

Thermodynamic Study of the Interaction of Cinnamylideneaniline and some of it's Derivatives with the Shift Reagent Ag(fod) by U.V Spectroscopy

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ABSTRACT

The U.V. spectra of a series of cinnamylidene (mono and di-substituted) anilines have been studied in CCl_4 with the shift reagent Ag(fod). A splitting of the main band into two bands was observed, which may be attributed to the complex formation with the Ag(fod). The equilibrium constant for the process was calculated using the method of Hartman. The U.V. spectra were measured at different temperatures (293-333 $^{\circ}K$), the results showed a decrease in K values with increasing temperature. The thermodynamic parameters (ΔG , ΔH and ΔS) were obtained. Application of Skalski method showed that the interaction with Ag(fod) was 1:1.

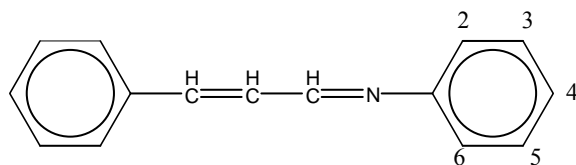
Ag(fod)

Ag(fod) ()
(333_293)
(ΔG , ΔH and ΔS) (K)
.1:1

INTRODUCTION

Cinnamylidene anilines are present mainly in the stable transform (Anteunis et al., 1972) The ^1H NMR study of these compounds after addition of the lanthanide shift reagent (LSR) $\text{Eu}(\text{fod})_3$ showed that they undergo isomerization to the less stable cis form (Saleem et al., 2000), In another studies (Saleem et al., 1992), (Saleem et al., 1997). it has been shown that cinnamylidene anilines can undergo isomerization to the cis form on irradiation by U. V. light at room temperature and the rate of isomerization was found to be a first order. The assigned cis signals for both methods (U.V. and ^1NMR) were found to be identical, which confirm the isomerization process. The interaction of Cinnamylidene anilines with $\text{Eu}(\text{fod})_3$ was also studied by U.V. spectroscopy and in different solvents (Saleem et al., 1989), (Saleem et al., 1999).

The thermodynamic parameters for such interaction have been determined (Sulaiman et al., 1998). The present work involves the study of the interaction of a



- | | |
|---------------------------|----------------------------|
| 1. 2, 3, 4, 5, 6 = H | 6. 3 = Me, 2, 4, 5, 6 = H |
| 2. 4 = Cl, 2, 3, 5, 6 = H | 7. 2, 3 = Me, 4, 5, 6 = SH |
| 3. 4 = F, 2, 3, 5, 6 = H | 8. 2, 4 = Me, 3, 5, 6 = H |
| 4. 4 = Br, 2, 3, 5, 6 = H | 9. 2, 5 = Me, 3, 4, 6 = H |
| 5. 4 = OH, 2, 3, 5, 6 = H | |

(Scheme 1)

EXPERIMENTAL

Cinnamylideneanilines were prepared by mixing an equimolar amounts of cinnamaldehyde with substituted anilines according to the procedure described by EI-bayoumi (E1-Bayotimi et al., 1971) and coworkers.

Preparation of the shift reagent $\text{Ag}(\text{fod})$:

(1,1, 1, 2, 2, 3, 3- Hepta fluoro -7, 7-dimethyl -4, 6- octanedion) silver(I). A solution of 9.6g (0.0324 mol) of $\text{Pr}(\text{fod})_3$ in 5 ml of methanol was neutralized with 8.1 ml of 4 M NaOH. The solution was added to a stirred solution of 5.5 g. (0.0324 mol) of silver nitrate in 75 ml of distilled water. A precipitate immediately separated, was collected by suction filtration, and was dried tinder Vacuum. (Belletete et al., 1982)

Sampling:

A stock solution of (5×10^{-3} M) Ag(fod) was prepared in CCl_4 , a solution of (5×10^{-4} M) of Schiff base was used for measurement. To 10 ml of (5×10^{-4} M) solution of Schiff-base a different amount of (4×10^{-3} M) Ag(fod) was added using a micro syringe.

