

Study of Charge Transfer Complexes of Salicylideneanilines and its Substituents with Pr(fod)3 in Cyclohexane by U.V. Spectroscopy

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ABSTRACT

Salicylidene aniline and its substituents form 1:1 charge transfer complexes with the lanthanide shift reagent Pr(fod)3 in cyclohexane indicated by the observation of a new band in their U.V. spectra located at longer wavelength ($\lambda_{\text{max}} = 430 \text{ nm}$) and with its low extinction coefficient. The colourless solutions of Schiff's-bases were changed to yellow on complexation with Pr(fod)3.

Equilibrium constant values (K) for the complexes were calculated by applying Benesi-Hildebrand equation at different temperatures, and the thermodynamic parameters ΔH , ΔS and ΔG were obtained. Negative values of ΔG indicates that the complexation occurs spontaneously.

Application of Hammet equation on K values for the para substituents show straight line with negative slope indicating that the electron donating groups enhances the reaction of complexation.

Pr(fod)3

1:1

Pr(fod)3

430 nm

 ΔG $\Delta G, \Delta S, \Delta H$

k

INTRODUCTION

The effect of lanthanide shift reagents (LSR) on the U.V. spectra of Schiff's-bases has been reported. Benzylidene anilines (Sulaiman et al., 1993; Saleem and Al-Razzak, 1996), cinnamylidene anilines (Sulaiman et al., 1998; Saleem and Al-Razzak, 1999), benzylidene aliphatic amines and cinnamylidene aliphatic amines (Sulaiman et al., 1997), benzylidene amino pyridine (Saleem et al., 2001) were studied with the LSR Eu(fod)₃ [Tris (1, 1, 1, 2, 2, 3, 3-heptafluoro-7, 7-dimethyl-4, 6-octanedione) europium(III)]. This effect resulted in a splitting of the absorption bands in their U.V. spectra into two well defined bands, and was attributed to the interaction between the schiff-base and the LSR resulting in a cis-trans isomerization.

The concept of cis-trans isomerization of Schiff-bases on addition of LSR has been earlier confirmed by NMR studies (Saleem, 1982; Al-Rawi and Saleem, 1989; Saleem and Omer, 1994; Saleem and Al-Razzak, 2000). It was also reported that the LSR Eu(fod)₃ resulted in the formation of charge transfer complexes with salicylidene aliphatic amines (Saleem et al., 2005).

The aim of the present work is to study the effect of the LSR Pr(fod)₃ on the U.V. spectra of a series of salicylideneanilines in cyclohexane. For this purpose the following compounds has been chosen.

1. Salicylidene aniline.
2. Salicylidene-*p*- methyl aniline.
3. Salicylidene-*p*- ethyl aniline.
4. Salicylidene-*p*- methoxy aniline.
5. Salicylidene-*p*- bromo aniline.
6. Salicylidene-*p*- chloro aniline.
7. Salicylidene-*m*- methoxy aniline.
8. Salicylidene-*m*- bromo aniline.
9. Salicylidene-*m*- chloro aniline.
10. Salicylidene-*o*- methoxy aniline.
11. Salicylidene-*o*- bromo aniline.
12. Salicylidene-*o*- chloro aniline.

EXPERIMENTAL

Salicylidene anilines were prepared (El-Bayoumi et al., 1971) by mixing equimolar amounts of purified anilines and salicylaldehyde in ethanol, the mixture was warmed for few minutes then left to cool. The product was recrystallized several times from alcohol.

Instrumentation:

The U.V. absorption spectra were recorded using Shimadzu U.V.-160 spectrometer and SP 800 U.V. spectrophotometer (unicam) connected with Haake thermostat type (000-4526) for temperature regulation, using 1 x 1 x 3 cm³ matched silica cells.

