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Study of Charge-Transfer Complexes of Salicylideneanilines with $Eu(fod)_3$ in Carbon Tetrachloride by U.V. Spectroscopy

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ABSTRACT

Salicylideneanilines in CCl_4 form 1:1 charge transfer complexes with $Eu(fod)_3$, indicated by the observation of a new longer wavelength band (~435 nm).

Equilibrium constant values (K) for the complexes were obtained by applying Benesi-Hildebrand equation at different temperatures. The thermodynamic parameters ΔH, ΔS and ΔG of the complex formation were determined at these temperatures.

دراسة معقدات الشحنة المنتقلة لتداخل قواعد شيف الساليسايلادين انيلين مع $Eu(fod)_3$ في رابع كلوريد الكاربون

الملخص

ادى تفاعل مركبات الساليسايلادين انيلين ومعوضاته مع كاشف الازاحة اللنثاني $Eu(fod)_3$ في مذيب رابع كلوريد الكاربون الى تكوين معقدات الشحنة المتنقلة الذي يترافق مع ظهور امتصاص لموجة جديدة عند الطول الموجي الاعلى (حوالي 435 نانوميتر).

تم حساب قيم ثوابت الاتزان (K) للمركبات المعقدة بالاستعانة بمعادلة بنسي- هيلدبراند عند درجات حرارية مختلفة. ثم تم حساب المتغيرات الثرموداينميكية ΔH، ΔS وكذلك ΔG لتكوين المركب المعقد عند هذه الدرجات الحرارية.

INTRODUCTION

The effect of $Eu(fod)_3$ and other lanthanide shift reagents on the UV spectra of cinnamylideneanilines (Sulaiman et al., 1998; Saleem et al., 1999), cinnaniylidenealiph-aticamines (Sulaiman et al., 1997), benzylideneanilines and benzylideneamin o-pyridines and (Saleem et al., 1996; Sulaiman et al., 1993 and Saleem et al., 2001), salicylidenealiph-aticamines (Saleem et al., 2005) was investigated. This effect resulted in splitting of the U.V absorption bands of the cinnamylideneanilines, cinnaniylidene-aliphaticamines, benzylidene- anilines and Benzylideneaminopyridine into two well-defined bands which are explained as being due to cis-trans isomerization of Schiff base molecules, and the formation of charge transfer complex with Salicylidene-aliphaticamine indicated by the appearance of new band at longer wavelength ($\lambda \simeq 430$ nm).

The aim of this work is to study the effect of Eu(fod)$_3$ on the UV spectra of a series of prepared salicylideneanilines in carbontetrachloride.

EXPERIMENTAL

The Schiff bases prepared and studied are:

1. Salicylideneaniline.
2. Salicylidene p-ethylaniline.
3. Salicylidene p-methylaniline.
4. Salicylidene p-methoxyaniline.
5. Salicylidene p-chloroaniline.
6. Salicylidene p-bromoaniline.
7. Salicylidene m-methoxyaniline.
8. Salicylidene m-chloroaniline.
9. Salicylidene m-bromoaniline.
10. Salicylidene m-nitroaniline.
11. Salicylidene o-methoxyaniline.
12. Salicylidene o-bromoaniline.
13. Salicylidene o-chloroaniline.

All anilines and salicylaldehyde are of pure type and were used as freshly distilled for liquid compounds.

Compound Preparation:

Salicylideneaniline was prepared by warming equimolar amounts of freshly distilled aldehyde and aniline in methanol (EL-Bayoumi et al., 1971). The product was recrystallized several times from alcohol. In the same way, the para- and meta-substituted aniline schiff bases were prepared except that the ortho-substituted aniline Schiff bases require a reflux for long time (few days). The solution was then cooled to precipitate the product and vacuum dried.

Instrumentation:

The UV absorption spectra were recorded using SP 800 UV spectrophotometer (Unicam) connected with Haake thermostat type 000-4526 for temperature regulation, using 1×1×4 cm silica cells.

Measurements:

A stock solution of 10^{-2}M of each Schiff base and a stock solution of 10^{-2}M Eu(fod)$_3$ were prepared in CCl$_4$.The UV spectra of schiff bases were recorded, the spectrum showed three absorption maxima in the range of 232-240, 269-275 and 341-346 nm. The spectra were recorded for samples with the optimum concentration of the schiff base which was fixed experimentally. To this solution, successive additions (10, 20, 30,……µl) of 10-2M Eu(fod)$_3$ were performed.

