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Study on Association Between o-methoxy-benzylidene-p-aminoaniline with phenols

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Abstract

The interactions of o-methoxy-benzylidene-p-aminoaniline (MBAA) with phenol, p-methoxyphenol ,and p-chlorophenol in n-hexane are studied by using UV spectroscopy . The study led to the formation of hydrogen bond species of types O – H·····O and O – H ····· N between MBAA with phenol and p-methoxyphenol . The last is appeared from the UV spectra record of MBAA with phenols stated at relative concentrations ratio of phenol / MBAA and p-methoxy phenol / MBAA of values 4/1 and 4/1 respectively. Similar result is obtained on using p-chlorophenol at relative concentration ratio of p-chlorophenol / MBAA of a value 4/1 , with additional appearance of two UV protonated bands at a wavelengths of 463 nm and 474 mm . These can be of type nitrilium ion $\overset{|+}{\underset{|}{-N-}}$ H or oxonium ion $\underset{\overset{|}{H}}{-\overset{\bullet\bullet+}{O}-}$,or both of them . The equilibrium constants for hydrogen bond formations of MBAA with phenols stated are included . The interactions of systems under study are confirmed by thermodynamic method . These show that $\overline{\Delta H}$ and $\overline{\Delta S}$ have a negative signs , as well as their values which support hydrogen bondings . Moreover , the processes of non spontaneous hydrogen bonding as observed and evident from the positive values of $\overline{\Delta G}$ are included . These final abnormal results are unexpected and discussed in details .

الخلاصة

يتضمن البحث دراسة تداخلات MBAA مع الفينول ، بارا ميثوكسي فينول وبارا كلورو فينول في مذيب الهكسان وبأستعمال مطيافية UV . اكدت الدراسة على تكوين اواصر هيدروجينية بنوعي O – H·····O و O – H ····· N بين MBAA مع الفينول ومشتقاته . الاواصر الهيدروجينة المذكورة توأ ظهرت من اطياف UV المسجلة للمركب MBAA وبنسب تراكيز 1/4 . بارا كلورو فينول اظهر نتائج متشابهة وعند نفس نسبة التركيز المذكورة مع ظهور حزمتي برتنة اضافية عند الاطوال الموجية 463nm

و 474 nm واللتان تعودان الى ايوني النتريليوم والاوكزونيوم . كما تضمن البحث تعيين ثوابت التوازن التداخلات المذكورة بين MBAA والفينولات والمثبتة بالطريقة الثرموديناميكية . دللت الاخيرة على أن اشارات $\overline{\Delta H}$ و $\overline{\Delta S}$ هي سالبة بأضافة الى قيمها والمؤكدة للاواصر الهيدروجينية بين الجزيئات المتداخلة . اشتمل البحت على حساب $\overline{\Delta G}$ والذي يؤكد ان التفاعل المذكور غير تلقائي . النتيجة الاخيرة كانت غير متوقعة ونوقشت بأسهاب .

Introduction

A survey of literature (1) reveals that association reactions are very important in DNA molecules and other polymeric systems . These may result in an increase in the stability (2) of many systems , change in absorption spectra (3-5) and other physico-chemical properties (2) .

It was expected that UV-visible spectrum of a molecule may be altered by formation of hydrogen bond , if a chromophore in a molecule is perturb by the hydrogen bond (6) .

In the last two decades , several studies (4,5,7-10) , were performed in our laboratory in the field of hydrogen bonding . Among them the thermodynamic and UV studies of association reaction between phenols and benzil mono benzylidene aniline (4), the thermodynamic study (8) of interaction of benzil di Schiff base with phenol and the UV absorption spectra of cinnamylidene n-butylamine (9) . These studies were showed that a hydrogen bond formation in these systems were accompanied by UV spectral changes .

The present investigation is an extension of the last three studies it deals with effect of phenol , p-methoxyphenol and p-chlorophenol on the UV absorption spectrum of o-methoxy-benzylidene-p-aminoaniline in n-hexane .The study includes the thermodynamic method for the investigation of a type of interaction in systems under study . This may open another subsequent future works on another studies .

Experimental

All chemicals used throughout this work are supplied from Fluka origin . They were used as supplied without any further purification , with an exception of phenol and o-anisaldehyde . The last were purified by distillation . Pure phenol and o-anisaldehyde have b.p 's of 70°C (12 torr) and 243 °C (760 torr)respectively .

