

Spectrophotometric Study of the Interaction between Tetraethylammonium Halides and Aza-15-crown-5 with I₂ and ICl in Acetonitrile Solution

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The interaction between tetraethylammonium chloride (TEACl) with ICl and tetraethylammonium iodide (TEAI) and aza-15-crown-5 (A15C5) with I₂ and ICl have been examined spectrophotometrically in acetonitrile solution. The results of TEACl-ICl indicate the formation of ICl₂⁻ through equilibrium reaction. In the case of TEAI-I₂ and A15C5-I₂, the equilibrium formation of I₃⁻ is confirmed. The interaction of TEAI-ICl begins with the simultaneous production of I₂ and ICl₂⁻ (at TEAI/ICl < 0.5) as well as continues with the simultaneous consumption of I₂ and formation of I₃⁻ (at TEAI/ICl > 0.5). Similar behavior is also observed for A15C5-ICl system. However, the changes are seen at A15C5/ICl mole ratios less and more than 0.66. Several equations have been suggested for the formation of detected species. The formation constants of various reactions were evaluated from the computer fitting of the absorbance-mole ratio data. IR spectra of A15C5 and 1:1 A15C5:ICl or A15C5:I₂ complexes are compared and the effect of complexation on absorption bands is discussed.

Key Words : Spectrophotometry, Aza-15-crown-5, Acetonitrile, Iodine monochloride, Iodine

Introduction

Crown ether chemistry has been started with accidental discovery by Pedersen for one member of macrocyclic polyethers.¹ During subsequent work,²⁻⁶ Pedersen gave these compounds, their trivial "crown" nomenclature, synthesized many members of their family and determined their properties as well as complexing ability with several metal ions. The most unique attribute for this class of neutral molecules is their ability to form complexes with many metal cations⁷⁻¹⁰ including all the alkali metal cations. The stability of these complexes relates to the size of cavity by the oxygen atoms in their ring.^{11,12}

Interesting of study in the electron donor-acceptor (EDA) complexes of crown ethers has been increased during the past two decades. Research in this area is strongly stimulated by the possibility of applications in separation processes, preparation of ion-selective electrodes, conversion of chemical reactions into optical or electronic signals, the mimicking of enzymes in their capability to bind substances rapidly and reversibly as well as catalysis of chemical reactions.¹³ The aza-substituted crown ethers show very interesting features among different macrocyclic ligands used for EDA complexation. It has been shown that the substitution of some of oxygen atoms in crown ether ring by nitrogen results in tremendous variations in their properties than those of ordinary crowns.¹⁴⁻¹⁶ However, the study of EDA complexes of aza-crown ethers is also attractive. To our knowledge, there is no published report on the complexation of aza-15-crown-5 and ICl in acetonitrile solution. The present work follows our previous investigations of the spectroscopic studies of molecular complexes of ordinary and aza-substituted crown ethers with halogens¹⁴⁻¹⁹ and some π -

acceptor molecules.^{20,21} In this paper, the results of spectral studies of interactions between aza-15-crown-5 with I₂ and ICl in acetonitrile solution have been studied. Since there are some similarities between TEAX-X₂ and azacrown-X₂ behaviors,¹⁴⁻¹⁹ the reactions of TEACl-ICl, TEAI-I₂ and TEAI-ICl have also been considered.

Experimental Section

Reagent grade iodine (Merck) was sublimed and stored in a desiccator over phosphorous pentoxide before use. Iodine monochloride, aza-15-crown-5 (A15C5) and tetraethylammonium iodide (TEAI) from Merck Company were used as received. Tetraethylammonium chloride monohydrate (TEACl·H₂O, Aldrich) was used without any further purification except in vacuum drying.

All UV-Vis spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer and absorbance measurements were made with a Philips PU875 spectrophotometer at 25 ± 1 °C.

In order to obtain UV-Vis spectra, 3 mL of 1.54 × 10⁻⁴ M iodine or 4.08 × 10⁻³ M iodine monochloride were transferred into 1.00 cm quartz cell and titrated with a concentrated solution of TEACl, TEAI and A15C5 by a 100- μ L Hamilton syringe. Each spectrum was recorded immediately after the titrant addition. The same procedure was followed for absorbance measurement. Neither TEAX, nor A15C5, did not show any measurable absorption in the 250-650 nm regions.

The conductometric measurements were made for 10 mL solutions with a Metrohm 660 conductometer with conductometric cell thermostated at 25 °C.

