Original Research Article

Spectrophotometric Study of Charge Transfer Complexes of Tetraethyleneglycol-bis-(8-quinolyl)ether with ICl$_3$ in some Nonaqueous Solvents

T. MADRAKIAN*, M. TORABBEIGI and M.A. ZOLFIGOL
Department of Chemistry, Faculty of Science, Bu-Ali Sina University, Zip code 65174, Hamadan, Iran

Abstract

The interaction between tetraethyleneglycol-bis-(8-quinolyl)ether (TEGQ) as a nitrogen and oxygen containing compound as a donor with ICl$_3$ as an acceptor has been investigated spectrophotometrically in chloroform, acetonitrile and dimethyl sulfoxide at different temperatures. The results of mole ratio plots and continuous variation data show the stoichiometry of complexation is 2:1 ICl$_3$/TEGQ. The formation constants of the resulting complexes and thermodynamic parameters have been determined. The results indicate the iodine trichloride complex with TEGQ is enthalpy stabilized but entropy destabilized.

Introduction

The macrocyclic polyethers, a class of compounds firstly synthesized by Pedersen [1], were shown to bind much more powerfully that, mono-functional and linear poly-functional ethers of similar basicity [2–5]. Studies on neutral molecule–macrocycles interaction have been far fewer in number than those on cation–macrocycle interactions. The motivation to study neutral molecule–macrocycle interactions is understandable because the function of neutral molecules is as important as that of charged molecules in many chemical and biochemical processes. In addition, there is increasing interest in molecular complexes of macrocyclic compounds by their possible application in different areas such as separation processes, catalytic chemical reactions, conversion of chemical reactions to optical or electronic signals and separate certain neutral molecules from environmental system [6–9].

Halogens and interhalogens form donor–acceptor complexes, with a range of Lewis bases. These charge transfer (CT) complexes first proposed by Muliken [10], are now recognized to play a key role in many chemical and biological processes. Consequently, many studies in spectral, thermodynamic, and other aspects of charge transfer complexes have been reported in the literature [11–13].

The preparation of molecular addition compounds of the type D·ICl and D·ICl$_3$, where D is a molecule of one of several heterocyclic amines, was reported in the literature [14]. Charge transfer complexes of iodine trichloride with pyridine, quinoline, and 2,6-lutidine were studied spectrometrically using Job's method of continuous variation [15, 16].

We have been recently involved in the spectroscopic study of molecular complexes of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), picric acid, thymol blue and bromo phenol blue with TEGQ [17].

In this paper, we report the results of a spectrophotometric investigation of the stiochiometry, thermodynamics of complex formation of ICl$_3$ with tetraethyleneglycol-bis(8-quinolyl)ether (TEGQ) in chloroform (CHCl$_3$), acetonitrile (AN) and dimethylsolfoxide (DMSO) solutions at different temperatures.

Experimental

Reagents

Reagent grade tetraethyleneglycol-bis-(8-quinolyl)ether (TEGQ) and iodine trichloride (ICl$_3$), (both from Merck) were of the highest purity available and used without any further purification. The structures of TEGQ and ICl$_3$ are shown in Scheme 1. Chloroform, acetonitrile and dimethysulfoxide (all from Merck) were used as solvents.

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* Author for correspondence. E-mail: madrakian@basu.ac.ir

TEGQ   ICl₃
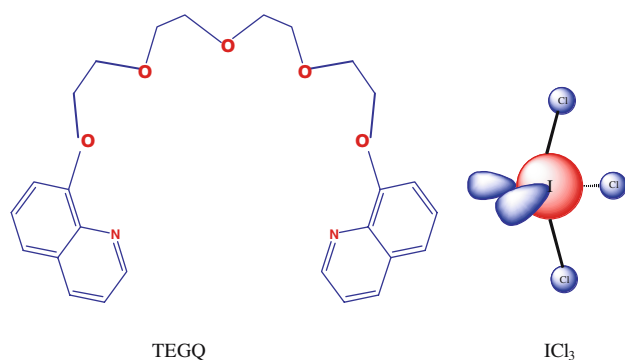
Scheme 1.

Apparatus

Recording all electronic spectra and the absorbance measurement at fixed wavelengths were carried out on a Shimadzu Model UV-265 UV–visible spectrophotometer equipped with a Shimadzu CPS controller Model 260 thermostat with 1 cm quartz cells. The mid-infrared spectra of TEGQ and its ICl_3 complex in the region 4000–400 cm^{-1} were recorded in nujol mulls dispersed on NaCl windows using a Perkin–Elmer FT-IR spectrometer Model spectrum GX.

