Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(4):322-328
(http://derpharmachemica.com/archive.html)

Viscometric and thermodynamic study of substituted-N,N'bis(salicyliden) arylmethanediamine in a binary system of 70% DMF-Water

A. S. Chandami, D. S. Hedaoo and M. P. Wadekar*

Applied Chemistry Division, Govt. Vidarbha Institute of Science and Humanities, Amravati,(MS), India

---

ABSTRACT

The viscometric and thermodynamic measurements of substituted- N,N'bis(salicyliden)-arylmethanediamines in a binary mixture were performed. Density and viscosity measurements were carried out in 70% DMF-Water mixture at different temperatures. The viscometric measurements were done with the help of Ostwald's viscometer. The data so obtained were analyzed by using Jones-Dole equation. This study helps to predict the molecular interaction in solution mixture. The present study deals with the determination of the thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS).

Keywords: Substituted-N,N'bis(salicyliden)-arylmethanediamines, Jones-Dole equation and thermodynamic parameters.

INTRODUCTION

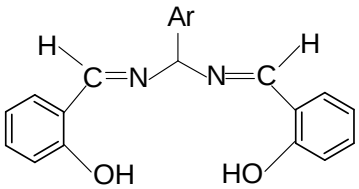
Viscosity is the measure of a substance's resistance to motion under an applied force. The shearing effect, that involves the movement of one layer of liquid over another, develops the viscosity. Viscosity is a principal parameter when any flow measurements of fluids, such as liquids, semi-solids, gases and even solids are made. Viscosity is also considered as the measure of the internal friction of a fluid. The importance of liquid viscosity in chemical process design makes it one of the most measured transport properties. Viscosity data on a material gives manufacturers the ability to predict how the material will behave in the real world. Viscosity measurements are used in the food industry to maximize production efficiency and cost effectiveness.

Viscosity measurements play an important role in pharmaceutical, medicinal and drug chemistry[1-2].The viscometric method gives primary information about structure, size, shape and molecular weight of compounds[3-4]. Viscometric studies of mixed ligand cobalt(III) complexes of certain diimine ligands bound to calf thymus DNA was performed[5]. Density and viscosity of drug Paracetamol (PAM) in various aqueous mixtures of ethanol have been determined[6]. The viscometric studies on the methyl cellulose-sodium dodecyl sulphate complex in aqueous solution was done[7].The complex formation between hydroxypropylcellulose and hexadecyltrimethylamonium bromide was studied by light scattering and viscometry[8]. Viscometric study of complexes of poly(vinyl pyrrolidone) with Co^{2+} Was also mentioned[9]. The interaction of β-cyclodextrin (β-CD) with the amphiphilic drug promazine hydrochloride (PMZ) by using conductometry and viscometry was studied[10]. The viscometric studies helps in the determination of shape parameter of Liposomes and DNA-Lipid complexes determined by utilizing small sample volumes[11]. The viscometric technique finds extensive application in polymer sciences. The coefficient of interaction between syndiotactic and isotactic poly(methyl methacrylate) was determined at 25°C in dioxan and chlorobenzene by instrinsic viscosity measurement in a polymer solvent[12]. Density (ρ) and viscosity (η) measurements were carried out for cefepime hydrochloride in water and 0.9 mass % normal saline from 278.15 to 313.15 K[13]. Similarly densities and viscosities of cefodizime sodium in water and normal saline was also known[14]. Literature survey shows the solute-solvent interaction by measuring the densities, viscosities, and ultrasonic velocities of solutions of sodium ibuprofen in water at various temperature and at atmospheric

pressure[15]. Viscometric study and thermal analysis of a schiff-based resin of 2-Methoxy-1-Napthaldehyde was known[16].

