THERMODYNAMIC PARAMETERS OF INTRA AND INTERMOLECULAR HYDROGEN BOND FOR A – NAPHTHOL AND ITS DERIVATIVES

Falah Shareif Abed Suhayl
Dept. of Chemistry, College of Pharmacy, University of Kufa

Abstract

Electronic absorption spectra of α– Naphthol , Nitronaphthol and Nitrosonaphthol in pure and mixed solvent show an obvious changes in their equilibrium constant (K), free energy change (ΔG) and enthalpy change (ΔH) .

Introduction

Ultraviolet spectroscopy (U.V.), an important method for studying the inter and intramolecular hydrogen bonding and effect of hydrogen bonding on the electronic absorption spectra.

In the present work was undertaken to investigate the effects induced by intermolecular hydrogen bonding on the electronic structure of an aromatic system. The electronic absorption spectra of α– Naphthol , Nitro–naphthol and Nitroso–naphthol in inert and proton–acceptor solvent are measured. The equilibrium constant (K) was determined[1] from the following equation:-

$$1/\varepsilon - \varepsilon_f = 1/K . 1/\varepsilon_b - \varepsilon_f . 1/C + 1/\varepsilon_b - \varepsilon_f$$

where εf , εb ere the molar extinction coefficient of free and hydrogen bounded molecules.

The free energy of hydrogen bond formation were calculated[2] by the following equation:-

$$\Delta G = - RT \ln K$$

The enthalpy also calculated[3] by the following equation:-

$$\Delta H = R d \ln K / d(1 / T)$$

Material and method

Naphthol derivatives (α – Naphtol , 2 – Nitro – 1 – naphthol and 2 – Nitroso – 1 – naphthol) , spectrophotometric pure Cyclohexane and Dioxane were supplied from B.D.H. spectrophotometric measurements were carried by using Pyunicam 8800 U.V. spectrophotometer with one cm. cell .

The concentration of Naphtholes were in range of 2.54×10^{-4} , 2.88×10^{-4} and 2.48×10^{-4} molar respectively. The Dioxane concentration was increased from (0.00 – 6.0 %) Percent . All the absorption measurements were carried out between 15-25 °C . The U.V. spectrophotometric measurements were done in the region from 290 nm to 240 nm with 5 nm increment.

Results and Discussion

In this work , the relationship proposed for evolution the equilibrium constant (K), free energy (ΔG) and enthalpy (ΔH) of α – Naphthol and its two derivatives involved in an intra and intermolecular hydrogen bonding either for free Naphtholes or bounded . The absorbance measurements show that the extinction coefficients (ε) of Naphtholes in cyclohexane increased in gradual increasing of Dioxane concentration , the value of absorption increases. Fig. (1,2,3) then tends to highest value of Dioxane concentration , indicating that intermolecular hydrogen bond formation is almost complete at such concentration with formation of 1:1 complex between Naphthol and Dioxane molecules[4] . To determination the thermodynamic parameters (K , ΔG , ΔH) for intermolecular hydrogen bond were calculated from equation (1) by plotting $1 / (\varepsilon - \varepsilon f)$ against $1 / C$. We show a straight line correlation Fig.(4,5,6) and these values are tabulated in table (1) .

The change of free energy (ΔG) of hydrogen bonding between proton donor (2 – Nitro – 1 – naphthol , 2 – Nitroso -1 - naphthol) and proton acceptor molecule (Dioxane) are small value than in case of α – Naphtol , due to the presence of nitro and nitroso groups which allowed to formation the intramolecular hydrogen bonding[5]