Measurements:

The U.V. spectra were measured by Unicam Sp 800 U.V. spectrometer using 1 cm silica cell. Measurements were performed against a blank solution containing only Ag(fod) of the same concentration as the sample in order to cancel the absorbance of the shift reagent. Variable temperature measurements were performed between 293-343 K⁰. Temperature control was carried out using a thermostat of a type HAAKE D₃ (± 0.1 Temp. accuracy).

RESULTS AND DISCUSSION

The U.V spectra of cinnamylidene anilines in CCl_4 (5×10^{-4} M) show a strong absorption band at wavelength ranging between (295-298 nm).

Addition of the shift reagent Ag(fod) (5×10^{-3} M) to cinnamylidene aniline (1) caused a splitting of the main band into two bands: band A₁ to the shorter wavelength (272 nm) and band A₂ to the longer wavelength (325 nm) (Figure 1).

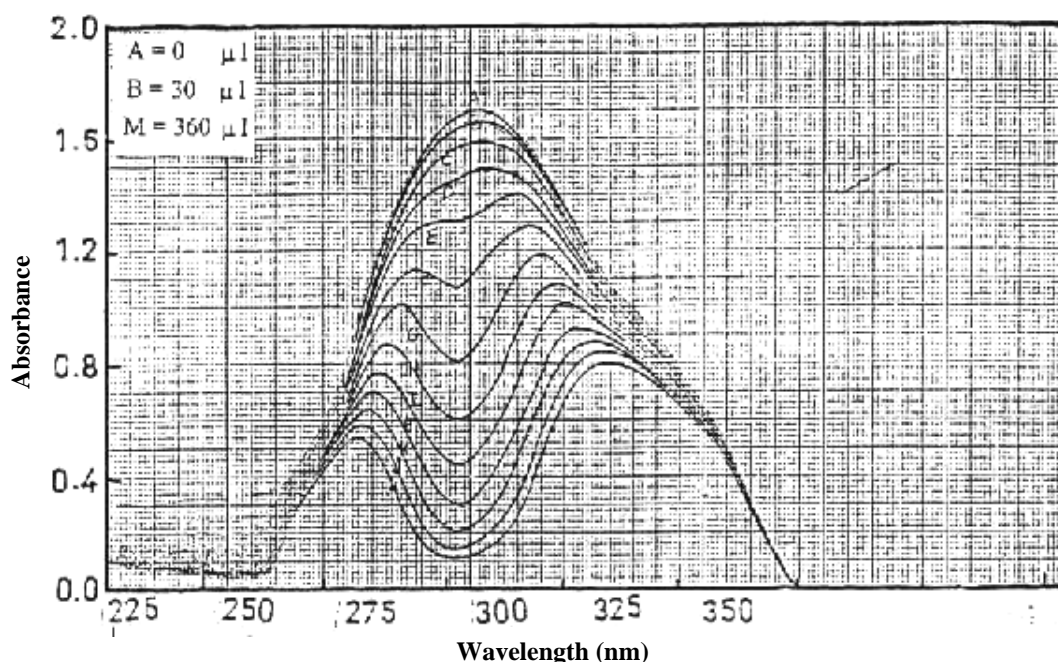


Figure 1: Absorption spectra of cinnamylideneaniline (5×10^{-4} M) with Ag(fod) in CCl_4 at 298 K⁰.

A. in the absence of Ag(fod) B. in the presence of Ag(fod)

Successive additions (30 μl) of (5×10^{-4} M) Ag(fod) tip to 360 μl resulted in a decrease in the absorbance of A_1 & A_2 , but the absorbance of band A_1 decreases more than band A_2 . The calculated values of $A_1\%$ and $A_2\%$ (Table 1) show a decrease in $A_1\%$ and increase in $A_2\%$ which may be due to complex formation of trans form with Ag(fod) followed by transformation to the complex of the less stable cis form.