Crude n-hexane was purified by standard method (11) . o-Methoxybenzylidene-p-amino-aniline was synthesized by standard method (4). Recrystillization of the product is performed in ethanol . Pure product has a m.p of 144 °C . The UV spectra are measured using Shimadzu UV – visible – 160 by using matched 1*1*3 cm^{3} . All UV spectra were measured against phenolic blank solutions . Also the IR spectrum of solid MBAA was measured by using computerized Tensor -27 and by KBr disk method. The linear plots were performed by using Excel computer program .

Results and Discussion

The IR spectrum of pure solid MBAA sample, shows a bands at wavenumbers values of 1102.83 (s) , 1599.35 (s) , 1615.36 (s) and 3400.74 (b) . They are assigned to the stretching frequencies of ether linkage, the aromatic ring , the azomethine group HC = N and the hydrogen bonding group of types O — H ….O or O — H ….N respectively . These confirm the chemical structure of MBAA .

The preliminary UV spectrum of 10^{-3} M MBAA in n-hexane is shown in Fig. 1, it shows a four bands at wavelengths values of (λ) nm with molar extension coefficient (ε) values . Similarly the UV spectrum of 10^{-3} M phenol in the same solvent shows two bands only . These results are collected in Table 1 .

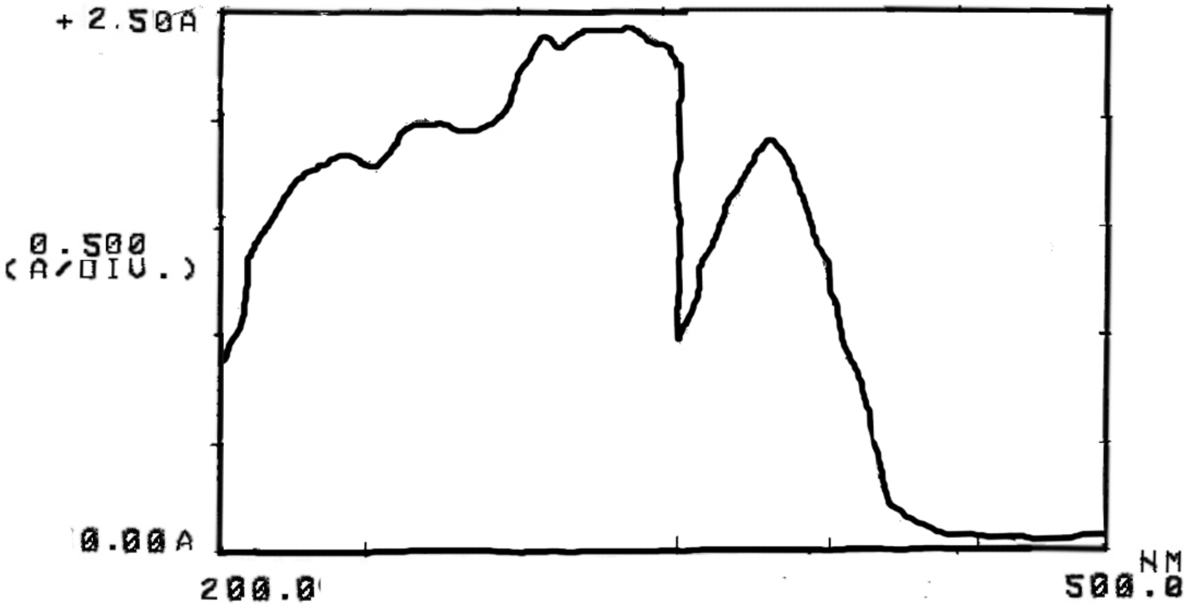


Fig.1 The UV spectrum of 10^{-3}M MBAA in n-hexane

Table 1 The UV spectra of 10^{-3} M MBAA and phenol in n-hexane

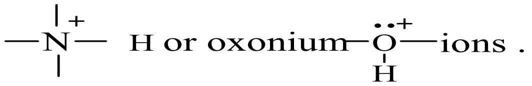
Compound	λ (nm)	ε (liter.mole^{-1}.cm^{2})
MBAA	382.5	1866
	331.5	2448
	264.5	1993
	239.5	1817
Phenol	261	1641
	219	1061