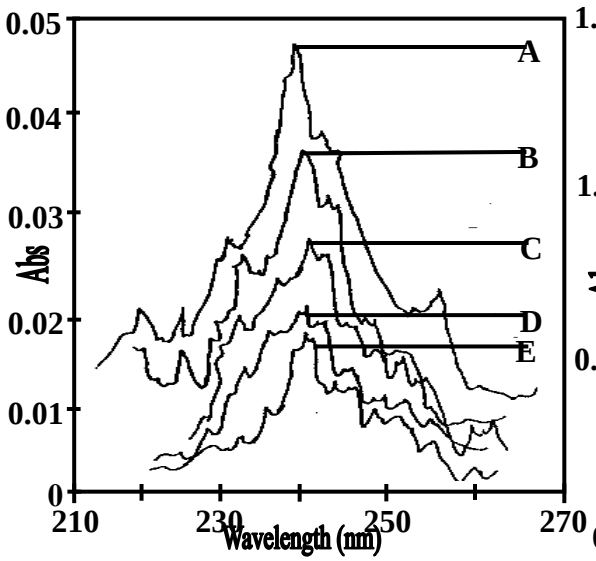

Fig.1 Absorption curves for α – Naphtol at 25° C , 2.486 × 10^{-4} mol. L^{-1} , Dioxane = (A) 0.07, (B) 0.047, (C) 0.023, (D) 0.0117, (E) 0.0 mol. L^{-1}

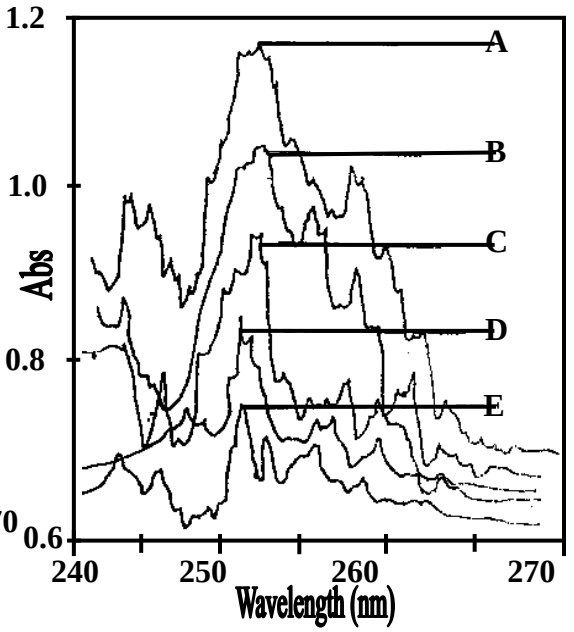

Fig.2 Absorption curves for 2-Nitroso-1-Naphtol at 25° C , 2.486 × 10^{-4} mol. L^{-1} , Dioxane = (A) 0.07, (B) 0.047, (C) 0.023, (D) 0.0117, (E) 0.0 mol. L^{-1}

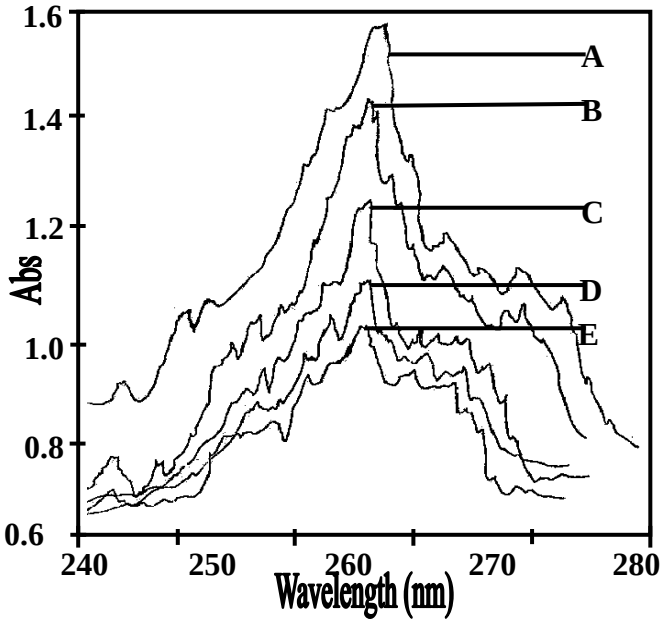

Fig.3 Absorption curves for 2-Nitro-1-Naphtol at 25° C , 2.486 × 10^{-4} mol. L^{-1} , Dioxane = (A) 0.07, (B) 0.047, (C) 0.023, (D) 0.0117, (E) 0.0 mol. L^{-1}

Table-1- Equilibrium constant and thermodynamic parameters for the hydrogen bonding of the system α - , 2 – nitro – 1 , 2 – nitroso – 1 – naphtholes in dioxane and cyclohexane .