The ligand N,N'bis(salicyliden)-arylmethanediamines, having imine linkage posses the antimalarial properties[17]. The antimicrobial activity of Schiff bases were also mentioned[18]. There are many reports were presented on the anti-inflamatory properties of compounds having imine linkage[19]. Some Schiff bases were found to posses anti-inflamatory as well as analgesic properties[20]. Phenylalanine analogus of Schiff bases were found to contain potent anti-inflammatory property[21]. Analgesic, anti-inflammatory and anti-ulcerogenic activities of certain novel Schiff's bases were also reported[22]. It is also well recognized that the azomethine functional group containing compounds shows a broad range of anti-HIV properties[23]. Istin Schiff bases were reported to possess anti- HIV properties[24]. Tridentate Schiff bases and their Co(II) complexes showed more pronounced DNA cleavage activity[25]. Chromone based Schiff bases with Pd(II) complexes cleave the pUC19 plasmid DNA[26]. DNA cleavage studies of metal complexes of chromone Schiff base with metals including Cu(II), Co(II), Ni(II) and Zn(II) were also reported[27]. It is also reported that some water-soluble copper(II) complexes of compounds showing imine linkage showed DNA cleavage, as well as protein binding activities[28].

In the present investigation deals with the viscometric study of substituted- N,N'bis(salicyliden)-arylmethanediamines at different temperatures by using their solutions of different concentrations.



Ligand A (L_A) = *N,N'bis(salicyliden)-arylmethanediamine*
Ligand B (L_B) = *N,N'bis(salicyliden)-furylmethanediamine*
Ligand C(L_C) = *N,N'bis(salicyliden)-nitroarylmethanediamine*
Ligand D (L_D) = *N,N'bis(salicyliden)-anisylmethanediamine*
L_A : Ar = $-C_6H_5$
L_B : Ar = $-C_4H_4O$
L_C : Ar = $-C_6H_5NO_2$
L_D : Ar = $-C_6H_6OCH_3$

MATERIALS AND METHODS

Analytical reagent (AR) chemicals were used for the present investigation, the chemical are pure in nature so they are used directly without any further purification. The substituted bis schiff bases ligands used for the study were synthesized by standard method[29]. Viscosities of the solutions are determined with the help of calibrated Ostwald viscometer (± 0.11% kgm-1s-1). The flow time of solutions is measured by using the digital clock (Racer Company) having an accuracy up to ±0.01Sec. Densities of solutions were determined by a bicapillary pyknometer (± 0.2 %) having a bulb volume of about 10 cm^3 and capillary having an internal diameter of 1mm and calibrated with deionised doubly distilled water. The accuracy of density measurements were within ± 0.1 kgm^3. Weighing was made one pan digital balance (petit balance AD-50B) with an accuracy of ± 0.001 gm.

RESULTS AND DISCUSSION

To determine the relative and specific viscosity, the different concentration of the substituted-N,N'bis(salicyliden)-arylmethanediamines solution were prepared and there viscosities were measured with help of the following mathematical relation

$$(\eta_r)=(ds \times ts/dw \times tw)\times \eta_w \quad (1)$$

Where,
η_r = Relative viscosity
η_w = Viscosity of water
ds = Density of solution
dw = Density of water
ts = Flow time for solution
tw = Flow time for water

From the calculated values of relative viscosities (η_r) and the temperature (T), the graph between log (η_r) vs 1/T can be plotted. The relative viscosities of solutions at different concentration are presented in table 1.

The viscosity data have been analyzed by Jones–Dole equation [30]

$$(\eta_r - 1) / \sqrt{C} = \eta_{sp}/\sqrt{C} = A + B\sqrt{C} \quad (2)$$

$$\eta_{sp} = (\eta_r - 1) \quad (3)$$

Where,
A = Falkenhagen coefficient
B = Jones-Dole coefficient
C = concentration of solutions

The Falkenhagen coefficient (A) measures the solute-solute interation while Jones-Dole coefficient (B) measures the solute-solvent interaction.