Table 2 Influence of excess phenols concentrations on the UV absorption spectra of 10^{-5} M MBAA in n-hexane

Phenols	Conc. Of MBAB (M)	Conc. Of phenol	Relative conc.	Wavelengths nm	Absorbance A	Relative absorbance
Phenol	10^{-5}	10^{-5}	1:1	367 347	0.026 0.027	0.96
	10^{-5}	2x10^{-5}	2:1	367 348	0.059 0.059	1.0
	10^{-5}	3x10^{-5}	3:1	364 349	0.109 0.125	0.872
*	10^{-5}	4x10^{-5}	4:1	365 347	0.097 0.125	0.78
	10^{-5}	5x10^{-5}	5:1	367 348	0.064 0.068	0.94
	10^{-5}	6x10^{-5}	6:1	365 348	0.074 0.081	0.91
	10^{-5}	7x10^{-5}	7:1	364 345	0.071 0.074	0.95
	10^{-5}	8x10^{-5}	8:1	365 348	0.065 0.071	0.91
p-methoxy phenol	10^{-5}	10^{-5}	1:1	367 347	0.093 0.097	0.95
	10^{-5}	2x10^{-5}	2:1	367 347	0.095 0.086	1.10
	10^{-5}	3x10^{-5}	3:1	367 347	0.09 0.09	1.0
*	10^{-5}	4x10^{-5}	4:1	367 347	0.039 0047	082
	10^{-5}	5x10^{-5}	5:1	367 347	0.055 0.055	1.0
p-chloro phenol	10^{-5}	10^{-5}	1:1	363 347	0.158 0.177	0.89
	10^{-5}	2x10^{-5}	2:1	364 348	0.141 0.165	0.85
	10^{-5}	3x10^{-5}	3:1	362 348	0155 0.182	0.85
*	10^{-5}	4x10^{-5}	4:1	360 348	0.151 0.221	0.68

Relative absorbance is estimated by diving absorbances of longer wavelength band by shorter wavelength .

The influence of excess different concentrations of phenol on the UV absorption spectra of 10^{-5} M MBAA in n-hexane are studied , by preparing a set of solutions containing a fixed concentration of MBAA and a variable excess quantities of phenol , or phenols , having a relative range ratio values between 1:1 – 8:1 . Then after the UV spectra for these eight solutions are measured versus phenolic blank for each mixture . The results obtained from such studies are collected in Table 2 . It is cleared from Table 2 that mainly two UV bands at longer wavelengths of range wavelengths values between (345 – 348) nm and (364 – 367) nm are obtained , beside other bands seen at shorter wavelength is seen in Fig 1 . These two bands mentioned are abbreviated A_1 and A_2 respectively . The lower relative absorbance ratio value of 0.78 for the bands mentioned are observed when the relative concentration of phenol \MBAA has a value of 4:1 as in Table 2 .The last is considered here , to represent the optimum condition for obtaining a greater UV changes , as compared with same UV band of MBAA listed in Table2 and with whole spectrum of MBAA seen in Fig 1 . Similar results are obtained by replacing p-methoxyphenol and p-chlorophenol in stead of phenol on the UV absorption spectra of MBAA with a maximum UV changes are obtained when relative concentrations of last phenols have a values of 4:1 and 4:1 respectively . Also the UV spectrum of MBAA is the presence of p-chlorophenol is resulted to the additional appearance of two weak absorptions at longer wavelengths values of 463 nm and 474 nm in n-hexane.They are assigned(4,12-13) to the nitrilium



$-\overset{|\,+}{\underset{|}{N}}-$ H or oxonium $-\overset{\cdot\cdot +}{\underset{H}{O}}-$ ions .