Solid complex was isolated from the solution containing

stoichiometric amounts of Al5C5 and ICl (1 : 1) followed by solvent vaporization. The solid was used to obtain IR spectra. The spectra were recorded on a Perkin-Elmer 781 spectrometer using KBr pellets.

Results and Discussion

A. TEACl-ICl: The electronic absorption spectrum of ICl in the 250-650 nm regions is shown in Figure 1A. The spectra of ICl in the presence of different quantities of TEACl are also shown in Figures 1B-1H. The following changes have been seen upon stepwise addition of TEACl:

- i) An isosbestic point is appeared at 370 nm.
- ii) A blue shift along with the increasing of the intensity of iodine monochloride band is also observed.

The observation of isosbestic point indicates an equilibrium reaction between TEACl and ICl.²² The blue shift of ICl band may be a direct result of the partial charge transfer of Cl⁻ to an antibonding orbital in the ICl that can develop its effective size so that the excitation energy is increased.²³ The higher ϵ of complexed than that of noncomplexed ICl (Fig. 1) origins from the development of effective size, which raise the absorption cross section.²⁴

The stoichiometry of the TEACl-ICl reaction was obtained from the absorbance-mole ratio and Job's methods.²⁵ The plots at 330 nm (Figs. 2 and 3) clearly show a 1 : 1 stoichiometry. Because of observation of an isosbestic point in the spectra of TEACl-ICl mixtures (Fig. 1), chemical reaction between Cl⁻ (from ionization of TEACl) and ICl can be formulated as follows:



For evaluation of formation constant of the resulting 1 : 1 complex (Eqn. 1), K_f from the absorbance-mole ratio data,

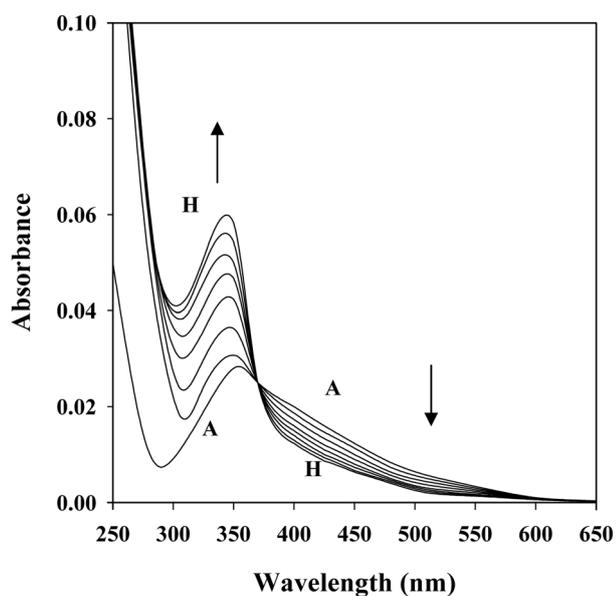


Figure 1. Absorption spectra of 1.36×10^{-4} M ICl in AN solution in different mole ratios of TEACl/ICl: (A) 0.00, (B) 0.10, (C) 0.20, (D) 0.30, (E) 0.40, (F) 0.50, (G) 0.60 and (H) 0.70.

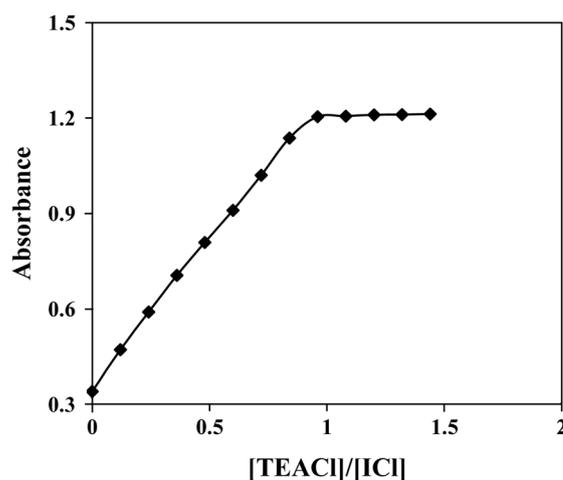


Figure 2. Absorbance-mole ratio plot for TEACl-ICl at $\lambda = 330$ nm.

