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Conductometric Studies of Charge Transfer Complexes Interaction of Amino Pyridine with π- Acceptors

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Abstract: *Charge Transfer Complexes of Amino Pyridine derivatives as donor with the organic π-Acceptors, maleic anhydride,α-nitroso-β-naphthol ,p-chloroaniline ,picric acid ,anthraquinone and p-bromoaniline in polar solvent have been determined . The study was performed in three different polar solvents namely N,N-dimethylformamide (DMF), acetonitrile (ACN) and dimethylsulfoxide (DMSO). The stoichiometric ratios of these complexes were found to vary from (1: 1) to (1: 1.5) (acceptor – donor) depending on the system solvent used and the (ασM) values has been examined . The distribution profiles of the various pyridine derivatives species and organic π-acceptors formed, are obtained.*

Keywords: *Charge transfer, molecular complexes, amino pyridine, organic π-acceptors , polar solvents,.*

I. Introduction

Electron donor – acceptors complexes play an important role in many biological processes [1-3] and in Medicinal Chemistry [4-6] . For instance enzyme catalysis, drug action and ion transfer through lipophilic membrances all involve complexation between two or more distinct molecules [7-13]. Stabilization of ferromagnetic exchange in molecular solids via admixing of the ground state with a virtual charge-transfer excited state are examined[14] . In particular, lattice dimerization in semiconducting crystals of alternately stacked donor and acceptor molecules results in creation of a ferroelectric chain with a large electric dipole [15]. Many authors studied the solvent effect on photochemically induced reaction between pyridine – carbonitrile and alkenes, pyridine – carbonitrile and primary or secondary aliphatic amines and pyridine – 2,4 – dicarbonitrile [16,17].

Spectral characteristic and stability constant of the formed C T complexes are examined [18-26]. The importance of conductometric studies of electron donor acceptor [EDA] complexes is increasing rapidly on account of their use as semi conductors[27-30].Many authors discussed the charge transfer complexes it was considered to be of interest to investigate the formation of charge transfer (CT) complexes of pyridine (D) as electron donor with π- acceptor [31-34]. Accordingly, it was considered to be interest to investigate the formation of CT complexes of 4-amino pyridine (L1) , 2-amino 5-chloro pyridine (L2) and 2,6 diamino pyridine (L3), as electron donor with the aromatic π-acceptors, maleic anhydride,α-nitroso-β-naphthol ,p-chloroaniline ,picric acid ,anthraquinone and p-bromoaniline.. The studies were carried out in dipolar aprotic solvents N,N-dimethylformamide(DMF), acetonitrile (ACN) and dimethylsulfoxide (DMSO) using conductometric titration technique. This technique based on the formed strong electron donor (D)-electron acceptor (A) inner CT complex DA may dissociate into ions giving rise to ionic conductivity which can be followed by measuring the charges in electrical conductivity of solution. The effect of solvent polarity, type of electron donor and acceptor has been examined. The site and type of CT interaction were also discussed.

II. Experimental

All the chemicals including acceptors , donors and solvents were A. R. products from BDH and Merck . The donor used were 4-amino pyridine (L1) 2-amino 5-chloro pyridine (L2) and 2,6 diamino pyridine (L3).The acceptors used were maleic anhydride,α-nitroso-β-naphthol ,p-chloroaniline ,picric acid ,anthraquinone and p-bromoaniline. . The conductance measurements were carried out on WPA CM35 Conductivity Meter using a conductivity cell fitted with platinized platinum electrodes. Standard stock solutions of donors [5×10^{-3} mol dm^{-3}] and acceptors [5×10^{-3} mol dm^{-3}] were prepared in the desired solvents . Stock solutions of donor L2 [3×10^{-3} mol dm^{-3}] and acceptors [3×10^{-3} mol dm^{-3}] were prepared in the DMF solvent. Titration were carried out by adding 1 ml of the acceptor solution to the 15 ml of the donor solution and vicr versa at an interval of 5 min. The value of molar concentrations of acceptors (MA) , donors (MB) and molar conductivity coefficient, σM were determined according equation [35].

III. Result And Discussion

III.1Conductometric titration

According to Gutmann et al [35],the formation of electron donor acceptor [EDA] complexes between an electron donor D and electron acceptor A is detected by the appearance of a peak in the conductivity-concentration (donor or acceptor) plot . The stoichiometry of the CT complex formed in solution has shown to be directly proportional to the position of the conductivity maximum of the obtained curves (Figs. 1-5) as a representative. The concentration of D and A at the well developed maximum are used to determine the stoichiometry of the complexes. It is found that, all curves obtained exhibit a maximum at a molar ratio of 1:1 in all solvents used indicating that only 1:1 CT complexes may be formed in our studies. The observed molar ratios for the conductivity peaks are listed in Tables (1-3). Among the molecules acting as electron donor those which are their donor properties to the presence of atoms processing one or more " lone pairs" of electrons – the "n donors" – are of particular significance . other types of donor molecules are also known, like unsaturated hydrocarbons, in particular aromatic hydrocarbons and some of their derivatives, molecules deriving their donor properties from the presence of comparatively loosely bond л electrons. The properties of electron donor - acceptor molecules display according to the nature of substituent of x -aromatic molecules moiety . Complexes of this kind are above all those formed by donor molecules containing atoms possessing "lone pair electrons" molecule .