The present study deals with the viscosity investigation of Ligand (L_A), Ligand (L_B), Ligand (L_C) and Ligand (L_D) in 70% DMF–Water mixture at different concentration. The results obtained are mentioned in table 1. Calculated values of A and B-coefficient are mentioned in table 2. From the results, it is observed that, the density and relative viscosity of ligand is directly proportional to concentration for ligand L_A, L_B, L_C and L_D for 70% DMF -Water mixture. This may be due to the solvation effect which interprets solute-solvent interaction.

The negative values of A and B-coefficient characterized as 'structure-breaker' indicating a solute-solvent interaction which is good for interactions in between the drug and the drug receptors shows best drug activity and drug effect.

The relation between viscosity ($\eta_{sp}/\sqrt{C}$) and concentration of solution ($\sqrt{C}$) represented by plotting the graph (fig. 1-5). These plotted graphs prove the validity of Jones-Dole equation for all systems by giving linear straight line

For the evaluation of the thermodynamic parameters, the viscosity measurement was carried out at different temperature.

The relationship between coefficient of viscosity of liquid and temperature is expressed as

$$\eta = Ae^{-\Delta G/RT} \quad (4)$$

The graphs are plotted between log η_r and 1/T and are presented in Fig.6 to 10.

The graphs obtained for each system gives linear straight line showing the validity of equation. The thermodynamic parameters i.e. free energy change (ΔG), enthalpy change(ΔH) and entropy change (ΔS) can be determine by using following relation,

$$\Delta G = -2.303 \times R \times slope \quad (5)$$

$$\log \eta_{r1} - \log \eta_{r2} = (\Delta H/2.303) \times (1/T_1 - 1/T_2) \quad (6)$$

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

These thermodynamic parameters for solution of ligands of different concentrations are represented in table 4 . The value ΔG and ΔH indicate reaction is spontaneous and exothermic and negative value of ΔS indicate there is a association of solvent molecule around the ligand mentioned in table 4 .

Table-1: Densites (d) and viscosities (η_r) of substituted-N,N'bis(salicyliden)-arylmethanediamines of different concentration in 70% (DMF+ water) solvent at 303K

Ligand L_A						
Conc(C) (mol/lit)	**√ C ($mol^{1/2}$ $lit^{-1/2}$)**	**Density (gm/cc)**	**Time Flow (s)**	**Relative Viscosity $\eta_r = \eta/\eta_0$**	**Specific Viscosity $\eta_{sp} = \eta_r - 1$**	**$\eta_{sp}/\sqrt{C}$**
0.01	0.1	1.0178	131	1.2885	0.2885	2.8851
0.005	0.0707	1.0150	127	1.2457	0.2457	3.4756
0.0025	0.05	1.0138	123	1.2050	0.2050	4.1013
0.00125	0.0354	1.0124	119	1.1642	0.1642	4.6403
0.000625	0.025	1.0115	116	1.1339	0.1339	5.3563
Ligand L_B						
Conc(C) (mol/lit)	**√ C ($mol^{1/2}$ $lit^{-1/2}$)**	**Density (gm/cc)**	**Time Flow (s)**	**Relative Viscosity $\eta_r = \eta/\eta_0$**	**Specific Viscosity $\eta_{sp} = \eta_r - 1$**	**$\eta_{sp}/\sqrt{C}$**
0.01	0.1	1.0204	158	1.558051	0.5580	5.5805
0.005	0.0707	1.0199	151	1.488294	0.4882	6.9065
0.0025	0.05	1.0183	140	1.37771	0.3777	7.5542
0.00125	0.0354	1.0172	138	1.356562	0.3565	10.0723
0.000625	0.025	1.0164	133	1.306383	0.3063	12.25
Ligand L_C						
Conc(C) (mol/lit)	**√ C ($mol^{1/2}$ $lit^{-1/2}$)**	**Density (gm/cc)**	**Time Flow (s)**	**Relative Viscosity $\eta_r = \eta/\eta_0$**	**Specific Viscosity $\eta_{sp} = \eta_r - 1$**	**$\eta_{sp}/\sqrt{C}$**
0.01	0.1	1.0128	132	1.2919	0.2919	2.9196
0.005	0.0707	1.0119	129	1.2614	3.6984	3.6984
0.0025	0.05	1.0113	127	1.2411	4.8237	4.8237
0.00125	0.0354	1.0109	124	1.2113	5.9714	5.9714
0.000625	0.025	1.0102	119	1.1617	6.4695	4.4695
Ligand L_D						
Conc(C) (mol/lit)	**√ C ($mol^{1/2}$ $lit^{-1/2}$)**	**Density (gm/cc)**	**Time Flow (s)**	**Relative Viscosity $\eta_r = \eta/\eta_0$**	**Specific Viscosity $\eta_{sp} = \eta_r - 1$**	**$\eta_{sp}/\sqrt{C}$**
0.01	0.1	1.0215	172	1.6979	0.6979	6.9793
0.005	0.0707	1.0206	167	1.6471	0.6471	9.153
0.0025	0.05	1.0198	160	1.5768	0.5768	11.5369
0.00125	0.0354	1.0191	153	1.5068	0.5068	14.317
0.000625	0.025	1.0188	148	1.4571	0.4571	18.286