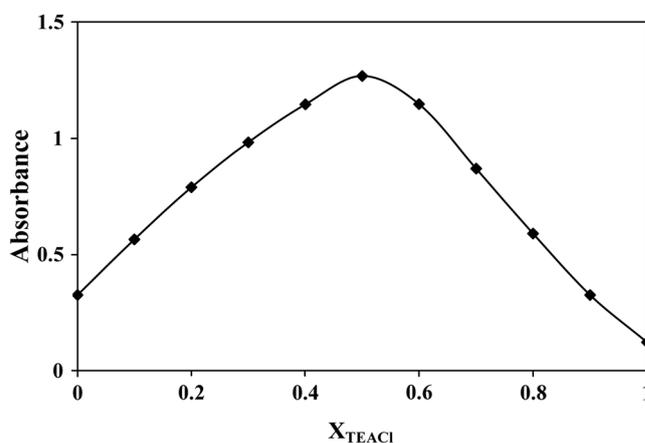


Figure 3. Continuous variation plot for TEACl-ICl at $\lambda = 330$ nm.

the nonlinear least square curve fitting program KINFIT was used.²⁶ The program is based on the iterative adjust of calculated to observed absorbance values by using either the Wentworth matrix technique²⁷ or the Powel procedure.²⁸ Adjustable parameters are K_f and ϵ , where ϵ is the molar absorption coefficient of complex. The output of program KINFIT comprises the refined parameters, the sum of squares and the standard deviation of data. The $\log K_f$ value obtained by this procedure is 6.11 ± 0.10 .

The high value of formation constant confirms a strong interaction between Cl⁻ and ICl. However, the spectra in Figure 1 are indicates of partial charge transfer from donor to acceptor. Thus, it can be concluded that charge transfer does not play an important role. Instead, the main role is due to ion (Cl⁻)-dipole (ICl) interactions.²⁹

B. TEAI-I₂: The absorption spectrum of iodine in acetonitrile solution in the 250-550 nm regions (Fig. 4A) shows three bands at 290, 364 and 460 nm. The 460 nm band is the locally excited visible I₂ band.³⁰ This band is appeared at 520 nm in n-heptane as an inert solvent and has a blue shift in acetonitrile solution.³¹ The blue shift has been attributed to the repulsion energy between the antibonding

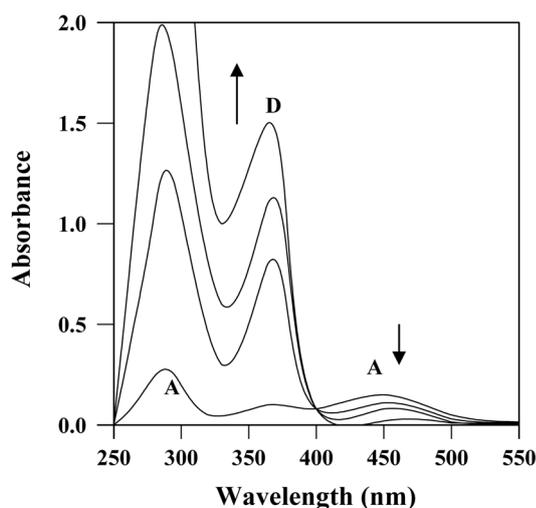


Figure 4. Absorption spectra of 1.54×10^{-4} M I_2 in AN solution in different mole ratios of TEAI/ I_2 : (A) 0.00, (B) 0.15, (C) 0.30 and (D) 0.45.

orbital of iodine and solvent. This energy is added to the usual energy of the excited iodine molecule that tends to the absorb energy of the excited iodine molecule.³⁰ On the other hand, the 290 and 364 nm bands are the well-known bands of triiodide ions.³¹⁻³⁴ This band indicates a chemical reaction between the solvent and iodine. The corresponding chemical equation can be written as follows:



The similar reaction between iodine and nitrogen containing compounds in inert solvents¹⁴⁻¹⁹ and increasing of the conductance of pure acetonitrile (from 1 to 4 $\mu\text{S}/\text{cm}^2$) in the presence of 1.16×10^{-3} M of iodine further supports the above reaction. In the other words, it can be concluded that in iodine solution of acetonitrile as a result of the reaction of iodine and solvent, a small fraction of iodine is converted to triiodide. It should be noted that in the case of solution of ICl in acetonitrile, neither the blue shift nor increasing in conductance is observed. It should be mentioned that the λ_{max} of ICl in chloroform is 360 nm³⁵ and the conductances of acetonitrile in the presence and absence of ICl are the same (1 $\mu\text{S}/\text{cm}^2$), which indicates that ICl and acetonitrile have a weak interaction.