The π-π interaction is asubset of donor –acceptor (EDA) intraction ,opposing π systems typically adopt a parallel –planer geometry .Following current understanding of the bonding forces , the ground state hybrid of the complex may be written as : D … A ={ D A $\rightleftharpoons$ $D^+ + A^-$}.The resonance structure D, A represents all nonbonding interaction ie,electrostatic forces ,repulsion ,dispersion induction and quadrapole inetraction between rings .By examining the results of the solvent effect reported in Tables(1-3), it is observed that dcrease an conductivity which follows the total number of ions carrying current at the stoichiometry of the CT complexes (σp values) decrease with increase dielectric constant of the solvent (ε) which follows the order:

DMF (ε = 36.7) > ACN (ε = 37.5) > DMSO (ε = 46.7)

It observe that the results on the solvents effect on the σp values are not in accordance the rate of electron transfer but is reinforce by the increase in solvent polarity[36]. Thus, a low stability of complex is expected to occur as the dielectric constant of the medium is increased. It is worth mentioning that due to the high basicity of *dimethylsulfoxide*, it is expected that the non-bonding electrons of sulfur and oxygen atoms of DMSO solvent can act as charge donor and will take part in DMSO-acceptor CT complex, which result in reducing the degree of ionic mobility in solution,this causes decrease the conductivity. In addition, the observed low conductivity in DMSO can be attributed to the large size of *dimethylsulfoxide* molecule compared to those of *dimethylformamide* or *acetonitrile*. This bahaviour is in accordance with the results reported previously [37] , which attributed to the greater electro relation results from the higher ability of a substance to store electrical energy in electric field of DMSO which lead to the interionic repulsion within the inner complex. The smaller σp values in ACN than those in DMF can be attributed to the higher ionizing power of ACN than DMF. This leads to increase the ion-solvent interaction in ACN which results in the formation of non-ionic complex as follows :-

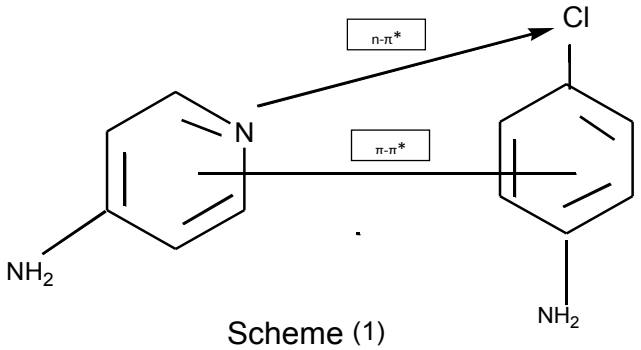
$$DA + ACN \rightleftharpoons D^{+}_{ACN} + A^{-}_{ACN}$$

Accordingly, the molecular size increases and consequently decrease in conductivity is observed [29] . Since, the σp values depend mainly on the solvent polarity and the donor (or acceptor) concentration, thus if the solvent polarity and the donor concentration are kept constant, thus σp values should reflect the electron affinity of the acceptors. On the other hand, if the acceptor concentration is kept constant, the σp values should reflect the donor strength or its basicity. As expected, the results listed in Tables (1-3) show that σp values follow the electron affinity order of the acceptors p-bromoaniline > p-chloroaniline which may be ascribed to salvation which would be expected to be more extensive with small ions where the charge is more concentrated compared to that with large ions.It is evident from Table (1-3) that the values of ασM of donor-acceptor complexes in DMF ,ACN and DMSO solvent increase by increasing the electron donating character of the substituents present in the pyridine in the following order:

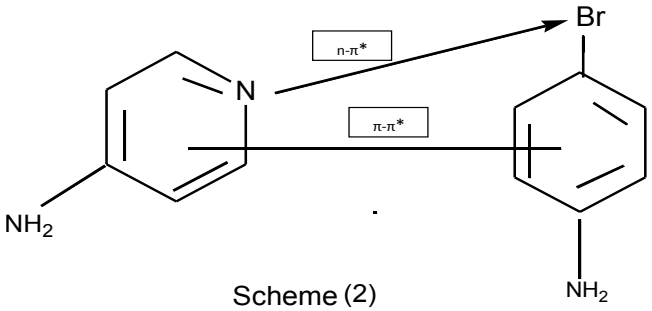
2,6 diamino pyridine > 4-amino pyridine > 2-amino 5-chloro pyridine