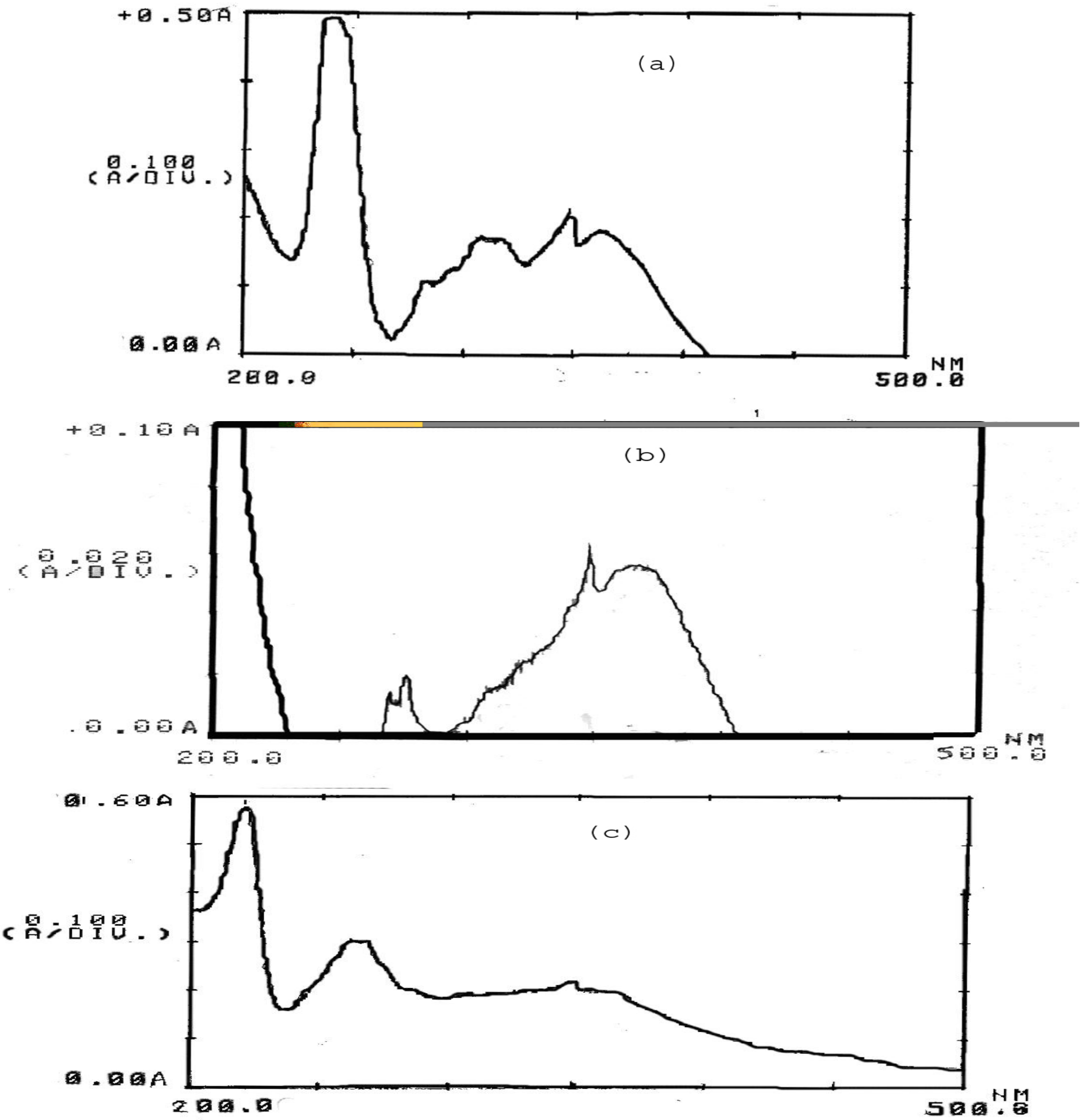


Fig.2 The UV absorption spectrum of 10^{-3}M BMAA in n-hexane after addition Of:

a- Phenol
b- P-methoxy phenol
c- P- chlorophenol

These polar ions are formed by proton$^{(3,14)}$ transfer reactions from phenol to an electronegative atoms , namely oxygen and nitrogen atoms available in MBAA . The weak intensities of absorptions for nitrilium and oxonium ions are due to low expected solubility of these ions in non polar n-hexane solvent . This is in accordance $^{(2)}$ to the rule like dissolves like .

Now the question which can be arise , why the UV spectra of MBAA are changed after addition of phenol , p-methoxyphenol and p-chlorophenol . Although the pka values$^{(15)}$ of last compounds have a values of 9.95 , 10.21 , 9.41 respectively . Actually , on can expect that these phenols are able to form a hydrogen bonding species by donor-acceptor mechanism $^{(2\text{-}4)}$ with different strengths . Phenol here is regarded as an acceptor species , while MBAA is a donor species . The formation of hydrogen bonding can be expected in this study to be of types O — H ….O or O — H …. N

These hydrogen bondings perturb the chromophore system of original MBAA and hence it not a strange to obtain UV spectral changes after additions of phenols . This is in a good agreement with other similar studies$^{(3\text{-}4)}$ in this field .