The absorption spectra of I_2 in the presence of different quantities of TEAI (Figs. 4B-4D) show an isosbestic point at 400 nm and increase in intensity of 290 and 364 nm bands. Such situation proves that TEAI and I_2 produce triiodide through an equilibrium reaction. The absorbance vs. TEAI/ I_2 mole ratio and Job's methods (Figs. 5 and 6) confirms 1 : 1 stoichiometry. The reaction between iodine and I^- (from ionization of TEAI) can be formulated as follows:



The logKf value of above reaction was also obtained by fitting the absorbance-mole ratio data. The calculated value is 5.73 ± 0.07 . Similar to Cl^- -ICl (Eqn. 1) a strong inter-

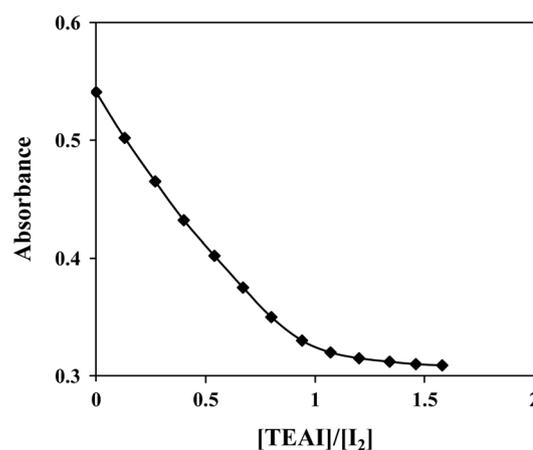


Figure 5. Absorbance-mole ratio plot for TEAI- I_2 at $\lambda = 460$ nm.

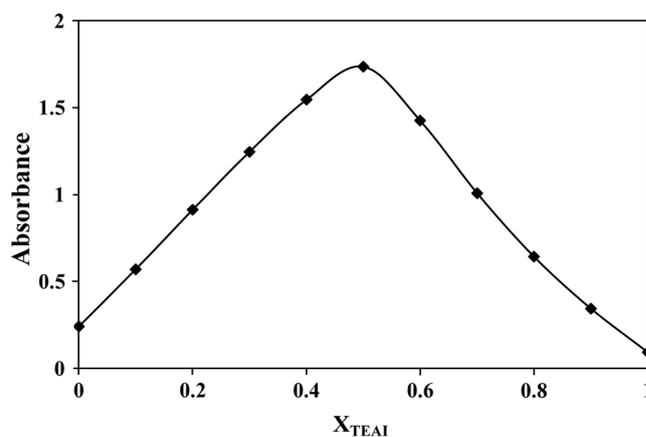


Figure 6. Continuous variation plot for TEAI- I_2 at $\lambda = 460$ nm.

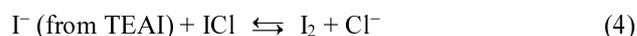
action is confirmed. However, because of absence of permanent dipole moment in iodine molecule and observation of charge-transfer band, the interaction can be assigned to charge transfer forces.

C. TEAI-ICl: The electronic absorption spectra of 1.36×10^{-4} M of ICl in the presence of different concentrations of TEAI (Fig. 7) shows the following features:

- i) Two isosbestic points at 400 and 350 nm.
- ii) The appearance of new band at 460 nm.
- iii) The blue shift of ICl band along increasing its intensity.

The existence of two-isosbestic point is indicative of two chemical equilibria.²² The appearance of new band at 460 nm confirms the realization of iodine (Fig. 4) and the blue shift of ICl band beside the increasing of its intensity can be attributed to the formation of ICl_2^- (Fig. 1).