Measurement:

A stock solution of 10⁻² M of the Schiff-base and a stock solution of 10⁻²M Pr(fod)₃ were prepared in cyclohexane. The U.V. spectra of salicylideneanilines show three absorption maxima in the range: 234-236, 269-272 and 340-347 nm, these spectra were recorded for samples containing the optimum concentrations of the Schiff-base which is fixed experimentally. To this solution successive additions of 10⁻² M of Pr(fod)₃ were performed.

Complex formation:

To prepare the complex between the Schiff-base and Pr(fod)₃ in cyclohexane, a certain volume of 10⁻²M of the Schiff-base (500, 800 or 1000 μl) was taken, successive volumes (50, 60, 70, 80, and 90 μl) of 10⁻²M Pr(fod)₃ were added in a total volume of 3ml. The u.v. spectra were measured against a reference blank of which the same volumes of Pr(fod)₃ were added.

The nature of complex:

The nature of the complex was determined by Job method. It was shown that the ratio of the Schiff-base to Pr(fod)3 is 1:1 .

Determination of k value:

K-values were estimated according to Benesi-Hildebrand equation (Benesi and Hildebrand, 1949) :-

$$\frac{[A_o]}{A_{com}} = \frac{1}{\varepsilon} + \frac{1}{k\varepsilon} * \frac{1}{[D_o]}$$

[Ao] : The molar concentration of Pr(fod)3.

[Do] : The molar concentration of the salicylidene aniline.

Acom : is the absorbance of the complex.

Plots were performed between $\frac{[A_o]}{A_{com}}$ against $\frac{1}{[D_o]}$, straight lines were obtained. From the

slope ($\frac{1}{k\varepsilon}$), the equilibrium constant k value of the complex was evaluated, and from the

intercept ($\frac{1}{\varepsilon}$), ε value (the molar extinction coefficient of the complex) was calculated.

The Thermodynamic parameters:

The enthalpy change (ΔH) was calculated from Vant-Hoff equation by plotting $\log K$ vs. $1/T$, from the (slope = $\frac{-\Delta H}{2.303R}$), ΔH was obtained.