Procedure

Photometric titrations of ICl_3 and TEGQ were performed at different temperatures under conditions of fixed ICl_3 concentration $(5 \times 10^{-4}$ mol l$^{-1})$ while the concentration of TEGQ in the reaction mixture was varied over the range $0.0–1.0 \times 10^{-3}$ mol l^{-1}. The yellow

color was appeared right after mixing and was stable at least for 1 h. The absorbance of the formed ICl_3 complex were measured in each case around 364 nm and plotted as a function of a TEGQ:ICl_3 ratio in order to determine the stoichiometry of the reaction according to the known method [18] as will be seen in the Results section. The stock solution of ICl_3 solution was freshly made on the day of measurements but TEGQ solution was stable for a lot of days.

Results and discussion

The electronic absorption spectra of TEGQ and ICl_3, $(5.00 \times 10^{-4}$ mol l$^{-1})$ in the different concentrations of TEGQ mole ratio (0–2) in chloroform solution at 25 °C are shown in Figure 1. Addition of donor to ICl_3 results in new absorption band at 364 nm shows itself as a shoulder band and none of the initial reactants show any measurable absorption in this region; these results presumably due to the formation of ICl_3–TEGQ complex. This change in absorbance at 364 nm, upon mixing the TEGQ and ICl_3 was found to increase with arise in the ICl_3:TEGQ mole ratio to reach a constant value at a mole ratio of 2:1. These results in different temperatures are shown in Figure 2. Such a ratio was also obtained for the reaction in AN and DMSO solutions under the same conditions. Figure 3 shows the continuous variations plot in $CHCl_3$ and shows a maximum at X_{TEGQ} value of 0.33 that emphasis on formation of a 2:1 ICl_3–TEGQ complex.

The formation constant of the 2:1 adduct was evaluated from the corresponding absorbance–mole ratio data as follows. When TEGQ reacts with ICl_3, it may from 2:1 complex as
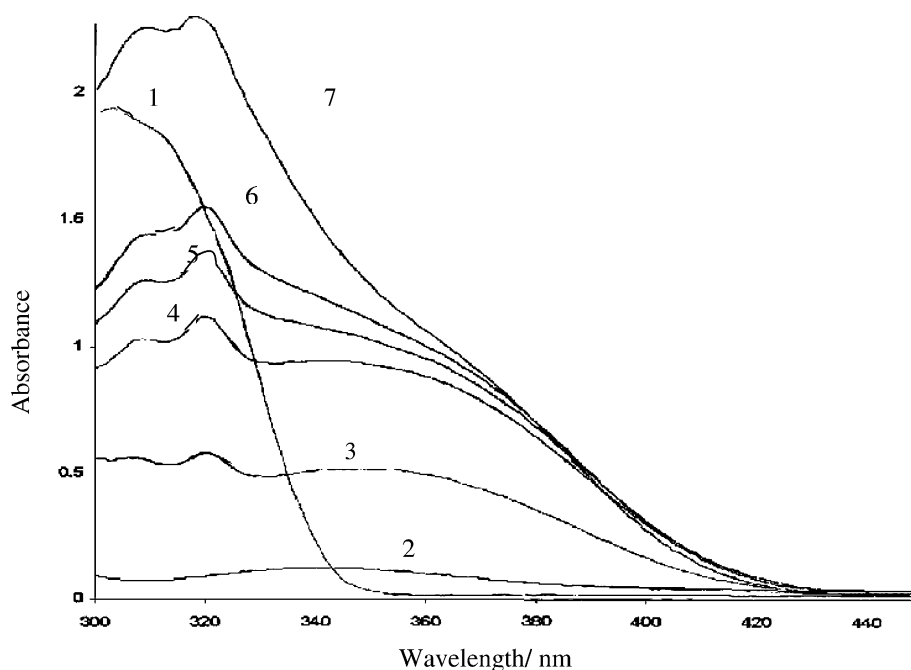

Figure 1. Absorption spectra of ICl_3 in chloroform in the presence of various mole ratios of TEGQ. (1) [TEGQ] = 2.5×10^{-5}, (2) [ICl_3] = 5×10^{-4}, (3) 0.2, (4) 0.52, (5) 0.6, (6) 0.8 and (7) 1.04 of C_{TEGQ}/C_{ICl_3} at 25 °C.