Based on these evidences, it can be concluded that at the onset of reaction of TEAI and ICl, free I_2 and ICl_2^- are produced through two simultaneous equilibria. The following equations are suggested for the production of the mentioned species:



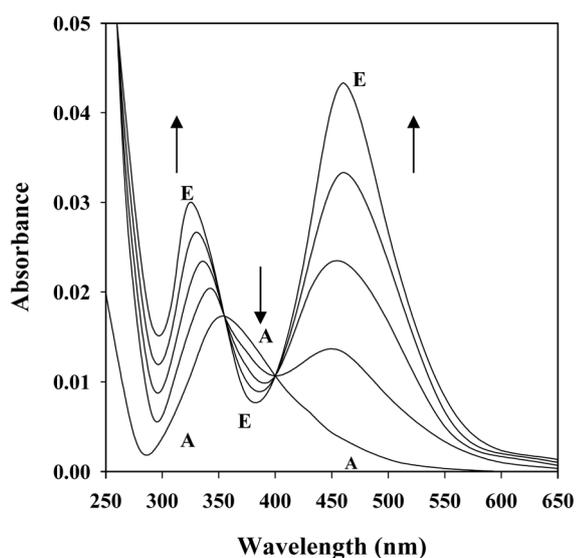


Figure 7. Absorption spectra of 1.36×10^{-4} M ICl in AN solution in different mole ratios of TEAI/ICl: (A) 0.00, (B) 0.085, (C) 0.170, (D) 0.255 and (E) 0.340.

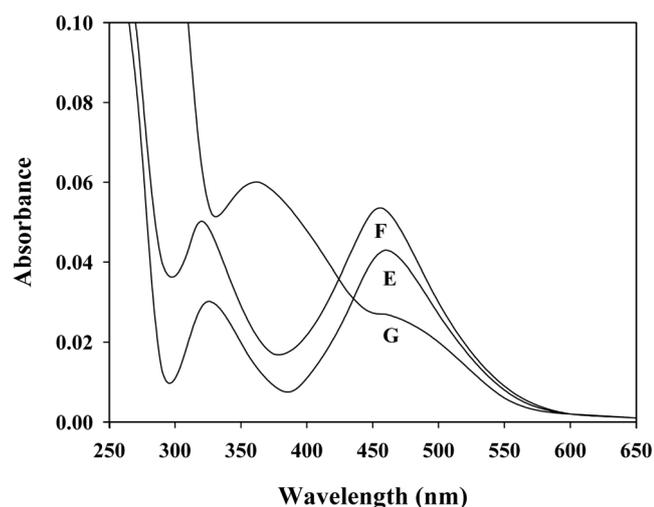


Figure 8. Absorption spectra of 1.36×10^{-4} M ICl in AN solution in different mole ratios of TEAI/ICl: (E) 0.340, (F) 0.425 and (G) 0.510.



Interestingly, at TEAI/ICl mole ratios more than 0.5, a new band at 364 nm is observed and the increasing trend of the intensity of 460 nm band is reversed (Fig. 8). This means that upon addition of further TEAI (TEAI/ICl > 0.5), new I_2 consumer and I_3^- producer reaction is occurred. Thus, it can be postulated that the excess I^- and free I_2 react at this stage (Eqn. 3).

Eqns. (6) and (3) are further confirmed by the plot of absorbance vs. TEAI/ICl mole ratio (Fig. 9). As it can be seen, three increasing, decreasing and plateau regions are appeared, respectively. The first region is related to production of I_2 and ICl_2^- (Eqn. 6), the second results from consumption of I_2 (Eqn. 3) and finally the third step

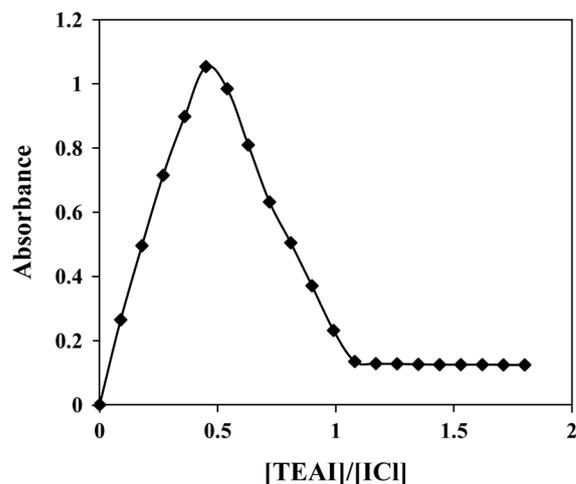


Figure 9. Absorbance-mole ratio plot for TEAI-ICl at $\lambda = 460$ nm.