Table-2: *A* = Falkenhagen coefficient, *B*= Jones-Dole coefficient values

Ligand	70% (DMF+ Water) system	
	A ($lit^{3/2}mol^{-1/2}$)	**B (lit/mol)**
L_A	25.08	-149.9
L_B	41.66	-261.8
L_C	10.71	-69.56
L_D	63.41	-428.3

GRAPHICAL REPRESENTATION

Fig-1: √ C Vrs $\eta_{sp}/\sqrt{C}$
(Ligand L_A in 70% DMF + Water)

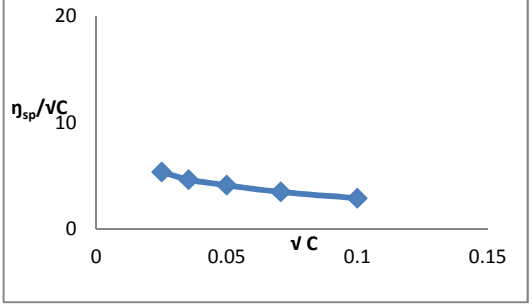
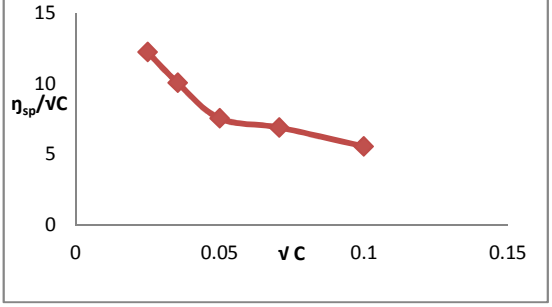
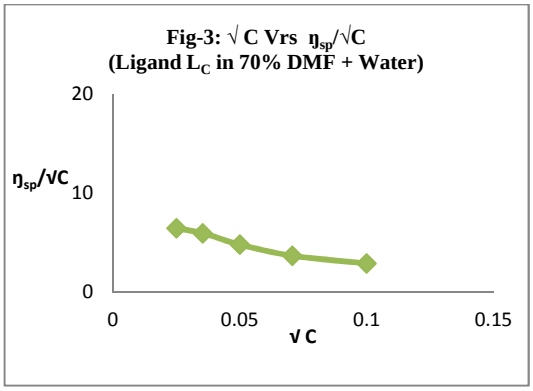
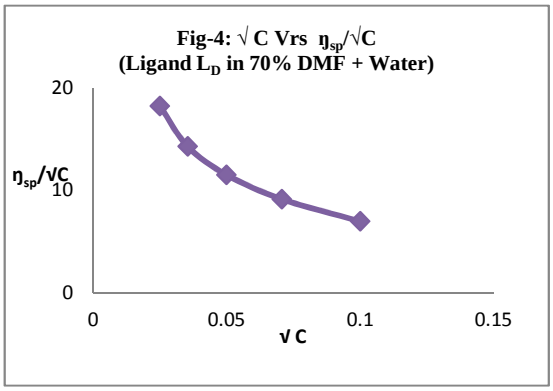