Table 1: Percent variation of complex due to addition Ag(fod) to cinnamylidene aniline (5×10^{-4} M) in CCl_4 .

Comp.	$A_1\%$ & $A_2\%$	Ag(fod) addition			
		120	150	180	210
1	$A_1\%$	48.32	44.84	41.72	39.85
	$A_2\%$	51.67	55.15	41.72	60.15
2	$A_1\%$	47.57	41.79	58.27	34.19
	$A_2\%$	52.42	58.20	36.52	65.80
3	$A_1\%$	48.33	44.44	63.47	36.77
	$A_2\%$	51.66	55.55	39.76	63.22
4	$A_1\%$	46.35	40.09	60.23	31.67
	$A_2\%$	53.64	59.90	34.48	38.32
6	$A_1\%$	48.36	41.37	35.00	31.46
	$A_2\%$	51.63	58.62	65.00	68.53

In order to calculate the thermodynamic parameters, variable temperature measurements were performed for solutions of cinnamylidene aniline (5×10^{-4} M) in CCl_4 with 210 μl of (4×10^{-3} M) Ag(fod).

The equilibrium constant was calculated using the method of Hartman (Hartman et al., 1968) in which the equilibrium constant is correlated with the absorptions of the two bands A_1 and A_2 as follows :

$$K = \frac{A_2 \alpha_1}{A_1 \alpha_2}$$

Where α_1 and α_2 represent the molar absorption coefficients of band 1 and 2 after addition of Ag(fod), A_1 and A_2 are the absorbances of bands 1 and 2 respectively. Plot of A_1 vs. A_2 at different temperatures (Figure 2) gave straight lines with slopes $\frac{\alpha_1}{\alpha_2}$ from which the values of K has been calculated and are given in Table 2.

The following thermodynamic relation was used to calculate the enthalpy and entropy of the complexes:

$$\log K = \frac{-\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R}$$

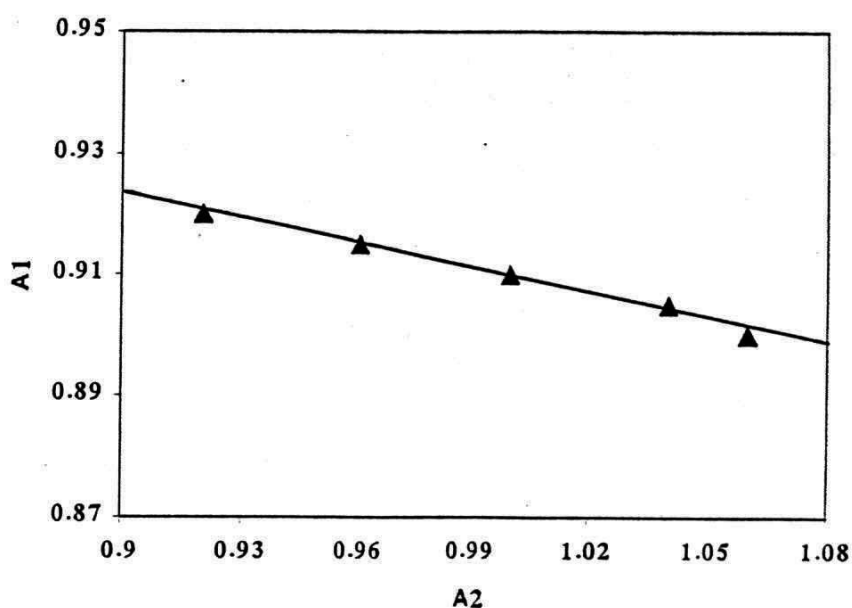


Fig. 2: Plots of A_1 against A_2 for cinnamylideneaniline in CCl_4 with $Ag(fod)$ at different temperature.

Plot of $\log K$ against $1/T$ give slopes of $\Delta H^0/2.303 R$ and an intercept $\Delta S^0/2.303R$. Such plot is shown in Fig (3) and the values of ΔH^0 and ΔS^0 are given in Table 2. From these results it can be seen that equilibrium constant values decrease on increasing temperature.