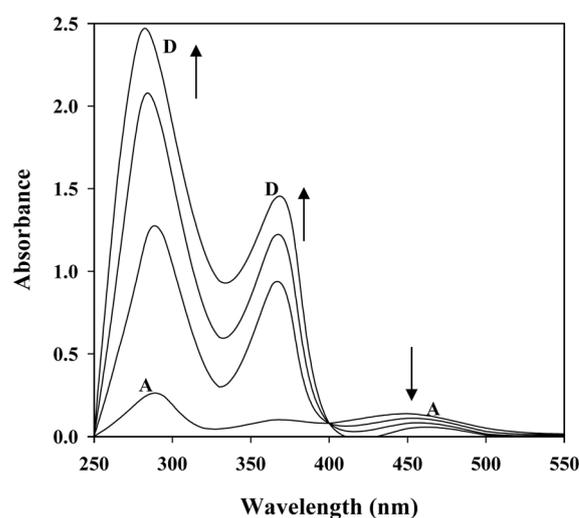


Figure 10. Absorption spectra of 1.25×10^{-4} M I_2 in AN solution in different mole ratios of A15C5/ I_2 : (A) 0.00, (B) 0.16, (C) 0.32 and (D) 0.48.

indicates the completeness of consumption reaction.

The absorbance-mole ratio data were fitted in the range of TEAI/ICl of 0 to 0.5 and the $\log K_f$ of Eqn. (6) was calculated as 7.35 ± 0.09 .

D. A15C5- I_2 : The absorption spectra of 1.25×10^{-4} M of iodine in the presence of different concentrations of A15C5 (Fig. 10) indicate similar spectral changes with those of iodine in the presence of different quantities (Fig. 4). On the other hand, the absorbance vs. A15C5/ I_2 mole ratio plot (Fig. 11) indicates a 1 : 1 stoichiometry. Based on these observations, the following equation is suggested for the A15C5- I_2 interaction.



Similar sandwich adduct has been reported previously¹⁴ and assigned to the strong affinity of I^+ ion for the soft NH group of the macrocycle ring.³⁶

Such as previous systems, the stability constant of A15C5-

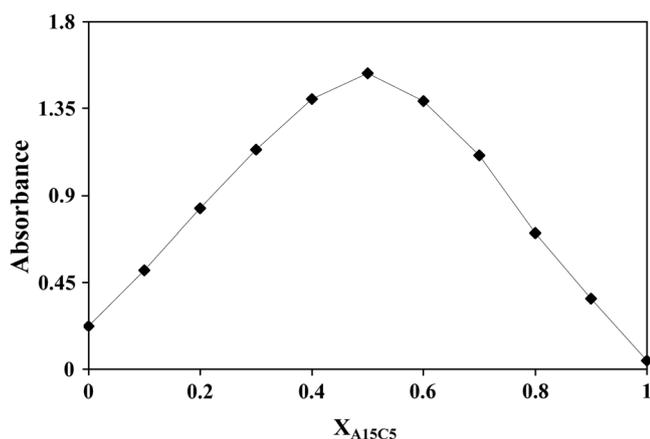


Figure 11. Continuous variation plot for A15C5-I₂ at $\lambda = 460$ nm.

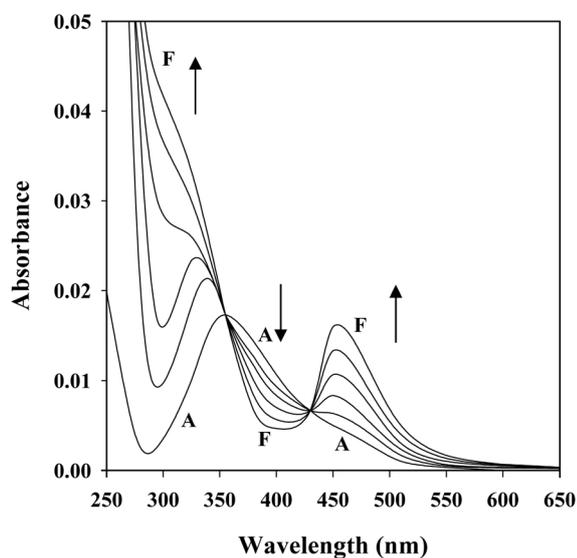


Figure 12. Absorption spectra of 1.36×10^{-4} M ICl in AN solution in different mole ratios of A15C5/ICl: (A) 0.00, (B) 0.10, (C) 0.20, (D) 0.30, (E) 0.40 and (F) 0.50.

I₂ reaction was obtained by computer fitting of absorbance-mole ratio data (Fig. 11) and the resulting value is $\log K_f = 4.59 \pm 0.02$.