Complex Formation:

To prepare the complex between the Schiff base and Eu(fod)$_3$ in CCl$_4$, 500µl of 10^{-2}M Schiff base was made 3ml total volume with CCl$_4$ and successive additions (10, 20, 30, 40 and 50 µl) of 10-2M Eu(fod)$_3$ to both sample and reference cells, the absorbance of the new band (Acom.) was measured.

Nature of Complexes:

The nature of the complexes were determined by Job method (a model shown below); it was found that the ratio of Schiff base to Eu(fod)$_3$ is 1:1.

ml 10^{-2}M salicylidene *p*-methylaniline	0.05	0.1	0.15	0.2	0.25
ml 10^{-2}M Eu(fod)$_3$	0.25	0.2	0.15	0.1	0.05
Absorbance	0.85	1.43	1.595	1.52	0.91

Determination of K-value:

To estimate K values, Benesi-Hildebrand equation was applied (Benesi and Hildebrand, 1949). [Ao]/Acom.= 1/ε +1/(K .ε) . 1/[Do]

[Do] : the molar concentration of Schiff base.

[Ao] : the molar concentration of Eu(fod)$_3$.

Acom. : Absorbance of the complex.

The plot of [Ao]/Acom.against 1/[Do] resulted a straight line and from the intercept =1/ε, ε the molar extinction coefficient of the complex was calculated. From the slope 1/(K.ε), the equilibrium constant K-value of the complex was evaluated.

RESULTS AND DISCUSSION

The UV absorption spectra of various amounts of 10^{-2}M per 3ml solution of salicylideneanilines compounds in CCl$_4$ showed absorption maxima at about 271-276 nm and the two other peaks of about 234-242 and 342-350 nm. The UV absorption spectrum of Eu(fod)$_3$ in CCl$_4$ showed absorption band at 295 nm. (Fig 1).

Successive additions of 10^{-2}M solution of Eu(fod)$_3$ in CCl$_4$ to a solution of salicylideneanilines caused a gradual decrease in the intensity of the observed bands of the whole Schiff base spectrum, accompanied by a gradual appearance of a new longer wavelength band at about 435-440 nm. The intensity of this band which is attributed to the charge transfer complex formation between the Schiff base and the Eu(fod)$_3$ increases as the amount of Eu(fod)$_3$ increased, (Fig. 2).

Complexes of compounds (1-13) with Eu(fod)$_3$ in CCl$_4$ were obtained as mentioned in the experimental part of this work. The absorbance of the formed complex band was measured and the equilibrium constant (K) values were calculated at 293, 303, 313 and 323 ^{o}K by the application of Benesi-Hildebrand equation. The results were shown in table (1).

Table 1 : The calculated equilibrium constant, molar extinction coefficient and λmax values of complexes of salicylidene anilines with Eu(fod)$_3$ at 20^{o}C.

Complex of compound	K (mole-1) at 20^{o}C	ε (lit.mole-1.cm-1)	λmax (nm)
S.A	585	170	435
S.p-Me.A	586	182	436
S.P-Ethyl.A	586	177	436
S.p-MeO.A	595	89	436
S.p-Cl.A	590	131	438
S.p-Br.A	588	73	440
S.m-MeO.A	584	162	435
S.m-Cl.A	597	80	436
S.m-Br.A	642	82	437
S.m-NO$_2$.A	295	54	440
S.o-Cl.A	597	44	423
S.o-Br.A	297	39	434
S.o-MeO.A	586	394	435

The low values of ε(<1000) together with the low intensity and long wavelength confirms this band to be n → π⋆ transition type and the interaction of Eu(fod)$_3$ with the Schiff base to be accomplished through the lone pair electrons of nitrogen or nitrogen and oxygen.Thus the availability of these electrons mainly affect the K-value of the complex.

The effect of temperature:

To evaluate the thermodynamic parameters for the complex formation between these Schiff bases and Eu(fod)$_3$, the equilibrium constants (K) had to be calculated at different temperatures (293, 303, 313 and 323 ^{o}K).

The enthalpy change ΔH was calculated using the Vant-Hoff equation by plotting logK versus 1/T where straight lines were obtained, and the

$$\text{slope} = -\Delta H/(2.303R)$$

hence ΔH was obtained. The value of ΔG was calculated from the equation $\Delta G = -RT\ln K$ while ΔS was obtained from the Gibbs equation

$$\Delta G = \Delta H - T\,\Delta S$$

The results were shown in table (2).