Table 2 :The thermodynamic parameters of cinnamylidene aniline with $Ag(fod)$ at different temperature in CCl_4 .

Comp. 1

Temp. K°	$1/T \times 10^{-3}$	A_2	A_1	$K_2 M^{-1}$	$-\ln K_2$	ΔG J/mole	ΔH J/mole	ΔS J/mole
293	3.412	1.06	0.900	0.1614	1.8233	4441.56	-3927.86	-28.56
303	3.300	1.04	0.905	0.1576	1.8474	4653.86		-28.32
313	3.194	1.00	0.910	0.1506	1.8928	4925.59		-28.28
323	3.095	0.96	0.915	0.1439	1.9384	5205.42		-28.27
333	3.003	0.92	0.920	0.1372	1.9863	5499.19		-28.30

* average value of $\Delta S = -28.35$

Comp. 2

Temp. K°	$1/T \times 10^{-3}$	A_2	A_1	$K_2 M^{-1}$	$-\ln K_2$	ΔG J/mole	ΔH J/mole	ΔS J/mole
293	3.412	1.19	0.81	0.2952	1.2201	2972.16	-5260.76	-28.09
303	3.300	1.16	0.82	0.2842	1.2580	3169.08		-27.82
313	3.194	1.13	0.83	0.2735	1.2962	3373.07		-27.58
323	3.095	1.06	0.84	0.2534	1.3725	3685.74		-27.69
333	3.003	1.00	0.85	0.2363	1.4423	3993.09		-27.78

* average value of $\Delta S = -27.79$

Comp. 3

Temp. K ^o	1/T x 10 ⁻³	A ₂	A ₁	K ₂ M ⁻¹	-ln K ₂	ΔG J/mole	ΔH J/mole	ΔS J/mole
293	3.412	1.14	0.81	0.4178	0.8725	2125.41	-4004.35	-20.92
303	3.300	1.12	0.82	0.4054	0.9028	2274.28		-20.72
313	3.194	1.09	0.83	0.3899	0.9417	2450.56		-20.62
323	3.095	1.05	0.84	0.3712	0.9908	2660.71		-20.63
333	3.003	1.01	0.85	0.3528	1.0417	2884.01		-20.68

* average value of ΔS = -20.71

Comp. 4

Temp. K ^o	1/T x 10 ⁻³	A ₂	A ₁	K ₂ M ⁻¹	-ln K ₂	ΔG J/mole	ΔH J/mole	ΔS J/mole
293	3.412	1.22	0.81	0.3945	0.9299	2265.23	-2884.12	-17.57
303	3.300	1.20	0.82	0.3833	0.9589	2415.60		-17.49
313	3.194	1.16	0.83	0.3660	1.0050	2615.29		-17.57
323	3.095	1.12	0.83	0.3534	1.0400	2792.83		-17.57

* average value of ΔS = -17.51

Comp. 5

Temp. K ^o	1/T x 10 ⁻³	A ₂	A ₁	K ₂ M ⁻¹	-ln K ₂	ΔG J/mole	ΔH J/mole	ΔS J/mole
293	3.412	1.19	1.11	0.6620	0.4123	1004.36	-2442.81	-11.76
303	3.300	1.18	1.13	0.6447	0.4388	1105.39		-11.71
313	3.194	1.17	1.14	0.6336	0.4562	1187.16		-11.59
323	3.095	1.14	1.15	0.6120	0.4909	1318.27		-11.64
333	3.003	1.12	1.16	0.5959	0.5175	1432.73		-11.63