ΔG was calculated using the equation: $\Delta G = -RT \ln K$

ΔS was obtained from Gibb's equation: $\Delta G = \Delta H - T\Delta S$

RESULTS AND DISCUSSION

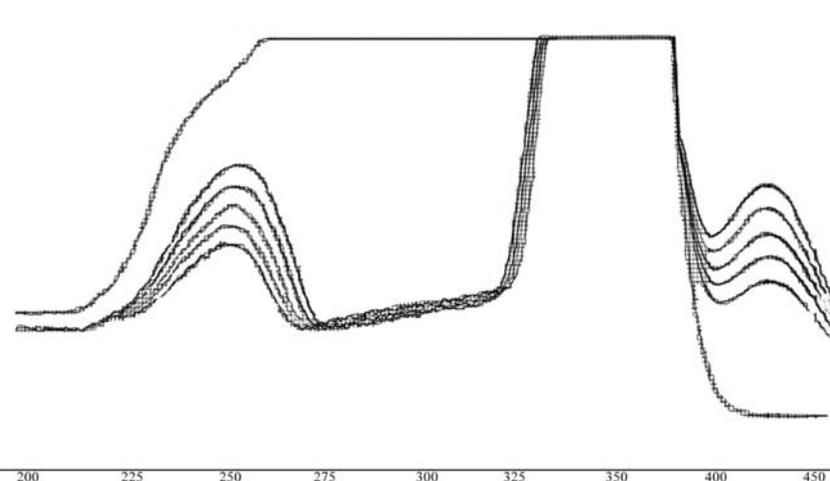
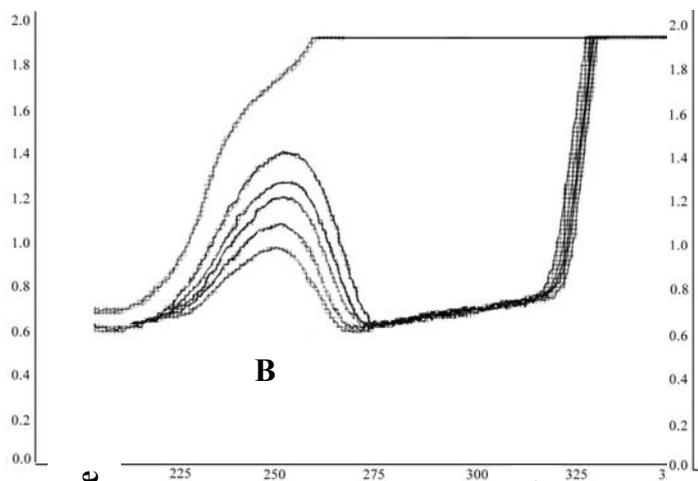
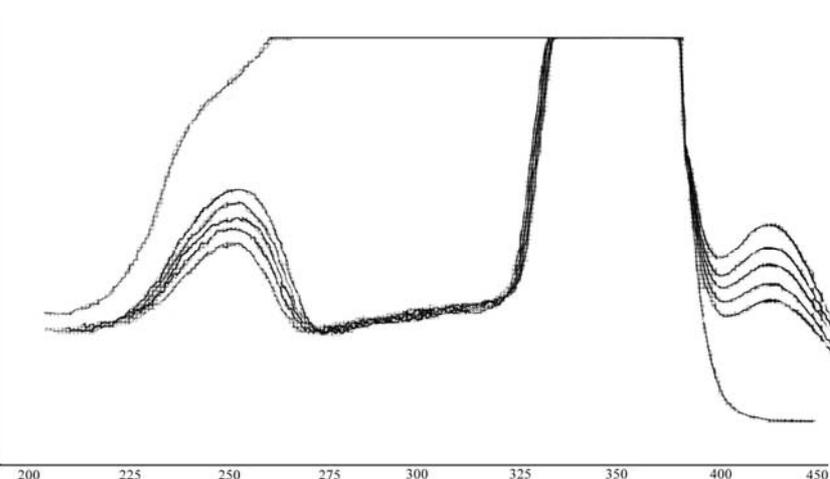
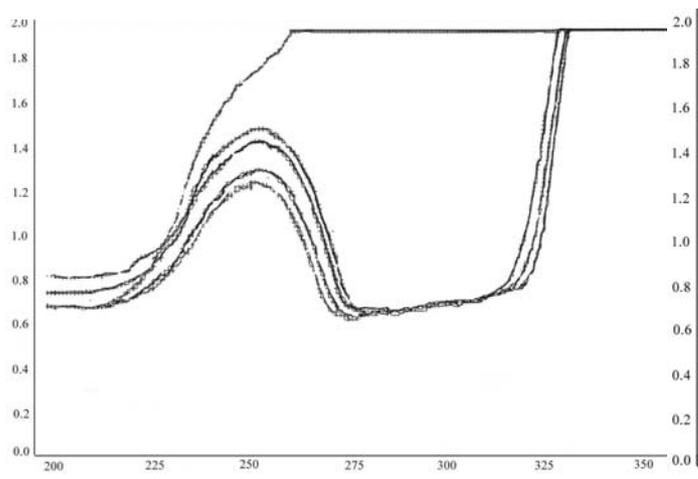
The U.V. absorption spectrum of 10⁻²M solution of salicylidene in cyclohexane show a maximum absorption at 270 nm and two other maxima at 236 nm and 340 nm. Successive additions of 10⁻²M solution of Pr(fod)3 in cyclohexane to the solution of salicylideneaniline caused a gradual decrease in the intensity of the whole spectrum accompanied by a gradual appearance of a new band at $\lambda_{max} = 430$ nm (see Fig. 1A). The intensity of this band increases with increasing the amount of the shift reagent.

Compounds 2 to 12 has also been studied with Pr(fod)3, their U.V. spectra show new bands at maxima ranging between 430-433 nm.