The donor character of the investigated compounds and the type of electron transition can be explained on the basis of previous reports [38], which suggest that the amino heterocyclic aromatic character which arise from the formation of three centered π-bonds resembling the π-system of benzene derivatives. Also, it is indicated that the NH_2 group is in resonance with the ring. The energy of NH_2 lone pair aromatic orbital are closer to π-levels of pyridine than π*-levels. This leads to increase the energy of π-MO'S. In addition, it was found that the tertiary N-atom is more basic than NH_2 or NH groups in the pyridine moiety ring [39]. Thus, the tertiary N-atom get protonated first taking into consideration the protonation of N atoms of the pyridine moiety

is that the same. Based on the above findings it is suggested that in the $L_3 > L_1 > L_2$,studied, the donation from the pyridine moiety is more proper than the phenyl ring. This donor part can undergo two different types of transitions, through intermolecular π-π* transition of electrons from the higher filled π-molecular orbital of the donor to the lowest unfilled π- π*-molecular orbital of the acceptor in the anodic direction whereas the positive hole moves to a molecule in cathodic direction. (Schemes 1,2).

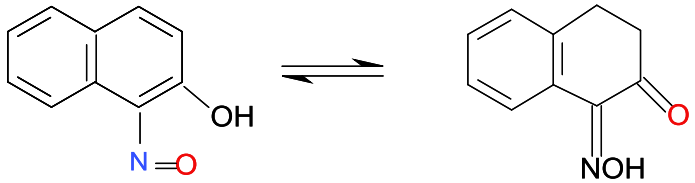


Scheme (1)



Scheme (2)

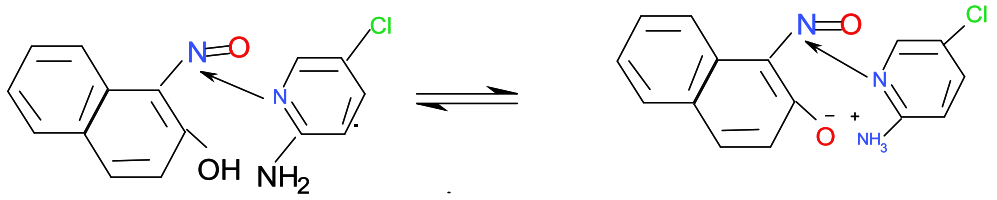
A Study of the Tautomeric Equilibria of Nitrosonaphthol-Naphthoquinoneoxime, systems can be explained on the basis of previous reports [40], where Nitroso is more stable than oxime. This statement is valid only if alpha hydrogen on carbon with respect to the nitrogen is not present in nitroso state. Otherwise both form exist equally in solution for the Nitroso compound. $R_2CH\text{-}N{=}O \rightleftharpoons R_2C = N\text{-}OH$,1-nitroso-2-naphthol (NNH) and its derivatives may exist in two tautomers, the nitroso and the oxime form NNH coordinates in the deprotonated state (NN−) as a monoanionic bidentate ligand. The coordinated anion can be referred to as an oximate or a phenolate. In both resonance forms the ligand may serve as charge transfer (CT) donor and acceptor. Nitroso groups provide acceptor functions [41], while phenolates are strong donors [42]. The oximate may also be viewed as a substituted ortho-quinone. Quinones are well known CT acceptors [43,44], but oximates have also donor properties [45](scheme 3).



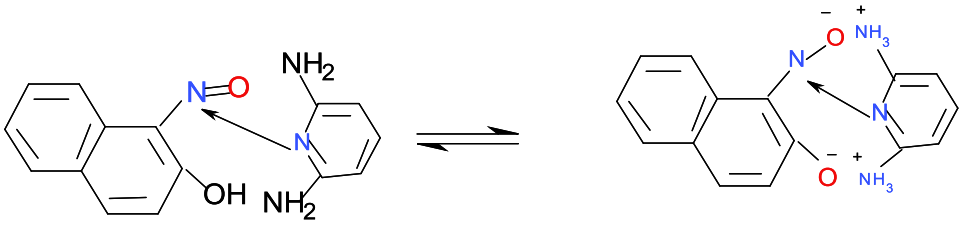
Tautomerisation in 1-nitroso -2-naphthol

Scheme (3)

On the other hand, the molecular complexes of substituents present in the pyridine derived from acidic acceptors can be stabilized by proton transfer from the OH group of the acceptor to the NH_2 group of the donor as represented in Schemes (4,5) which is shown below. The complete proton transfer is not believed to occur then; partial protonation seems to be more probable mechanism for complex formation. Protonation of NH_2 group rather than the tertiary nitrogen atoms can be attributed to the higher π-charge density on NH_2 group than that on hetero N-atom [46,47].