Table 2: Calculated thermodynamic parameters of the complexes of salicylideneanilines Schiff bases with Eu(fod)$_3$ in CCl$_4$ at different temperatures.

Complex of compound	**T(°K)**	**K**	**ΔH (J.mol-1)**	**ΔS (J.mol-1.K-1.)**	**ΔG (J.mol-1)**
S.A	293	585	-3181.738	42.139	-15528.383
	303	576		42.361	-16017.155
	313	548		42.284	-16416.729
	323	520		42.157	-16798.348
S.p-Me.A	293	586	-3149.331	42.270	-15534.402
	303	583		42.567	-16047.182
	313	579		42.842	-16558.812
	323	514		42.158	-16766.252
S.p-ethyl A	293	586	-1268.909	48.663	-15527.269
	303	584		48.774	-16047.680
	313	575		48.787	-16539.186
	323	557		48.654	-16984.171
S.p-MeO.A	293	595	-1055.406	49.527	-15566.786
	303	560		49.131	-15942.214
	313	491		48.149	-16126.115
	323	461		47.739	-16475.130
S.p-Cl.A	293	590	-502.644	51.341	-15545.622
	303	588		51.360	-16064.586
	313	587		51.393	-16583.777
	323	578		51.328	-17081.663
S.p-Br.A	293	588	-719.828	50.562	-15534.402
	303	585		50.605	-16052.982
	313	580		50.604	-16558.812
	323	572		50.560	-17050.741
S.m-MeO.A	293	584	-1002.408	49.548	-15519.890
	303	582		49.634	-16042.222
	313	581		49.724	-16566.026
	323	559		49.512	-16994.799
S.m-Cl.A	293	597	-727.376	50.670	-15573.673
	303	587		50.618	-16064.586
	313	589		50.675	-16588.777
	323	580		50.652	-17087.848
S.m-Br.A	293	642	-381.529	52.444	-15747.586
	303	638		52.449	-16273.443
	313	634		52.431	-16792.541
	323	633		52.450	-17322.860
S.m-NO2.A	293	295	-691.342	44.922	-13853.557
	303	290		44.870	-14287.032
	313	289		44.919	-14750.997
	323	286		44.910	-15197.237
S.o-MeO.A	293	586	-2978.372	42.578	-15453.581
	303	584		42.892	-15974.637
	313	560		42.834	-16385.514
	323	526		42.584	-16733.153
S.o-Cl.A	293	597	-437.112	51.661	-15573.673
	303	593		51.652	-16087.793
	313	589		51.641	-16600.764
	323	588		51.665	-17124.955
S.o-Br.A	293	297	-1039.144	43.801	-13872.869
	303	295		43.876	-14333.581
	313	291		43.870	-14770.419
	323	285		43.804	-15187.771

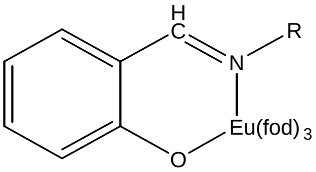
According to the estimated K-values,the calculation of the enthalpy change (ΔH) showed negative values (exothermic) and the temperature rise caused as expected a decrease in the K- values of the complexes and there was considerable agreement with these results.

The calculated entropy change (ΔS) showed positive values which indicated that an increase in the disorder on complexation with $Eu(fod)_3$ which could be explained as due to the possibility of intra and inter molecular hydrogen bonding in the salicylideneanilines Schiff base molecules before the complexation process which restricted the molecular freedom. On complexation a type of free molecular or part of the molecular motion persist that resulted in an increase in random and thus a positive ΔS value of the complex was obtained.

The calculated free energy change of the complex were negative values indicating the possible spontaneous process at the mentioned experimental conditions.

CONCLUSIONS

As a result it could be concluded that salicylideneanilines formed 1:1 charge transfer complexes with $Eu(fod)_3$ in CCl_4 and the complexation could be either through the nitrogen Lone pair electron or together with the Lone pair of oxygen of the hydroxyl group of salicylidene part of the Schiff base as suggested by the following expected structure of the complex.



According to the calculated thermodynamic parameter ΔH, ΔS and ΔG this process could occur spontaneously.