The initial molar concentration of the donors (salicylidene anilines), the acceptor [Pr(fod)3] and the measured absorbance of the complexes formed (A com.) are given in Table 1 (A, B and C) for compounds (1 to 4), 5 and 6, (7 to 12) respectively.

Plots were performed between [Ao/Acom.] vs. 1/[Do], according to Benesi-Hildebrand equation, and straight lines were obtained. K values were obtained from their slopes and ε max. values obtained from their intercepts. These values are tabulated in Table (2), for all complexes at 293 Ko.

From Table (2), it can be seen that ε max. values are all below 103 indicating that the complexes show n- π^* transition. It can also be seen that k values for the ortho substituted salicylidene aniline complexes are close except for the ortho methoxy aniline which has a lower value, similarly close values were obtained for the meta substituted complexes whilst for the para substituted complexes different values were obtained, but generally speaking, K values for the ortho and meta substituents are less than those for the para substituents.



5
4
3
2
1

B

← 1
← 2
← 3
← 4
← 5

← 5
← 4
← 3
← 2
← 1

T = 303 K^o

Wave length (nm)

D

Absorbance

← 1
← 2
← 3
← 4
← 5

← 5
← 4
← 3
← 2
← 1

T = 323 K^o

Wave length (nm)

Table 1: The measured absorbance of complexes of salicylidene anilines (1 to 12) on addition of different amounts of Pr(fod)₃ at 293K_o

(A)

[Do] x10 ⁻² schiff-bases	[Ao] x 10 ⁻⁴ Pr(fod) ₃	Acom.			
		1	2	3	4
0.1639	1.6393	0.74	0.69	0.72	1.02
0.1634	1.9608	0.86	0.78	0.85	1.20
0.1629	2.2801	0.99	0.84	0.95	1.36
0.1623	2.5974	1.09	0.90	1.07	1.49
0.1618	2.9126	1.20	0.98	1.18	1.62
Intercept * 1.300x10 ⁻³		4.69x10 ⁻³	4.55x10 ⁻³	1.30x10 ⁻³	1.30x10 ⁻³
Slope* 2.6416		8.06x10 ⁻⁶	7.85 x10 ⁻⁶	2.52x10 ⁻⁶	2.35x10 ⁻⁶
R* 0.9931		0.9795	0.9956	0.9700	0.9921

(B)

[Do] x10 ⁻²	[Ao] x10 ⁻⁴	Acom.	
		5	6
0.2623	1.6393	0.49	0.52
0.2614	1.9608	0.54	0.58
0.2606	2.2801	0.59	0.63
0.2597	2.597	0.63	0.69
0.2589	2.9126	0.68	0.73
Intercept		6.73x10 ⁻³	5.95x10 ⁻³
Slope		1.85x10 ⁻⁵	1.64x10 ⁻⁵
R*		0.9977	0.9960

(C)

[Do]x 10 ⁻² schiff-bases	[Ao] x10 ⁻⁴ Pr(fod) ₃	Acom.					
		7	8	9	10	11	12
0.3279	1.6393	0.82	0.45	0.43	0.62	a	0.27
0.3268	1.9608	0.89	0.50	0.46	0.70	0.29	0.29
0.3257	2.2801	0.97	0.54	0.50	0.80	0.30	0.30
0.3247	2.5974	1.07	0.58	0.54	0.86	0.31	0.31
0.3236	2.9126	1.17	0.62	0.57	0.96	0.32	0.32
0.3226	3.2258					0.33	
Intercept *		3.49x10 ⁻³	7.68x10 ⁻³	9.10 x10 ⁻³	2.70 x10 ⁻³	2.25 x10 ⁻³	2.13 x10 ⁻³
Slope*		1.21x10 ⁻⁵	2.63 x10 ⁻⁵	3.12 x10 ⁻⁵	9.90 x10 ⁻⁵	7.57 x10 ⁻⁵	7.20 x10 ⁻⁵
R*		0.9706	0.9980	0.9946	0.9685	0.9992	0.9989

a for compound 11 the started concentration of the Schiff base is (0.3268 x 10⁻²M)