Scheme (4)



Scheme (5)

III.2 Distribution diagrams

The distribution profiles of the various pyridine (D) species as donor and free π -acceptors, (A) formed through the change of the concentrations of their solutions, are obtained from the plots of [L] values of the ligand solution as function of the calculated concentration percentage (α %) of each ligand species using the dissociation constant (ασM) values of these ligands. A typical species-distribution graph are represented in Figs (6-10). For binary systems graphs are shown in Fig. (6) the obtained curves are generally showing that, in presence of low concentration of the ligand L_1 [1×10^{-6} mol dm^{-3}] in DMSO, all the π –acceptors free ions maleic anhydride, anthraquinoneine and p-bromoaniline will be present as free ions (αA 99.9%). On increasing donor[D] [1×10^{-3} mol dm^{-3}] , the acceptor concentration [A] will begin to decrease(α ≈ 59.3% , 65. 4%and 74.5%) while that of [DA] species tends to increase at (α_A≈ 40.7%, 34.6% and 25.5%) .When the [D] = 1/KDA value, the α_A and α_{AL} will become equal. On increasing [L] above 1/KDA value, the [DA] will exceed that of [A] because the reaction will shift toward [DA] formation. At high concentration of the ligand [0.1 mol dm^{-3}], the acceptors ions is completely disappeared (α ≈1.43% ,1.86% and 2.03%) .On the addition of L_1 solution[3.16×10^{-5} mol dm^{-3}] to a solution containing in α-nitroso-β-naphthol and p-bromoaniline in ACN all the π –acceptors free ions will be present as free ions (α_A 98.1% and 97.3%) respectively in fig (7). On increasing donar ligand [1×10^{-3} mol dm^{-3}] , the acceptor concentration [A] will begin to decrease(α ≈ 61.9% , and 53.2%) while that of [DA] species tends to increase at (α ≈ 38.1% and 46.8 %) and at concentration of the ligand0 [0.1 mol dm^{-3}] , the acceptors ions is completely disappeared (α ≈ 1.6% and 1.12%) . Distribution digram of L2pecies in DMF with maleic anhydride,α-nitroso-β-naphthol and p- chloroaniline the obtained curves Fig(8) are generally showing that, in presence of low concentration of the ligand D [1×10^{-5} mol dm^{-3}] will be present as free ions (α_A 98.2% and 99 %) . On increasing donar[D] [3×10^{-4} mol dm^{-3}]., the acceptor concentration [A] will begin to decrease(α_A ≈ 80.6% , 88.2 %and 75.5%) while that of [DA] species tends to increase at (α_{DA} 19.4% ,11.8%and 24.5%) . At high concentration of the ligand [o.1 mol dm^{-3}], the acceptors ions is completely disappeared (α_A ≈1.3% ,2.32% and 0.97%). On the addication of L_2 in DMSO concentration at very low [3.16×10^{-5} mol dm^{-3}],α-nitroso-β-naphthol ,picric acid and p-bromoaniline ,almost all the acceptor ion will be present as free ions (α_A≈ 98.4% , 99.2% and 96.9%) Fig(9).On increasing the concentration of the ligand [L] =1×10^{-3} mol dm^{-3}, the concentration of the acceptor tends to decrease ,while the concentration of the complex tendes to appear (α 33,3% , 44.9% and 24.2%) ,at higher high concentration of the ligand[0.1 mol dm^{-3}], the acceptors ions is completely disappeared (α ≈,1.96 % , 1.2 % and 3.03%) . For binary systems graphs are shown in Fig. (10) distribution digram of ligand(L_3) pecies in DMF with p-chloroaniline and p-bromoaniline, the obtained curves are generally showing that, in presence of low concentration of the ligand D [1×10^{-5} mol dm^{-3}] will be present as free ions (α_A 98.9% and 99 %) . On increasing donor [D] [1×10^{-3} mol dm^{-3}], the acceptor concentration [A] will begin to decrease(α ≈ 42.1% and 49.3%) while that of [DA] species tends to increase at (α_{DA} 57.9% and 50.7%) .When the [D] = 1/KDA value, the α_A and α_{AL} will become equal. On increasing [L] above 1/KDA value, the [DA] will exceed that of [A] because the reaction will shift toward [DA] formation. At high concentration of the ligand, the acceptors ions is completely disappeared (α_A ≈ 0.72% and 0.96%) .

IV. Conclusion

Aconductometric titration has been used to study the stoichiometry of charge Transfer Complexes of the 4-amino pyridine , 2-amino 5-chloro pyridine and 2,6 diamino pyridine with the maleic anhydride,α-nitroso-β-naphthol ,p-chloroaniline ,picric acid ,anthraquinone and p-bromoaniline.in DMF, ACN and DMSO. The Protonation of NH_2 group rather than the tertiary nitrogen atoms can be attributed to the higher π-charge density on NH_2 group than that on hetero N-atom. The stoichiometric ratios of these complexes were found to vary from (1: 1) to (1: 1.5) (acceptor – donor) and σp values decreases with an increase in the dielectric constant of solvent are in the order DMF>ACN> DMSO. The distribution profiles of the various pyridine derivatives species and organic π-acceptors formed, are obtained.