* average value of ΔS = -11.67

Comp. 6

Temp. K ^o	1/T x 10 ⁻³	A ₂	A ₁	K ₂ M ⁻¹	-ln K ₂	ΔG J/mole	ΔH J/mole	ΔS J/mole
293	3.412	1.20	1.04	0.5332	0.6287	1531.51	-3338.07	-16.61
303	3.300	1.18	1.05	0.5193	0.6551	1650.28		-16.46
313	3.194	1.16	1.07	0.5013	0.6904	1796.61		-16.40
323	3.095	1.13	1.08	0.4837	0.7261	1949.88		-16.37
333	3.003	1.09	1.09	0.4625	0.7711	2134.83		-16.43

* average value of ΔS = -16.45

Comp. 7

Temp. K ^o	1/T x 10 ⁻³	A ₂	A ₁	K ₂ M ⁻¹	-ln K ₂	ΔG J/mole	ΔH J/mole	ΔS J/mole
293	3.412	0.83	1.07	0.1590	1.8386	4478.83	-2574.51	-24.07
303	3.300	0.82	1.07	0.1571	1.8503	4661.16		-23.88
313	3.194	0.79	1.065	0.1520	1.8835	4901.39		-23.88
323	3.095	0.77	1.06	0.1489	1.9039	5112.77		-23.79
333	3.003	0.73	1.05	0.1426	1.9476	5392.05		-23.92

* average value of ΔS = -23.91

Comp. 8

Temp. K ^o	1/T x 10 ⁻³	A ₂	A ₁	K ₂ M ⁻¹	-ln K ₂	ΔG J/mole	ΔH J/mole	ΔS J/mole
293	3.412	0.78	1.11	0.3852	0.9538	2323.45	-1437.49	-12.83
303	3.300	0.77	1.10	0.3841	0.9566	2409.81		-12.69
313	3.194	0.75	1.09	0.3775	0.9739	2534.36		-12.68
323	3.095	0.73	1.08	0.3704	0.9930	2666.62		-12.70
333	3.003	0.71	1.07	0.3638	1.0110	2799.01		-12.72

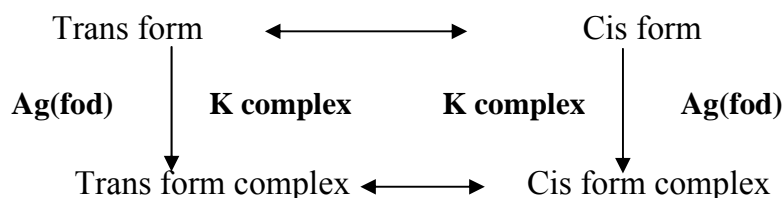
* average value of ΔS = -12.72

Comp. 9

Temp. K ^o	1/T x 10 ⁻³	A ₂	A ₁	K ₂ M ⁻¹	-ln K ₂	ΔG J/mole	ΔH J/mole	ΔS J/mole
293	3.412	0.94	1.190	0.1025	2.2772	5547.26	-2060.37	-25.96
303	3.300	0.92	1.190	0.1004	2.2976	5787.98		-25.90
313	3.194	0.91	1.185	0.0997	2.3054	5999.30		-25.74
323	3.095	0.88	1.180	0.0968	2.3345	6269.11		-25.78
333	3.003	0.85	1.180	0.0936	2.3687	6557.89		-25.88

• average value of ΔS = -11.67

The positive value of ΔG⁰ indicate that the equilibrium prefers the backward transformation (cis complex back to trans see scheme 2). The negative values of ΔS⁰ indicate that the complex form is more ordered (more rigid).



Scheme (2)