Now it is important to prove the type of interaction between MBAA and phenols by thermodynamic method . The equilibrium reactions occure between MBAA and phenols added before UV measurements of solutions outlined before , and are expected to be of forms ; $\text{MBAA} + \text{Phenols} \rightleftharpoons \text{complex molecule or ions}$.

The equilibrium constant K of the interaction reaction stated above is evaluated from the UV spectrum from the relationship :

$$K = \frac{A2}{A1} \quad ……….(1)$$

A_2 and A_1 are absorbance of bands generated after addition of optimized quantity of phenols seen in this work respectively .

Table (3) shows the equilibrium constant values of interactions of MBAA with phenol, p-methoxyphenol and p-chlorophenol in n-hexane and at a temperatures range (283-323) K . They have a direct relationship with the inverse of absolute temperatures . This facilitates the evaluation of heat of reaction ΔH from Vant hoff equation of the form as in equation (2) :

$$\text{Ln K} = \text{constant} - \frac{\Delta H}{RT} \quad ……..(2)$$

By using excel computer program , the plots of lnK versus T^{-1} for phenol , p-methoxyphenol and p-chlorophenol .They show a straight lines of R^2 values 0.9530,0.9655 and 0.9294 respectively.

These straight lines collected in Fig (3) . From the last plots are shown to fit an equation (3-5) , for phenols mentioned above respectively .

$$\text{Lnk} = 138.5\,X - 0.5012 \quad ………..(3)$$

$$\text{lnK} = 198.35\,X - 0.7761 \quad ………..(4)$$

$$\text{lnK} = 849.35\,X - 2.9798 \quad ……….(5)$$

Hence $X = - \Delta H \backslash R$

Equations (3-5) allow the evaluations the heats of interactions for MBAA with the phenols at any temperature . They have an average values of $\overline{\Delta H}$ equal to -1148.7 , -1658.9 and -6993.4 J. mole^{-1} for phenol , p-methoxyphenol and p-chlorophenol respectively .

The Gibbs free energy ΔG is calculated from equation (6) of the form :

$$\Delta G = - RT \ln K \quad …………….(6)$$

All average $\overline{\Delta G}$ values have a positive range values between (128.2 – 513.2) J. mole^{-1} . Their positive signs are far away of our expectations , since mixing MBAA with phenols generate bands A_2 and A_1 spontaneously . In other words , that the interacting molecules under study is occur by a non spontanous process . An acceptable explanation for such abnormal result is given here , by the fact of magnitude A_2 absorbance has a lower value if compared with A_1, for any interacting equilibrium systems seen in Table (3) at any constant temperature . This produces K of a value lower than unity according to equation (1) , or hence its logarithmic numbers must be negatives . Finally a positive ΔG values are appeared in (3) for all systems from equation (3) . These positive ΔG values are in agreement [(4)] with other similar system as the interaction benzil monobenzyliden aniline with 2,4-dimethylphenol and phenol at some elevated temperature of 293 and 298 K . Another explanation for the smaller A_2 value of complex molecule or ions products for the interacting systems is by the assumption of smaller stabilities of interacting products by hydrogen bonding . This proposal may be to the steric hindarance of ortho methoxy group presents in MBAA . The last results due to the difficulty for phenolic protons to approach the hetero oxygen or nitrogen atoms in MBAA or to the smaller absorbance A_2 values of interacting products .

The ΔS values for systems above are estimated for Gibbs equation [(7)] of a form :

$$\Delta G = \Delta H - T\,\Delta S \quad \ldots\ldots\ldots\ldots\ldots\ (7)$$

All ΔS values listed in Table (3) have a negative signs and are agreed with the interacting systems in this study .

Now both the values and the negative signs of $\overline{\Delta H}$ and $\overline{\Delta S}$ thermodynamic parameters are in full agreement [(3,4,6)] with hydrogen bondings $O - H \cdots\cdots O$ or $O - H \cdots\cdot N$ available in this study .