E. A15C5-ICl: Figure 12 shows the absorption spectra of ICl in the presence of different concentrations of A15C5. Comparison of the recent spectra with those of TEAI-ICl mixtures (Fig. 7) indicates similar spectral changes in two systems. For example, in both cases two isosbestic points, appearance of new band at 460 nm and the simultaneous blue shift and increasing of ICl band, are observed. Thus, the initial products of the TEAI-ICl and A15C5-ICl interactions are the same.

By monitoring the spectral variations of A15C5-ICl mixtures at higher A15C5/ICl mole ratios (Fig. 13), appearance of I₃⁻ band at 364 nm and decrease of the iodine band at 460 nm are observed. This behavior is also similar to TEAI-ICl system (Fig. 8).

The plot of absorbance vs. A15C5/ICl mole ratio (Fig. 14), further confirms the identical of TEAI-ICl and A15C5-ICl

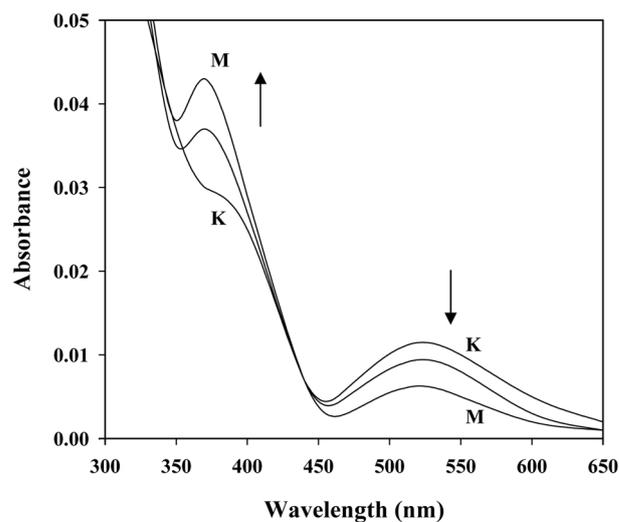


Figure 13. Absorption spectra of 1.36×10^{-4} M ICl in AN solution in different mole ratios of A15C5/ICl: (K) 0.75, (L) 0.85 and (M) 0.95.

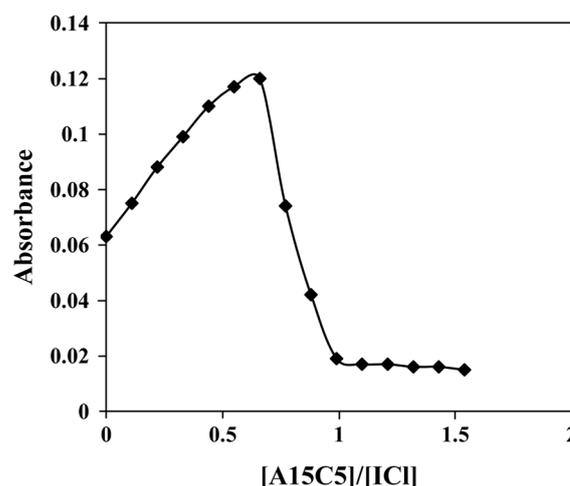
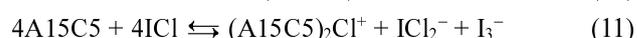
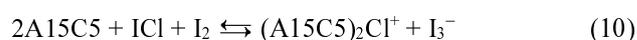
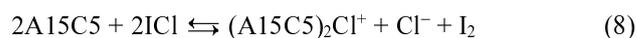


Figure 14. Plot of variations of absorbance vs. mole ratio of A15C5/ICl at $\lambda = 460$ nm.

systems. However, in contrast to TEAI-ICl system, instead of 0.5 and 1 (Fig. 8), the breaks are seen at 0.66 and 1 (Fig. 14).