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Graphical Abstract

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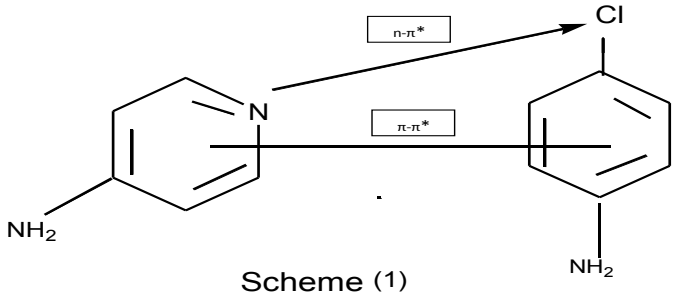


Scheme (1)

Synopsis

A conductometric titration has been used to study the stoichiometry of charge transfer complexes formed by pyridine derivatives as donors and the organic π-acceptors, maleic anhydride,α-nitroso-β-naphthol ,p-chloroaniline ,picric acid ,anthraquinone and p-bromoaniline in polar solvents. The stoichiometric ratios of these complexes were found to vary from (1: 1) to (1: 1.5) (acceptor – donor) depending on the system solvent used.The dissociation constant (ασM) values of the formed complexes have been calculated, and the effects of solvents as well as types of electron donors on their conductance σp-values have been examined The distribution profiles of the various pyridine derivatives species and organic π-acceptors formed, are obtained.

Table (1): Conductance Data* for Ligands-Complexes in Dimethylformamide, at 25ºC.

System	Stoichiometry of the complex	Conductance (μ mho)			$\alpha\sigma_M$ (dm^3mol^{-1})
		σ_p	σ_o	$\sigma_p - \sigma_o$	
		L_1 (4-amino pyridine) with			
Maleic anhydride	**1.13 : 1**	**272.00**	**90**	**182.00**	**763.102**
α-nitroso-β-naphthol	**1.27 : 1**	**358.75**	**120**	**238.75**	**710.029**
p-chloroaniline	**1 : 1**	**76.40**	**20**	**56.400**	**1128.000**
Picric acid	**1.5 : 1**	**497.92**	**120**	**377.90**	**1049.778**
Anthraquinone	**1 : 1**	**82.40**	**25**	**57.400**	**918.400**
p-bromoaniline	**1 : 1**	**82.90**	**27**	**68.200**	**1010.370**
		L_2 (2-amino 5-chloro pyridine) with			
Maleic anhydride	**1 : 1.07**	**86.00**	**41**	**45.00**	**756.939**
α-nitroso-β-naphthol	**2.37: 1.4**	**68.00**	**36**	**32.00**	**421.274**
p-chloroaniline	**1 : 1.09**	**146.25**	**48**	**98.25**	**1026.786**
Picric acid	**1 : 1**	**54.00**	**60**	**126.0**	**969.231**
Anthraquinone	**1 : 1**	**191.00**	**23**	**31.00**	**898.550**
p-bromoaniline	**1.24 : 1**	**68.80**	**26**	**42.80**	**991.659**
		L_3 (2,6 diamino pyridine) with			
Maleic anhydride	**1 : 1.09**	**565.83**	**150**	**415.83**	**1159.916**
α-nitroso-β-naphthol	**1 : 1.09**	**148.00**	**40**	**108.77**	**1129.707**
p-chloroaniline	**1 : 1.09**	**150.00**	**35**	**115.00**	**1374.776**
Picric acid	**1 : 1.63**	**191.00**	**60**	**131.00**	**1149.12**
Anthraquinone	**1 : 1.34**	**64.00**	**20**	**44.00**	**1028.037**
p-bromoaniline	**0.92 : 1**	**60.00**	**26**	**58.80**	**1029.050**

*** Stock solutions of A and D were 5×10^{-3} mol dm^{-3} in L_1 ,L_3 .**
*** Stock solutions of A and D were 3×10^{-3} mol dm^{-3} in L_2**

Table (2): Conductance Data* for Ligands-Complexes in Acetonitrile, at 25ºC.