Table 2: K values and ϵ max. values for Salicylidene aniline complexes after addition of $\text{Pr}(\text{fod})_3$ at 293 Ko

Compound No.	K (mol^{-1})	ϵ max. ($\text{l.mol}^{-1}.\text{cm}^{-1}$)
121	469	213
2	579	217
3	578	769
4	551	769
5	363	149
6	362	169
7	288	286
8	291	130
9	291	109
10	289	370
11	297	444
12	296	469

If a comparison is made for K values of the para substituted salicylideneanilines. It is noticed that these values are greater for the *p*-methoxy, *p*-ethyl and *p*-methyl substituents than those for the *p*-bromo and *p*-chloro substituents. This could be explained in terms of the electron donating power of the earlier one's which facilitate the interaction with $\text{Pr}(\text{fod})_3$.

Similar experiments were performed with $\text{Pr}(\text{fod})_3$ at different temperatures: 303, 313 and 323 Ko for salicylidene aniline see Fig. (1) (B to D) and for the other salicylidene anilines. Table (3) show k values for the complexes calculated at different temperatures. It can be seen that these values decrease with increasing the temperature except for compounds (3, 9 and 10). This decrease in K values is expected because increasing the temperature will cause dissociation of the complex which is formed.

Table 3: K-values for Salicylidene aniline complexes at different temperatures.

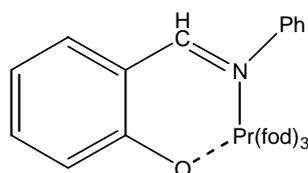
Comp. No.	K values at			
	293	303	313	323
1	469	458	433	417
2	579	573	550	545
3	578	575	565	560
4	551	546	539	532
5	363	356	351	349
6	362	359	355	353
7	288	274	267	262
8	291	289	287	284
9	291	292	295	296
10	289	278	275	270
11	297	296	295	291
12	296	295	294	292

Vant Hoff plots were performed between $\log K$ vs. $1/T$, straight lines were obtained from their slopes ΔH values were obtained. The average values of ΔH , ΔG and ΔS for the complexes are given in Table (4). From these values it can be seen that, ΔS has positive values, this increase in ΔS values may be attributed to the possibility of inter or intra hydrogen bonding in the salicylideneanilines before complex formation which result in a restriction of the molecular motion, ΔG values are negative indicating that reaction take place spontaneously.

Table 4: The average values of the thermodynamic parameters for the complexes of salicylideneanilines with the lanthanide shift reagent $\text{Pr}(\text{fod})_3$ in cyclohexane at different temperatures.

Comp. No.	ΔH (KJ.mole)	ΔS (J.mole ⁻¹ .K ⁻¹)	ΔG (KJ.mole ⁻¹)
1	-3.217	40.16	-14.98
2	-1.7937	46.81	-16.34
3	-0.866	49.87	-16.21
4	-0.9034	49.41	-16.12
5	-1.0410	45.44	-15.03
6	-0.6907	46.64	-15.05
7	-2.4422	38.28	-14.36
8	-0.6498	44.97	-14.50
9	0.4707	48.77	-14.55
10	-1.7323	41.20	-14.41
11	-0.5027	48.65	-14.56
12	-0.3599	46.95	-14.56

The results indicate that salicylidene anilines form 1:1 charge transfer complexes with $\text{Pr}(\text{fod})_3$ in cyclohexane and the complexation occur through the lone pair of electrons of nitrogen or through the lone pair of electrons of nitrogen together with the lone pair of oxygen of the hydroxyl group of salicylidene part of the Schiff base as shown in the following suggested structure.