System	T°C	K	–ΔG Kcal. mol^{-1}	ΔH Kcal.mol^{-1}
α – Naphtol	15	40.608	2.12	14.230
	20	28.469	1.95	
	25	17.646	1.70	
2 – Nitro – 1 – naphthol	15	8.88	1.25	9.885
	20	6.613	1.10	
	25	4.973	0.95	
2 – Nitroso – 1 – naphthol	15	4.903	0.91	7.810
	20	3.883	0.79	
	25	3.099	0.67	

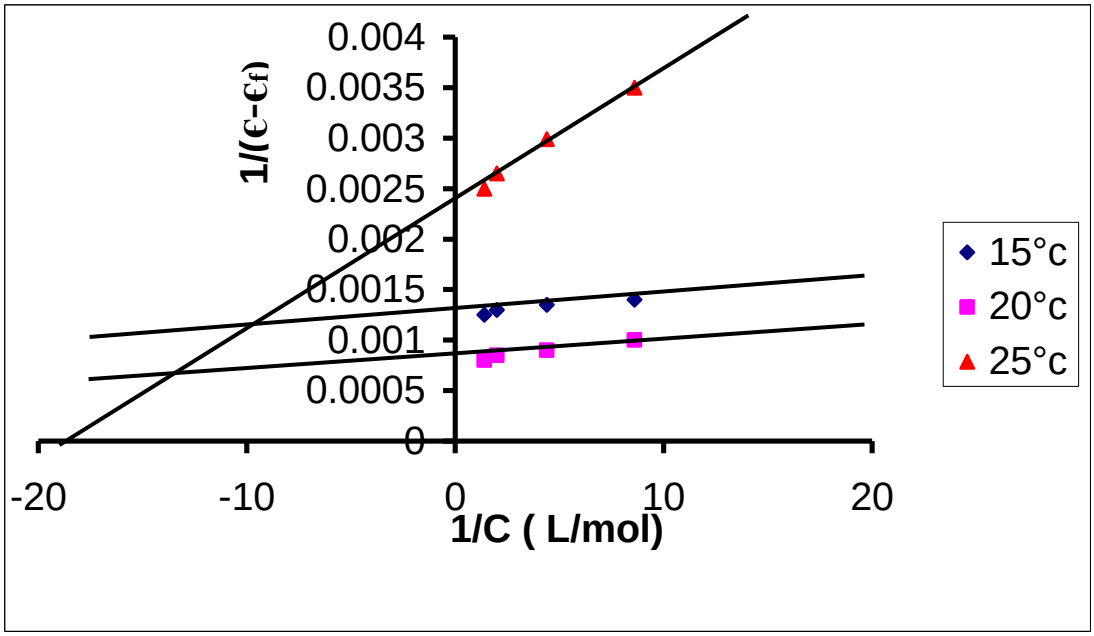

Fig.4 Plot of $1/(\varepsilon-\varepsilon f)$ against 1/C of Dioxane for the determination of K For α-Naphthol .