System	Stoichiometry of the complex	Conductance (μ mho)			$\alpha\sigma_M$ (dm^3mol^{-1})
		σ_p	σ_o	$\sigma_p - \sigma_o$	
		L_1 (4-amino pyridine) with			
Maleic anhydride	**1.08 : 1**	**153.77**	**52**	**101.717**	**752.344**
α-nitroso-β-naphthol	**1 : 1.17**	**116.0**	**46**	**70.000**	**661.163**
p-chloroaniline	**1.5 : 1**	**82.60**	**19**	**63.600**	**1115.789**
Picric acid	**1 : 1.27**	**177.483**	**56**	**121.483**	**986.063**
Anthraquinone	**1 : 1**	**92.00**	**30**	**62.000**	**826.667**
p-bromoaniline	**1 : 1**	**11.20**	**35**	**7.700**	**880.000**
		L_2 (2-amino 5-chloro pyridine) with			
Maleic anhydride	**1 : 1.22**	**75.00**	**28**	**47.00**	**746.032**
α-nitroso-β-naphthol	**1 : 1**	**39.56**	**15**	**24.56**	**654.933**
p-chloroaniline	**1 : 1.5**	**90.00**	**28**	**62.00**	**1107.143**
Picric acid	**1 : 1.5**	**86.00**	**30**	**56.00**	**933.333**
Anthraquinone	**1 : 1.09**	**52.29**	**20**	**32.29**	**675.439**
p-bromoaniline	**1 : 1.09**	**48.79**	**20**	**28.79**	**602.301**
		L_3 (2,6 diamino pyridine) with			
Maleic anhydride	**1.5 : 1**	**90.00**	**27.0**	**6.30**	**777.778**
α-nitroso-β-naphthol	**1.34 : 1**	**163.33**	**47.5**	**115.83**	**903.158**
p-chloroaniline	**1.5 : 1**	**90.00**	**20.0**	**70.00**	**1166.667**
Picric acid	**1.5 : 1**	**534.67**	**130.0**	**404.67**	**1037.605**
Anthraquinone	**1.34 : 1**	**72.80**	**20.0**	**52.80**	**923.077**
p-bromoaniline	**1.27 : 1**	**53.60**	**15.0**	**38.60**	**919.040**

*** Stock solutions of A and D were 5×10^{-3} mol dm^{-3}.**

Table (3): Conductance Data* for Ligands- Complexes in Dimethylsulfoxide, at 25ºC.

System	Stoichiometry of the complex	Conductance (μ mho)			$\alpha\sigma_M$ (dm^3mol^{-1})
		σ_p	σ_o	$\sigma_p - \sigma_o$	
	L_1 (4-amino pyridine) with				
Maleic anhydride	**1 : 1**	**474.40**	**160.00**	**314.40**	**687.72**
α-nitroso-β-naphthol	**1.09 : 1**	**358.75**	**135.00**	**223.75**	**635.02**
p-chloroaniline	**1.09 : 1**	**80.83**	**32.00**	**48.830**	**584.65**
Picric acid	**1.37 : 1**	**584.55**	**180.00**	**404.55**	**899.00**
Anthraquinone	**1.09 : 1.41**	**77.00**	**35.00**	**42.00**	**342.86**
p-bromoaniline	**1.07 : 1.43**	**90.00**	**37.00**	**53.00**	**572.97**
	L_2 (2-amino 5-chloro pyridine) with				
Maleic anhydride	**1 : 1.09**	**73.00**	**33**	**40.00**	**507.16**
α-nitroso-β-naphthol	**1.5 : 1**	**75.00**	**30**	**45.00**	**500.00**
p-chloroaniline	**1.09 : 1**	**82.50**	**40**	**42.50**	**408.65**
Picric acid	**1.04 : 1**	**49.92**	**16**	**33.92**	**813.37**
Anthraquinone	**1 : 1**	**36.00**	**20**	**16.00**	**320.00**
p-bromoaniline	**1.09 : 1**	**82.40**	**35**	**47.40**	**541.70**
	L_3 (2,6 diamino pyridine) with				
Maleic anhydride	**1 : 1**	**92.8**	**3.2**	**58.8**	**691.765**
α-nitroso-β-naphthol	**1.27 : 1**	**103.5**	**4.0**	**66.5**	**641.892**
p-chloroaniline	**1.50 : 1**	**127.0**	**32.0**	**95.0**	**989.583**
Picric acid	**1 : 1.5**	**191.0**	**3.58**	**126.0**	**969.231**
Anthraquinone	**1 : 1**	**52.0**	**3.50**	**30.0**	**545.455**
p-bromoaniline	**1 : 1**	**91.6**	**3.40**	**63.6**	**908.571**

*** Stock solutions of A and D were 5×10^{-3} mol dm^{-3}**

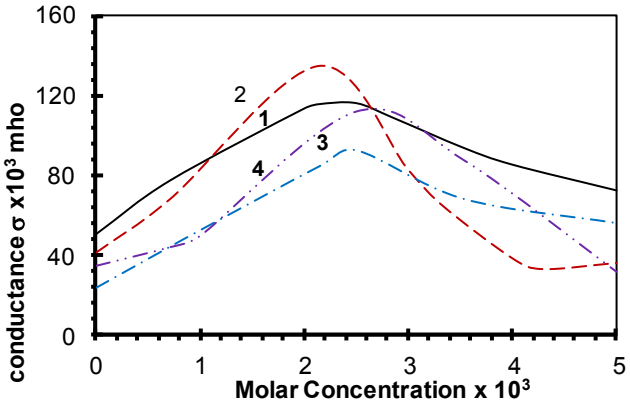


Fig (1): Plot of conductance of L_1 in ACN with 1- *α*-Nitroso-*β*-naphthol , 2 *p*-Chloroaniline, 3- Anthraqunone and 4- *p*-Bromoaniline