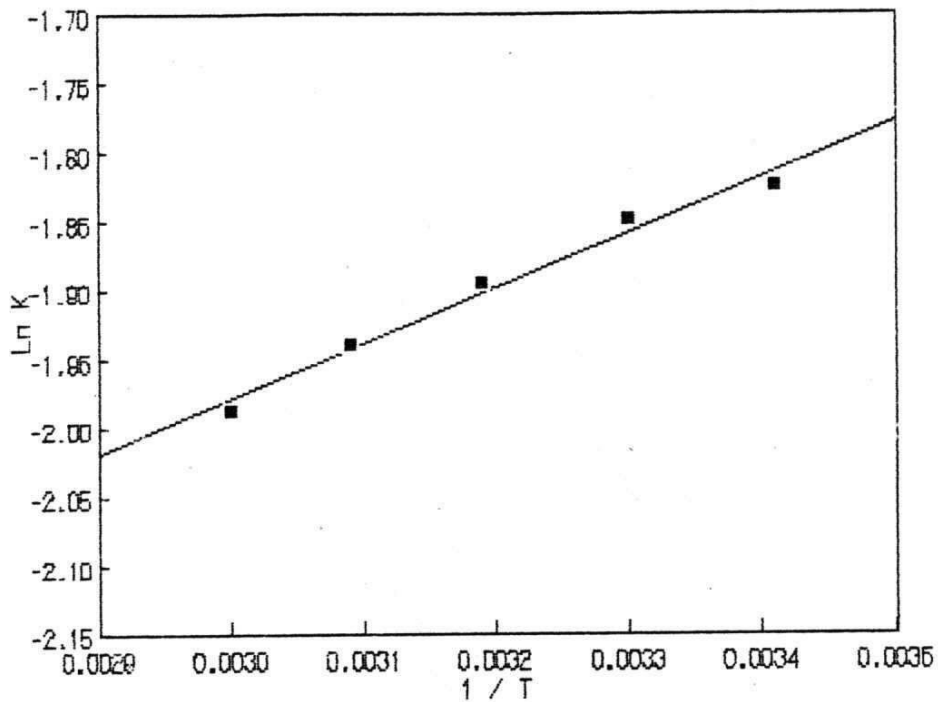


Fig. 3: Plot of $\ln K$ vs. $1/T$ for cinnamylideneaniline with $\text{Ag}(\text{fod})$ in CCl_4 .

Stoichiometry (complex formation) of cinnamylideneaniline (1) with $\text{Ag}(\text{fod})$:

In addition to the splitting of the main band into two bands which was observed on adding $\text{Ag}(\text{fod})$, a blue shift for the band A_1 to the shorter wave length and a red shift for the band A_2 to the longer wave length was also observed. The plot of frequency shift ($\Delta\nu$) against the added amount of $\text{Ag}(\text{fod})$ shows a linear correlation which have been obtained for both A_1 and A_2 (Figure 4).

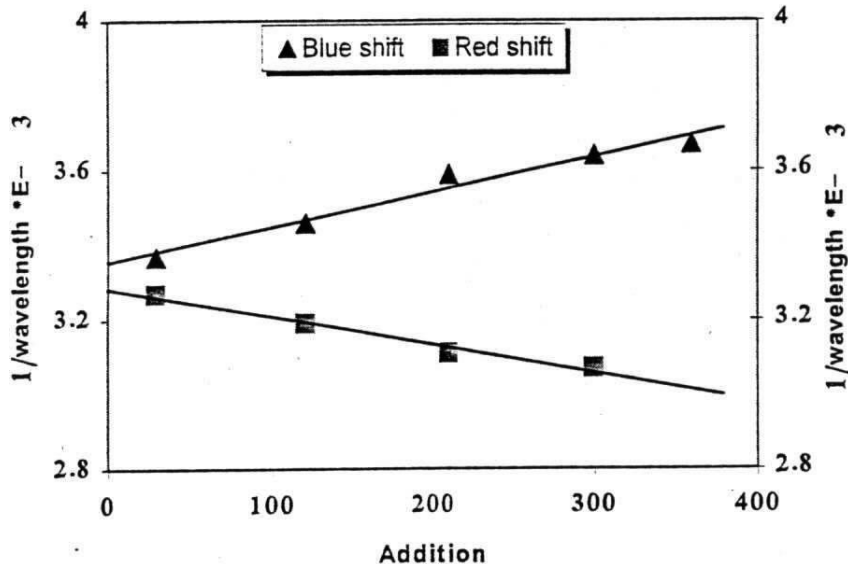


Fig. 4: Plots of frequency shift ($\Delta\nu$) against additions of $\text{Ag}(\text{fod})$ of cinnamylideneaniline for both bands (A_1 and A_2).