This suggestion is supported by a previous study (Saleem et al., 2005) regarding the different factors affecting K values, using a multiple and linear regression equations, which show that the main two factors affecting K values are the charge on nitrogen and the charge on oxygen.

Finally, Hammett equation (Hammett, 1980) was applied on K values for the para substituted salicylidene anilines. Plot between $\log K$ vs. σ , Table (5), show straight line with negative slope see (Fig. 2), indicating that the interaction between salicylidene anilines with $\text{Pr}(\text{fod})_3$ is accelerated by the electron donating groups, since these groups increase the basicity of the compounds and thus result in stronger interaction with $\text{Pr}(\text{fod})_3$.

Table 5: Effect of Hammett substituents σ on the equilibrium constant of the C.T.C. of the para substituted salicylideneanilines with the lanthanide shift reagent $\text{Pr}(\text{fod})_3$ in cyclohexane at 293K° .

Compounds	σ	K	Log K
Salicylidene aniline	0	469	2.671
Salicylidene- <i>p</i> -methyl aniline	-0.17	579	2.763
Salicylidene- <i>p</i> -ethyl aniline	-0.15	578	2.762
Salicylidene- <i>p</i> -methoxy aniline	-0.27	551	2.741
Salicylidene- <i>p</i> -bromo aniline	0.23	363	2.560
Salicylidene- <i>p</i> -chloro aniline	0.23	362	2.559

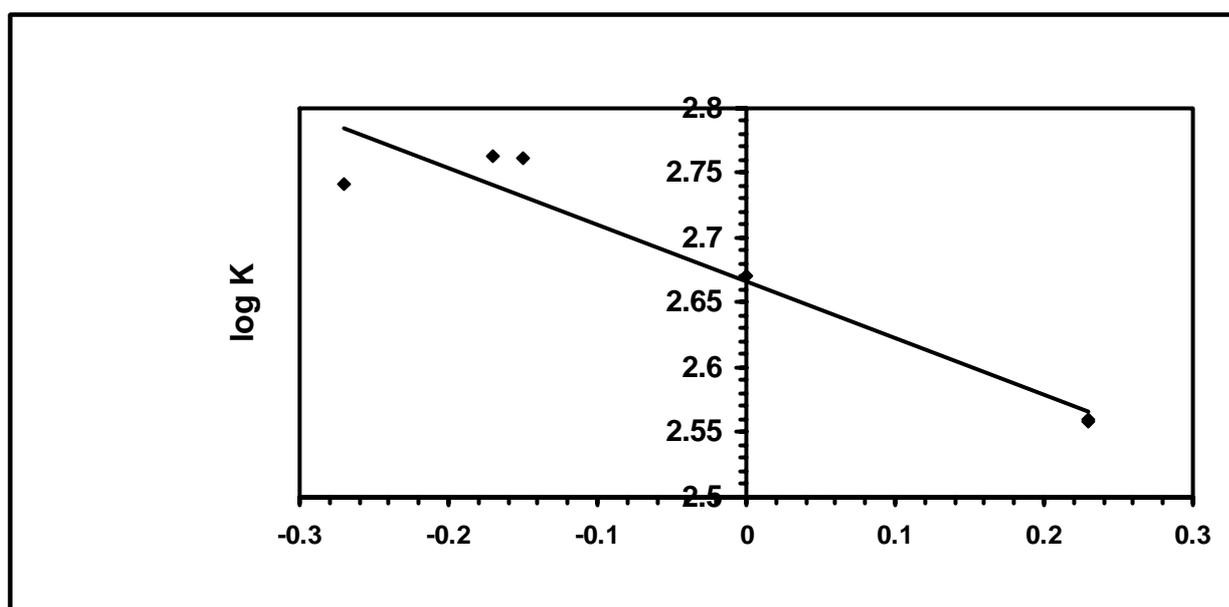


Fig. 2: plot of log K against σ for salicylidene aniline complexes, substituted in the para position, with $\text{Pr}(\text{fod})_3$ in cyclohexane

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