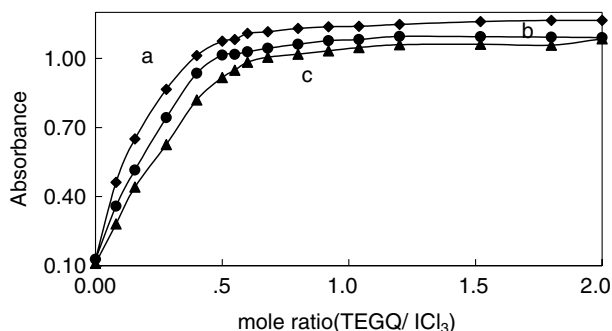*Figure 2.* Plots of absorbance vs. C_{TEGQ}/C_{ICl_3} mole ratio in chloroform at (a) 10 °C, (b) 15 °C and (c) 20 °C. Concentration of ICl_3 was 5.00×10^{-4} mol l^{-1}.
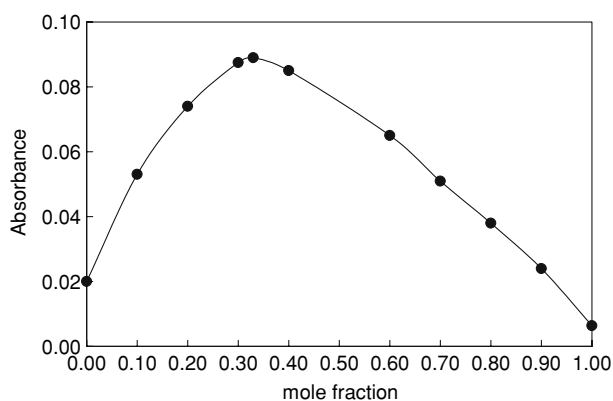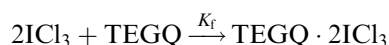

Figure 3. Continuous variation plot of TEGQ/ICl_3 mole fraction in chloroform at 25 °C.

$$2ICl_3 + TEGQ \xrightarrow{K_f} TEGQ \cdot 2ICl_3$$

$$K_f = \frac{[TEGQ \cdot 2ICl_3]}{[TEGQ][ICl_3]^2} \qquad (1)$$

The mass-balance equations are written as Equations (2) and (3)

$$C_{ICl_3} = [ICl_3] + 2[TEGQ \cdot 2ICl_3] \qquad (2)$$

$$C_{TEGQ} = [TEGQ] + [TEGQ \cdot 2ICl_3] \qquad (3)$$

Substitution of Equation (1) into Equations (2) and (3) and rearrangement yields Equation (4)

$$K_f[ICl_3]^3 - [ICl_3]^2(2K_f C_{TEGQ} - K_f C_{ICl_3}) + [ICl_3]$$
$$- C_{ICl_3} = 0 \qquad (4)$$

The observed absorbance of the solution is also given by

$$A = \varepsilon_{TEGQ \cdot 2ICl_3}[TEGQ \cdot 2ICl_3] \qquad (5)$$

The free [ICl$_3$] calculated from Equation (4) by means of a Newton Raphson procedure. Once the value of [ICl$_3$] had been obtained the concentrations of all other species involved were calculated from the corresponding mass-balance equations by using the estimated value of K_f at the current iteration step of the program. Refinement of the residuals between calculated and observed absorbance values for all experimental points was minimized. The output program KINFIT [19] comprises the refined parameters, the sum of squares and the standard deviations of the data. A sample computer fit of the mole ratio data for 5×10^{-4} ICl$_3$ and 0–2 mole ratio TEGQ/ICl$_3$ in DMSO solution is shown in Figure 4. A fair agreement between the observed and calculated absorbances further supports the occurrence of a 1:2 complexation between TEGQ and ICl$_3$. The fitting of curves was acceptable and the formation constant of complex in various temperatures was obtained. The formation constant of the resulting complex in various temperatures in chloroform, acetonitrile and DMSO are listed in Table 1. As Table 1 shows, TEGQ forms stable 1:2 complexes with ICl$_3$ in all the investigated solvents.

In order to have a better understanding of the thermodynamics of the complexation reactions of iodine trichloride with TEGQ, it is useful to consider the enthalpic and entropic contributions to this reaction. The enthalpy and entropy values of complex formation
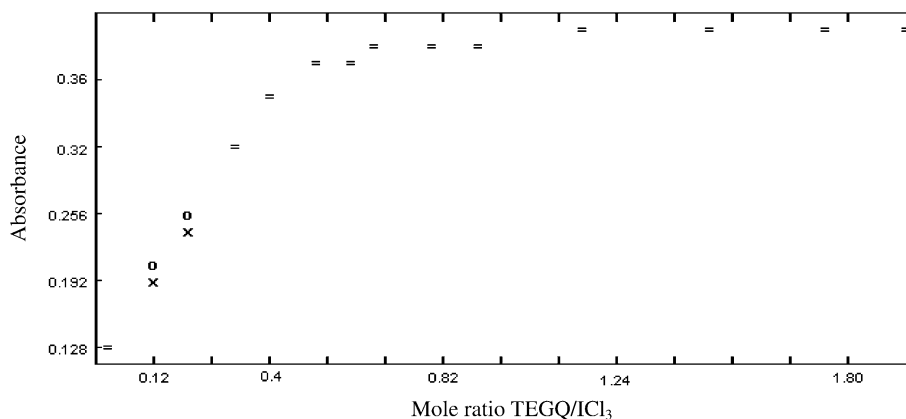