Fig-2: √ C Vrs $\eta_{sp}/\sqrt{C}$
(Ligand $L_B$in 70% DMF + Water)







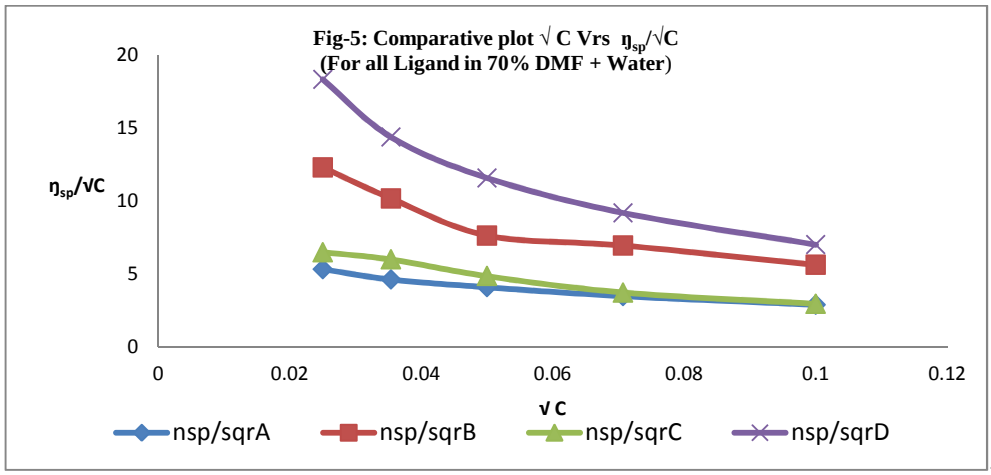


Table-3: Densites(d) and relative viscosities(η_r) of substituted-N,N'bis(salicyliden)-arylmethanediamines of 0.01M concentration in 70% (DMF+ Water) solvent at different temperature (*T*=303, 305,307 and 309K)