Finally it is of great importance to study the influence of chloro and methoxy substitutents on the $\overline{\Delta H}$ and $\overline{\Delta S}$ thermodynamic parameters of association system under study . The higher acidity of p-chlorophenol as seen above by its low pKa value as compared with p-methoxyphenol , results to a larger negative values of thermodynamic parameters mentioned as shown in Table (3) . In other words , that p-chlorophenol produces a more stable and more order products after association of p-chlorophenol with MBAA .

Table (3) Thermodynamic of hydrogen bonding interactions of MBAA with phenols in n-hexane

Accepter	10^3 \T K^{-1}	A_2	A_1	$K=\frac{A2}{A1}$	$\ln\frac{A2}{A1}$	ΔG $J.mol^{-1}$	$\overline{\Delta G}$ $J.mol^{-1}$	ΔH $J.mol^{-1}$	$\overline{\Delta H}$ $J.mol^{-1}$	ΔS $J.mol^{-1}.K^{-1}$	$\overline{\Delta S}$ $J.mol^{-1}.K^{-1}$
Phenol	3.09	0.055	0.059	0.932	-0.0704	189.1	128.2	-1156.9	-1148.7	-4.2	-4.2
	3.19	0.072	0.076	0.947	-0.0545	141.8		-1162.4		-4.2	
	3.30	0.076	0.080	0.950	-0.0513	129.2		-1170.8		-4.3	
	3.40	0.050	0.052	0.962	-0.0387	94.3		-1126.7		-4.2	
	3.50	0.080	0.083	0.964	-0.0367	86.4		-1126.7		-4.3	
p-methoxy-phenol	3.09	0.175	0.202	0.866	-0.1430	384.0	296.2	-1700.1	-1658.9	-6.5	-6.5
	3.19	0.208	0.241	0.863	-0.1470	382.5		-1637.1		-6.5	
	3.30	0.231	0.259	0.892	-0.1140	287.2		-1667.9		-6.5	
	3.40	0.076	0.084	0.905	-0.1000	243.6		-1647.0		-6.5	
	3.50	0.246	0.266	0.925	-0.0780	183.5		-1642.5		-6.5	
p-chloro phenol	3.09	0.015	0.022	0.682	-0.3820	1025.8	513.2	-6976.2	-6993.4	-24.8	-24.8
	3.19	0.037	0.046	0.804	-0.2180	567.3		-7187.0		-24.8	
	3.30	0.039	0.047	0.830	-0.1860	468.6		-7038.0		-24.8	
	3.40	0.051	0.056	0.911	-0.0930	226.5		-7032.3		-24.8	
	3.50	0.064	0.072	0.889	-0.1180	277.6		-6733.4		-24.8	