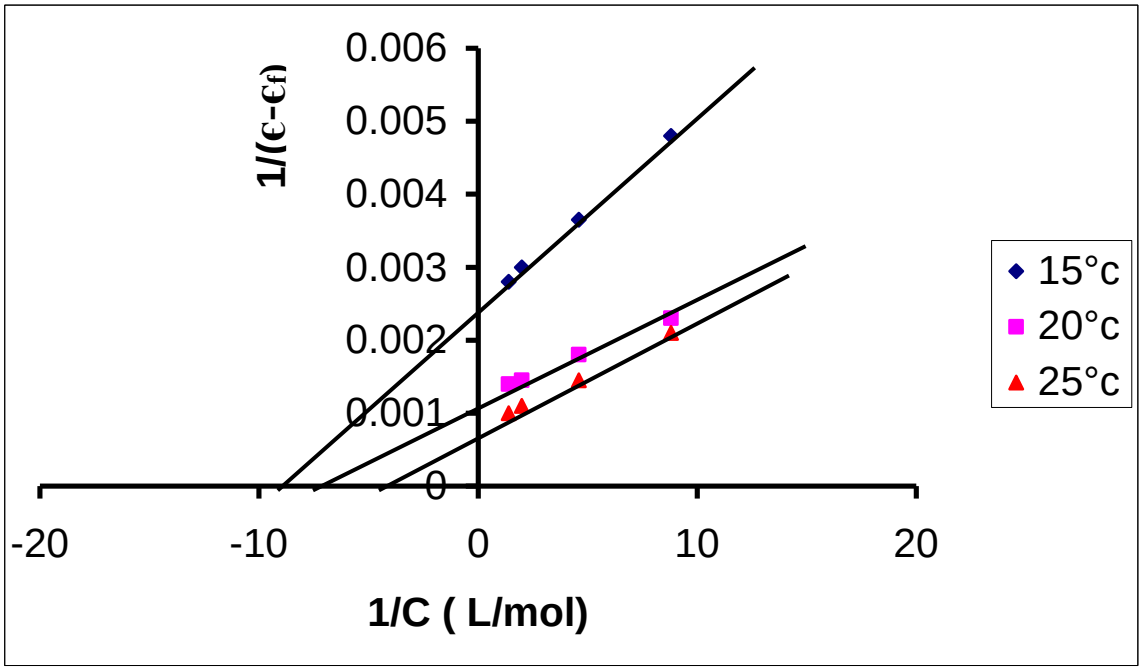

Fig.5 Plot of $1/(\varepsilon-\varepsilon f)$ against 1/C of Dioxane for the determination of K For 2-Nitro-1-naphthol .

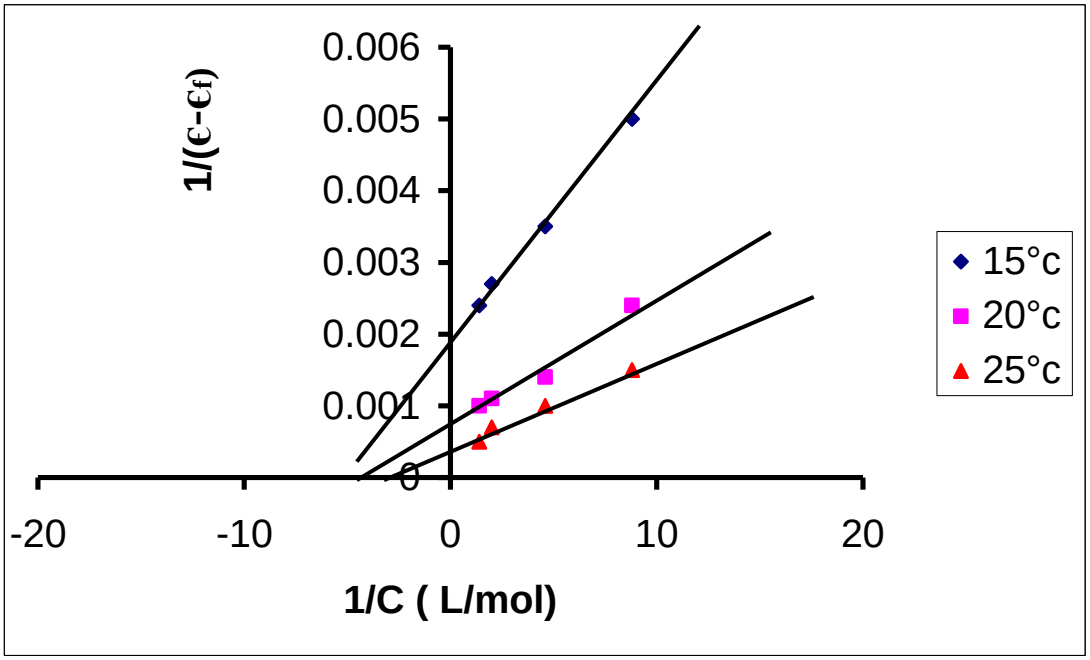

Fig.6 Plot of $1/(\varepsilon-\varepsilon f)$ against 1/C of Dioxane for the determination of K For 2-Nitroso-1-naphthol

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الخلاصة

في هذا البحث تم دراسة التغيرات في الدوال الثرموديناميكية لقيم ثابت الاتزان (K) والطاقة الحرة (ΔG) والمحتوى الحراري (ΔH) عن طريق القياسات الطيفية بتقنية أطياف الامتصاص الالكترونية لمركبات (الفا– نفثول ، 2– نايترو–1– نفثول ، 2– نايتروزو – 1 نفثول) في مذيب السايكلوهكسان النقي وامزجة مختلفة النسب من الدايكوسان ، سايكلوهكسان.