According to (i) the observed similarities in the spectra and absorbance-mole ratio plots of two systems and (ii) the difference in absorbance-mole ratio plots, the following equations are suggested for the interaction of A15C5 and ICl:



The suggestion of the formation of $(\text{A15C5})_2\text{Cl}^+$ in the above equations is reasonable. In fact, the ionic radius of Cl^{+37} is much less than the cavity sizes of A15C5³⁸ and the ion in the hole-model is not applicable.³⁹ In addition, it has a

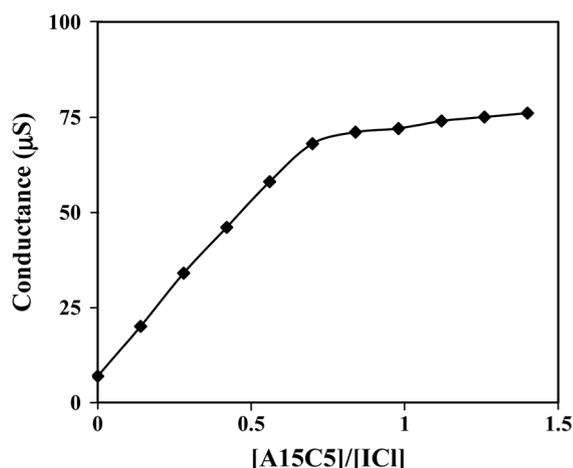


Figure 15. Plot of variations of conductance vs. mole ratio of A15C5/ICl in AN solution.

high charge density. Therefore, instead of insertion in the cavity, location between two nitrogen is preferred and consequently a sandwich adduct is formed. Evidence for the formation of such product has been reported previously.¹⁴ The formation constant of reaction (11) measured as $\log K_f = 7.69 \pm 0.15$.

The plot of conductance vs. A15C5/ICl mole ratio (Fig. 15) is in accordance with spectrophotometric results and further supports the presented Eqns. (8-10). As seen, three regions with different slopes are appeared. The first region relates to production of $(A15C5)_2Cl^+$ and ICl_2^- (Eqns. 8 and 9). The second region indicates the formation of I_3^- (Eqn. 10) and third region shows the completeness of reaction. The size of I_3^- is larger than ICl_2^- . Thus, the ion mobility of the former is less than the latter, which causes the decrease in the slope of conductance-mole ratio plot in the second relative to first region (Fig. 11).

F. IR Spectra: IR spectra of A15C5 and its 1 : 1 complex with ICl are compared in Figure 16. As seen, (i) a new band is appeared at 500 cm^{-1} , (ii) the CN band shifted to lower frequencies and (iii) the intensity of bands have been changed. The 500 cm^{-1} band can be attributed to $Cl^+ \cdots N$ bond stretching.⁴¹ The second effect results from electrodonation of nitrogen atom¹⁷ and the last effect is a con-

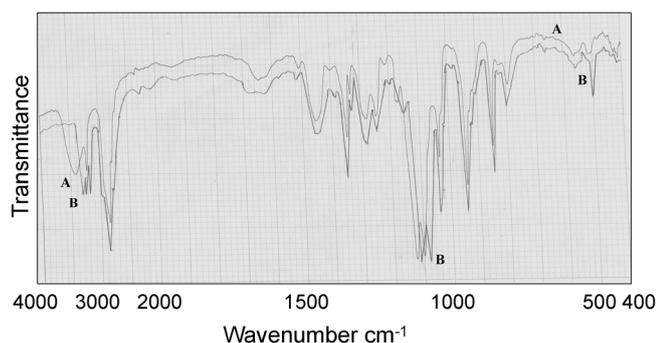


Figure 16. IR spectra of A15C5 (A) and its 1 : 1 complex with ICl (B).

sequence of change of symmetry of molecule during complexation.⁴² Comparison of IR spectra of A15C5 and A15C5- I_2 complex shows similar effects. However, in the latter, $I^+ \cdots N$ stretching bond is located at 560 cm^{-1} .

G. Conclusion: According to the results and discussion in sections A-F it can be concluded:

i) Iodine reacts with solvent, and iodine monochloride do not have any reaction with the solvent. This is confirmed by the appearance of triiodide bands in the spectrum of iodine in acetonitrile and increasing of conductance of pure acetonitrile upon addition of iodine. These effects are not seen for the solution of ICl in acetonitrile. Such a difference in behavior can be related to the soft character of both nitrogen atom of acetonitrile and I_2 .

ii) The charge transfer absorption band is observed in the case of I^-I_2 interaction. However, the interaction of Cl^-ICl only involves the partial charge transfer from Cl^- to ICl.

iii) Both Cl^-ICl and I^-I_2 form strong complexes. However, in the former ion-dipole and in the later charge transfer have the main role.

iv) A15C5 and TEAI have similar behavior with ICl and in both cases so that formation of I_3^- in the next observed.

v) The usefulness study of tetraalkylammonium halides-halogen (or interhalogen) interaction beside the macrocycle-halogen is reconfirmed.

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