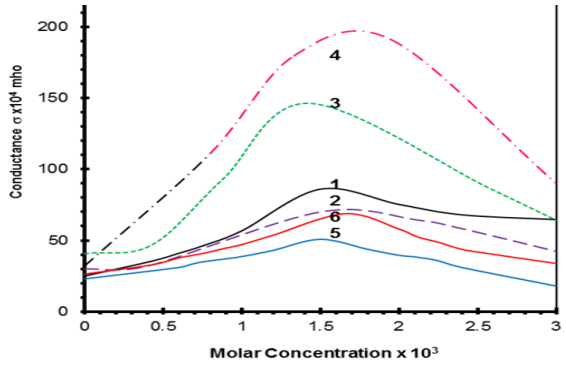


Fig (2): Plot of conductance of L_2 in DMF with 1- Malic anhydride, 2- *α*-nitroso-*β*-naphthol, 3- *p*-Chloroaniline, 4- Picric acid, 5- Anthraqunone and 6- *p*-Bromoaniline.

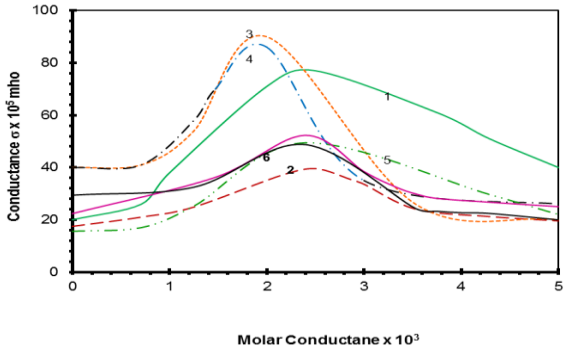


Fig (3): Plot of conductance of L_2 in ACN with 1- Malicanhydride, 2- α-nitroso-β-naphthol, 3- p-Chloroaniline, 4- Picric acid, 5- Anthraqunone and 6- p-Bromoaniline.

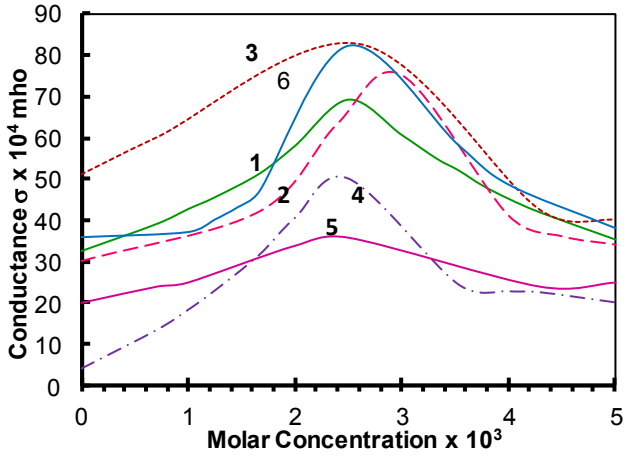


Fig (4): Plot of conductance of L_2 in DMSO with 1- Malic anhydride, 2-α-nitroso-β-naphthol, 3-p-Chloroaniline, 4- Picric acid ,- 5- Anthraqunone and 6-p-Bromoaniline.

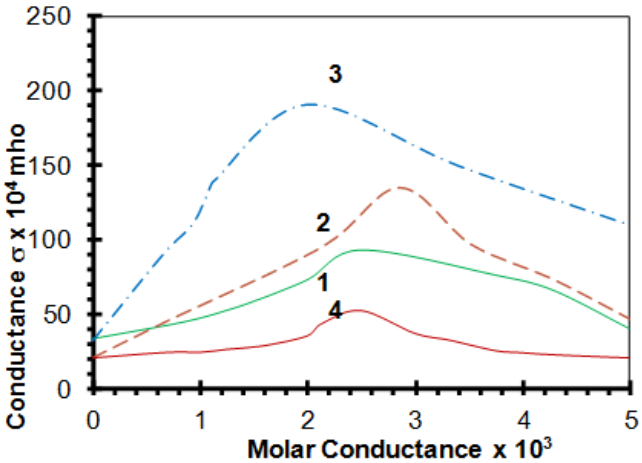
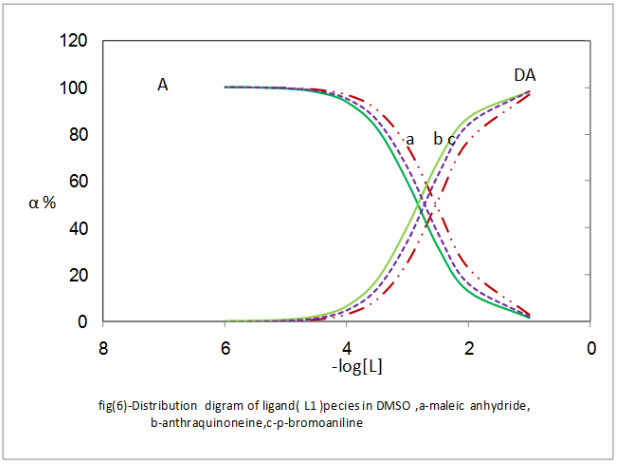
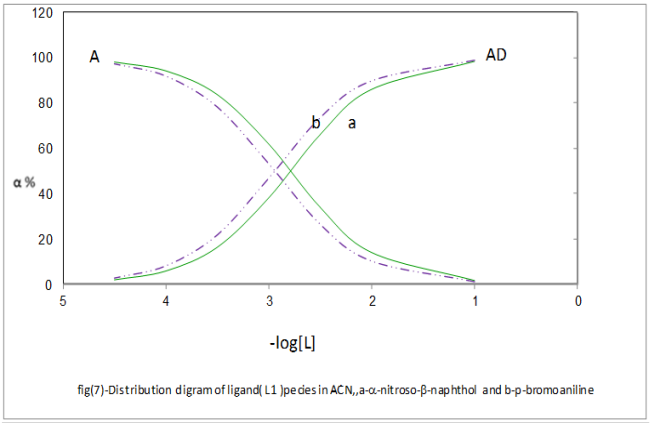