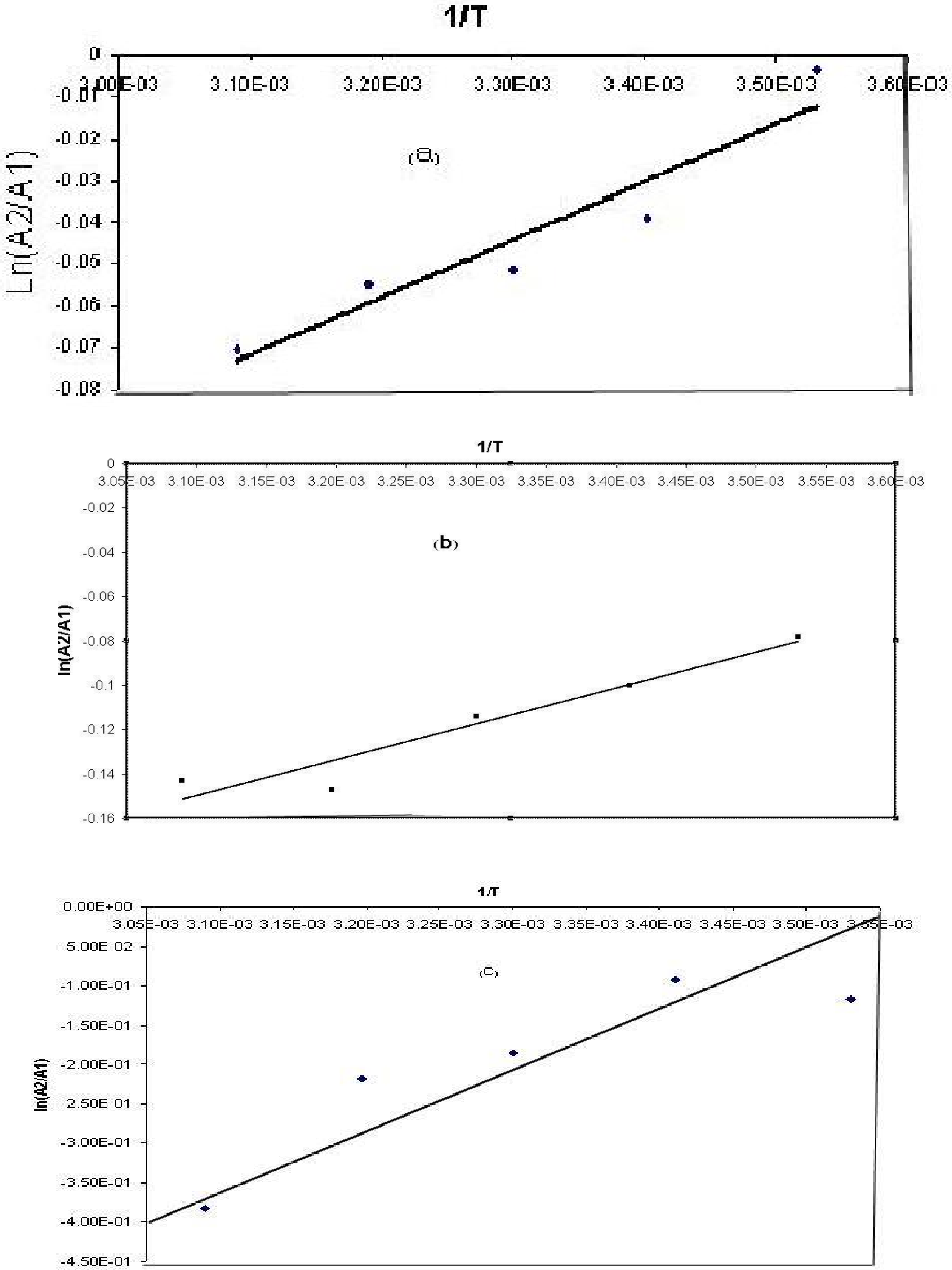
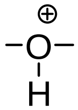
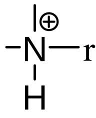


Fig.3 Vant Hoff equations plots for the interactions of MBAA in n – hexane With :-

- **a- phenol.**
- **b- p-Methoxy phenol.**
- **c- p-Chlorophenol.**

Conclusions

1. The interactions of MBAA with phenol , p-methoxyphenol and p-chlorophenol are studied by UV spectroscopy and thermodynamic method .
2. At optimal relative concentrations values of 4/1 for phenol /MBAA and 4-methoxyphenol / MBAA , generate two new UV bands are observed in the UV spectrum of MBAA . They are assigned to the complex molecule or ions formed by the hydrogen bonding species , and the non hydrogen bonding species in reacting molecules .
3. The interactions in the reactants molecules by hydrogen bonding are of types O ····· H – O and N ····· H – O . These perturb the chromopher of MBAA and results to the appearance of a new UV band after addition of phenols .
4. p-Chlorophenol shows a similar behavior to those given for phenol and p-methoxyphenol with additional appearance of diprotonated UV bands at wavelength of 463 nm and 474 nm. They are arised from oxonium or nitrilum ions of types  $-\overset{\oplus}{\underset{H}{O}}-$ and  $-\overset{\oplus}{\underset{H}{N}}-$ respectively by proton transfer reactions(4.14)
5. Both negative signs of $\overline{\Delta H}$ and $\overline{\Delta S}$ calculated thermodynamic parameters for the equilibrium interacting systems under study , support (3, 4, 6) the interaction processes by hydrogen bondings .
6. The observed entropy changes $\overline{\Delta S}$ for the interactions of phenol , p-methoxyphenol and p-chlorophenol with MBAA have a negative values of 4.2, 6.5 and 24.8 cal.mole^{-1}.K^{-1} . The last smaller value supports the hydrogen bonding as well as the diprotonated UV bands shown above and in Fig.2.c .

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