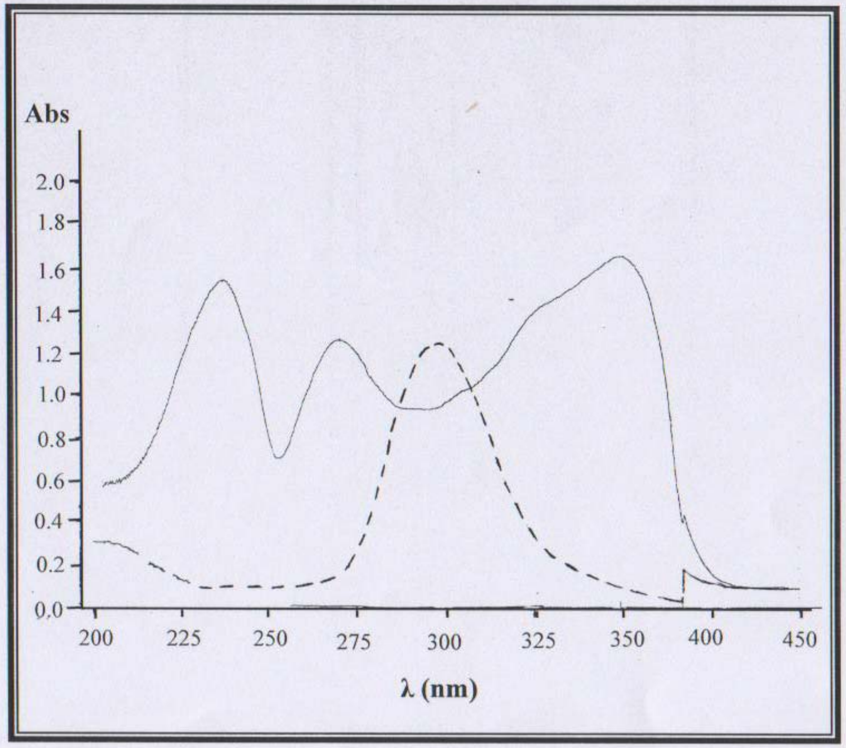


Fig (1): The U.V Spectrum of salicylidene-*p*-methoxy aniline (___) and Eu(fod)$_3$ (-----) in CCl$_4$

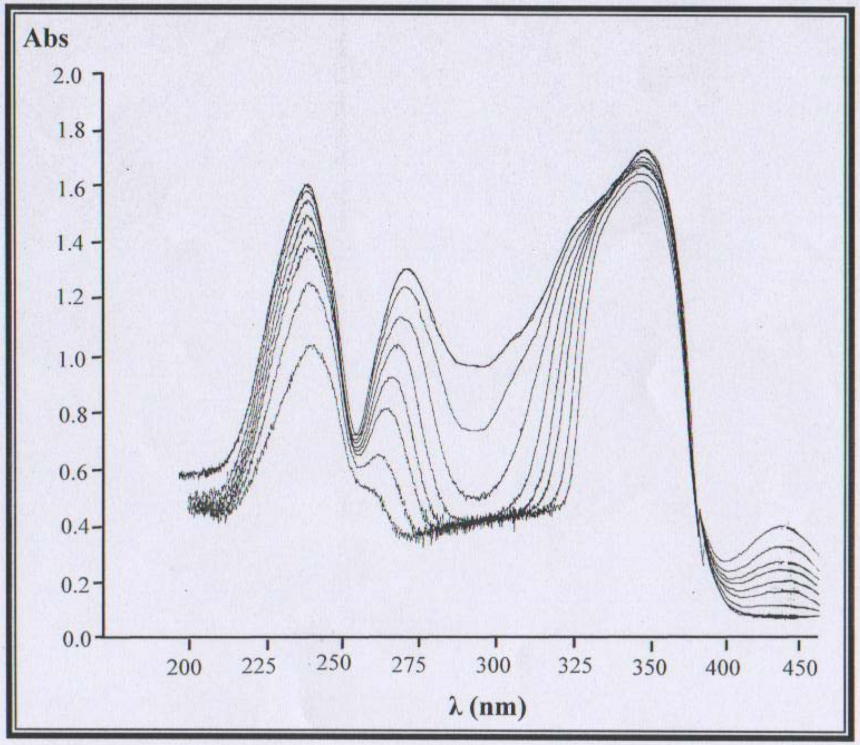


Fig (2): The effect at Eu(fod)$_3$ addition on the U.V Spectrum of salicylidene-*p*-methoxy aniline in CCl$_4$

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