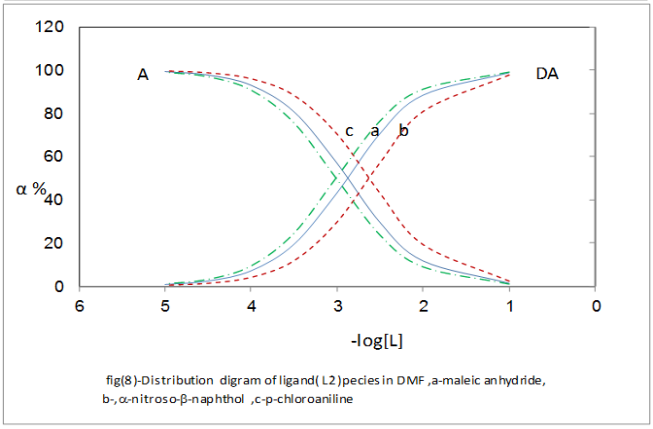
Fig (5): Plot of conductance of L_3 in DMSO with 1-Malic anhydride, 2- α-nitroso-β-naphthol, 3- Picric acid and 4- Anthraqunone.



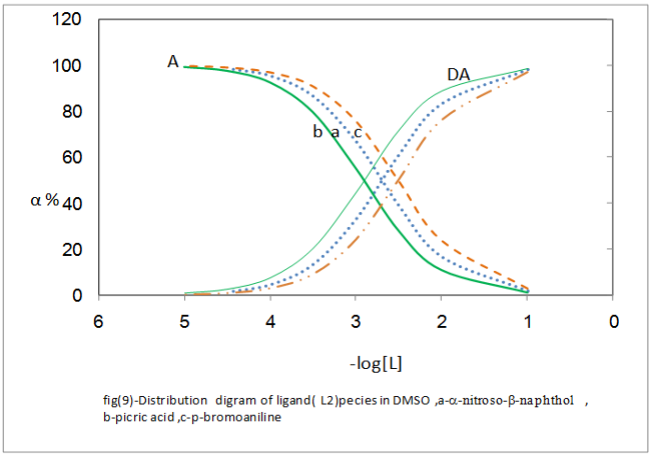
fig(6)-Distribution digram of ligand(L1)pecies in DMSO ,a-maleic anhydride, b-anthraquinoneine,c-p-bromoaniline



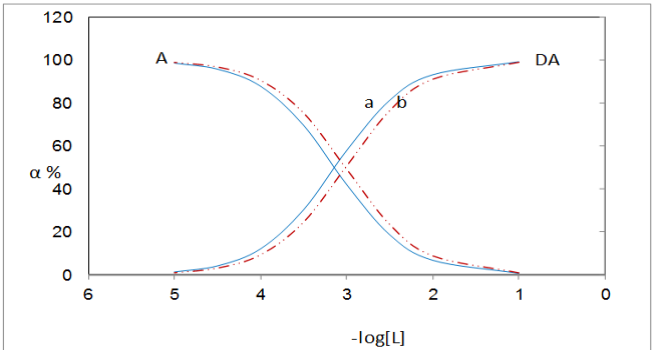
fig(7)-Distribution digram of ligand(L1)pecies in ACN,,a-α-nitroso-β-naphthol and b-p-bromoaniline



fig(8)-Distribution digram of ligand(L2)pecies in DMF ,a-maleic anhydride, b-, α-nitroso-β-naphthol ,c-p-chloroaniline



fig(9)-Distribution digram of ligand(L2)pecies in DMSO ,a-α-nitroso-β-naphthol , b-picric acid ,c-p-bromoaniline



fig(10)-Distribution digramof ligand(L3)pecies in DMF ,a-p-chloroaniline , b -p-bromoaniline