The slope of the plot for both bands A_1 and A_2 was found to be (9×10^{-7}) . This result indicates that both bands A_1 and A_2 show similar effect on complexation with $\text{Ag}(\text{fod})$. In order to find the stoichiometry of these complexes a plot of $A_0 - A / [\text{Ag}(\text{fod})]^n$ against A [where A_0 = the absorbance of the Schiff base at a particular wave length in the absence of $\text{Ag}(\text{fod})$], the absorbance in the presence of $\text{Ag}(\text{fod})$] was obtained with a linear correlation when $n=1$ (Fig. 5) which represent the no. of $\text{Ag}(\text{fod})$ molecules involved in the complex.

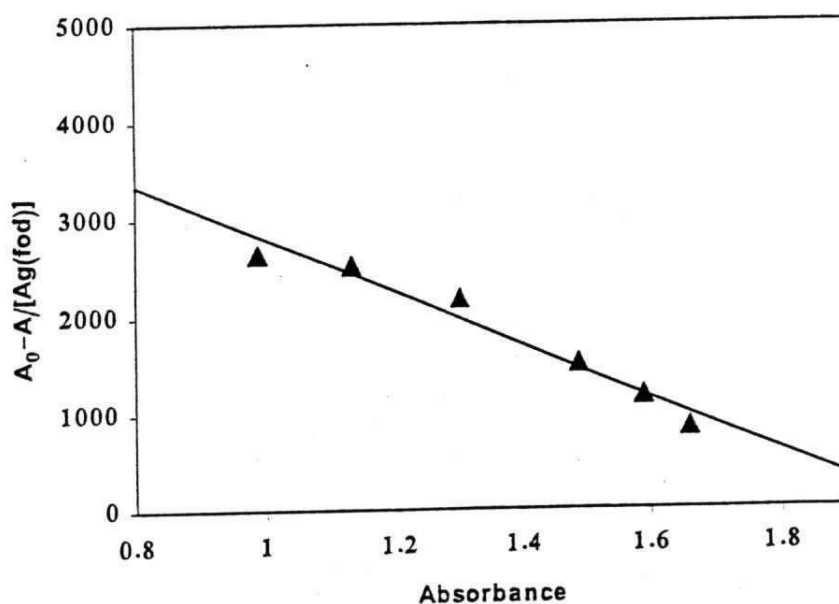


Fig. 5: Plots of $(A_0 - A) / [\text{Ag}(\text{fod})]$ against absorbance for cinnamylideneaniline in CCl_4 at 293 K° .

CCl_4

REFERENCES

- M. Anteunis and A. DeBryne, *J. Magn. Res.* 8, pp.7-14 (1972).
 L. M. N. Saleem, A. Y. Al-Razzak, *Raf. J. Sci.* 3, 8-14, 2000.
 L M N. Saleern and A. S. Authman, *Spec Lett.* 25, 799-809(1992), *Spectr. Lett.* 25, 799-809 (1992).
 L. M. N. Saleern, *J. Ed. Sci.* 26,63-71(1997).
 L. M. N. Saleern and A. O. Ornar, *Iraq. J. Sci.*, 30, 9-16 (1989).
 L. M. N. Saleem and A. Y. Al-Razzak, *Raf. J. Sci.* 10, 12-16 (1999).
 S. T. Sulaiman, L. M. N. Saleern, A. S. Authman, *Iraq. J. Chem.*, 24, 49-53 (1998).
 M. A. El-Bayotimi, M. EJ-Asser and F. Abdel-Halirn, *J. Am. Chem. Soc.*, 93, 586-590 (1971).
 M. Belletete and G. Durocher, *Can. J. Chern.*, 60, 2332-2339 (1982).
 K. O. Hartman, g. L. Cariso, R. E. Witkowski and W. G. Fateley, *Spectrochimica Acta*, Vol. 24A, 1 57-167(1968).