Figure 4. Computer fit of absorbance vs. TEGQ/ICl$_3$ mole ratio in DMSO solution at 25 °C. (o) calculated point; (×) experimental point; (=) experimental and calculated points are the same within the resolution of the plots.

Table 1. Formation constants of TEGQ·2ICl$_3$ complex in different temperatures at various solvents

Solvent	log K_f[a]						
	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
DMSO	–	6.15	6.09	5.85	5.75	5.58	5.40
AN	7.64	7.35	7.19	6.90	6.75	–	–
CHCl$_3$	8.59	8.17	7.93	7.50	–	–	–

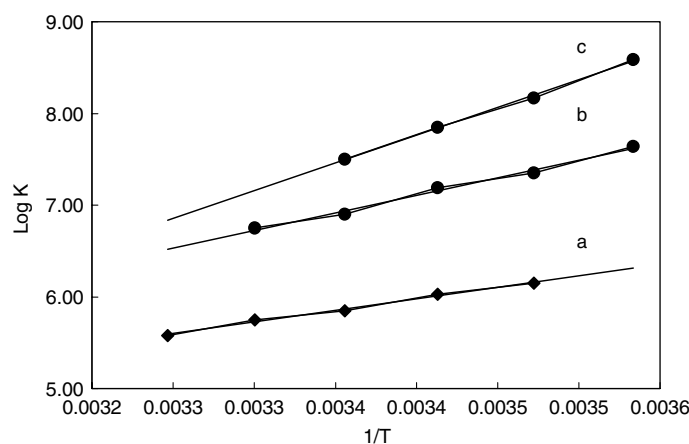[a]SD on log K_f values is at the most ±0.05.

Figure 5. Van't Hoff plots for (a) DMSO, (b) acetonitrile and (c) chloroform solutions.

Table 2. Thermodynamic parameters of TEGQ·2ICl$_3$ complex in different solvents

Solvent	DN[a]	$\varepsilon/\varepsilon_0$ [a]	ΔH^0/kJ mol^{-1}	ΔS^0/J K mol^{-1}
DMSO	29.8	45	−53.5 ± 2.8	−66.1 ± 5.5
AN	14.1	36	−73.4 ± 3.9	−113.1 ± 9.2
CHCl$_3$	–	4.8	−113.4 ± 6.1	−236.3 ± 12.4

[a]Ref. [20].

were evaluated by measuring the formation constants as a function of temperatures. The plots of log K_f vs. 1/T for CHCl$_3$, AN and DMSO solution are shown in Figure 5. The enthalpy and entropy values of complex formation were evaluated from the slopes and intercepts of the resulting linear plots, respectively, and the results are also included in Table 2. It is obvious that the stability of complex decrease very significantly with increasing temperature and with increasing donor number and dielectric constant of solvent. The formation constant of complex is the highest in chloroform and is the lowest in DMSO.

The solvent plays a donor role in DMSO solution, which decreases the formation constant of complex.

As can be seen in Table 2, the iodine trichloride complex with TEGQ is enthalpy stabilized but entropy destabilized. Based on the proposed mechanism for the formation of TEGQ–2ICl$_3$ complex, it seems reasonable to assume that the main reason for the relatively large negative entropy of complexation is the decrease in the conformational entropy of the TEGQ upon formation of the complex.

The IR spectra data of TEGQ and charge transfer complex are presented in Table 3. As can be seen, the (C = N) stretching, ν(C–O–C), ν(C–O)$_{ar}$ and ν(C–H) of TEGQ show a measurable shift to either lower (10–20 cm^{-1}) or higher (10–30 cm^{-1}) frequencies, upon molecular complex formation with TEGQ.

The NMR spectra of complex were very broader than the NMR spectra of TEGQ that shown the complex was formed.

Table 3. Infrared wavenumbers (cm^{-1}) and tentatives assignments for (TEGQ) and (TEGQ·2ICl$_3$)

	TEGQ (cm^{-1})	Complex (cm^{-1})
ν(C–O–C)	1108	1098
ν(C–O)$_{ar}$	1570	1549
ν(C = N)	1613	1634
ν(C–H)	3041	3054

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