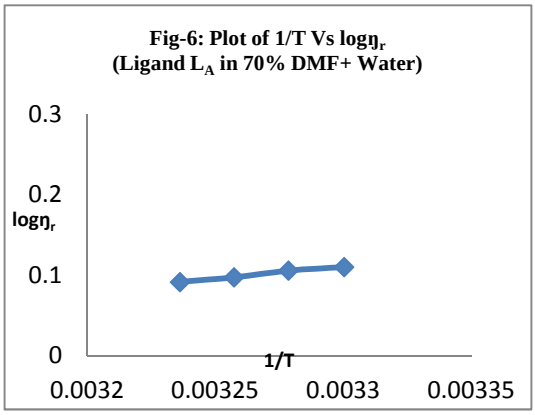
Medium: 70% DMF-Water

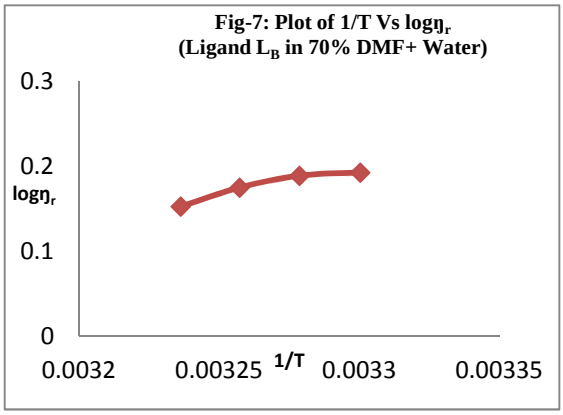
Ligand L_A					
Temp (K)	**1/T x 10^{-3}**	**Density (gm/cc)**	**Time Flow (s)**	**Relative Viscosity (η_r)**	**log η_r**
303	3.300	1.0178	131	1.2885	1.1008
305	3.279	1.0162	126	1.2756	1.0571
307	3.257	1.0155	121	1.2515	0.9744
309	3.226	1.0142	118	1.2350	0.9167
Ligand L_B					
Temp (K)	**1/T x 10^{-3}**	**Density (gm/cc)**	**Time Flow (s)**	**Relative Viscosity (η_r)**	**log η_r**
303	3.300	1.0204	158	1.5581	1.9258
305	3.279	1.0200	152	1.5446	1.8880
307	3.257	1.0197	144	1.4956	1.7481
309	3.226	1.0192	135	1.4199	1.5226
Ligand L_C					
Temp (K)	**1/T x 10^{-3}**	**Density (gm/cc)**	**Time Flow (s)**	**Relative Viscosity (η_r)**	**log η_r**
303	3.300	1.0128	132	1.2920	1.1125
305	3.279	1.0123	125	1.2606	1.0057
307	3.257	1.0119	119	1.2265	0.8866
309	3.226	1.0114	112	1.6900	0.6781
Ligand L_D					
Temp (K)	**1/T x 10^{-3}**	**Density (gm/cc)**	**Time Flow (s)**	**Relative Viscosity (η_r)**	**log η_r**
303	3.300	1.0215	172	1.6979	2.2992
305	3.279	1.0209	166	1.6883	2.2745
307	3.257	1.0201	153	1.5897	2.0131
309	3.226	1.0195	145	1.5255	1.8342

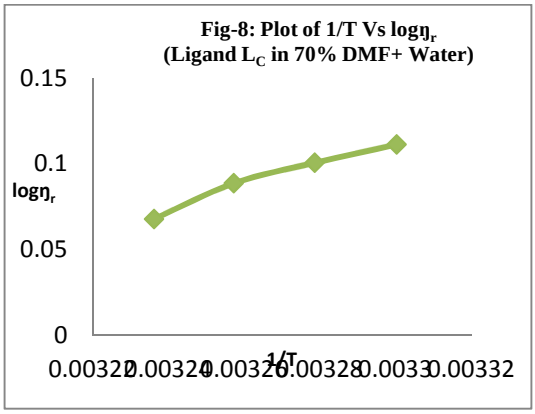
Table-4:Values of thermodynamic parameters for temperature difference 307K – 309K

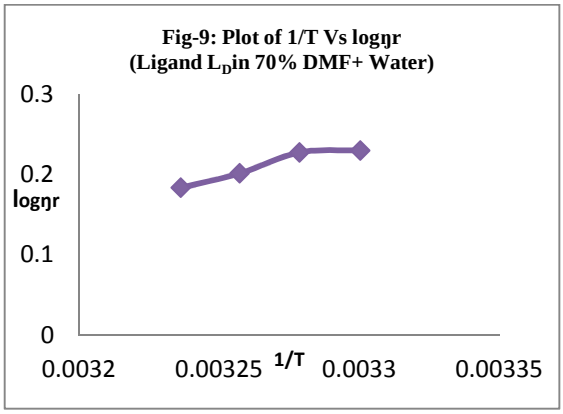
System	ΔG (J mol^{-1} K^{-1})	ΔH (J mol^{-1} K^{-1})	ΔS (J mol^{-1} K^{-1})
L_A	-7907.0	-21512.2	-0.9521
L_B	-9920.0	-10213.5	-0.9494
L_C	-12843.9	-13081.2	-0.7680
L_D	-14844.8	-13929.8	-0.9612

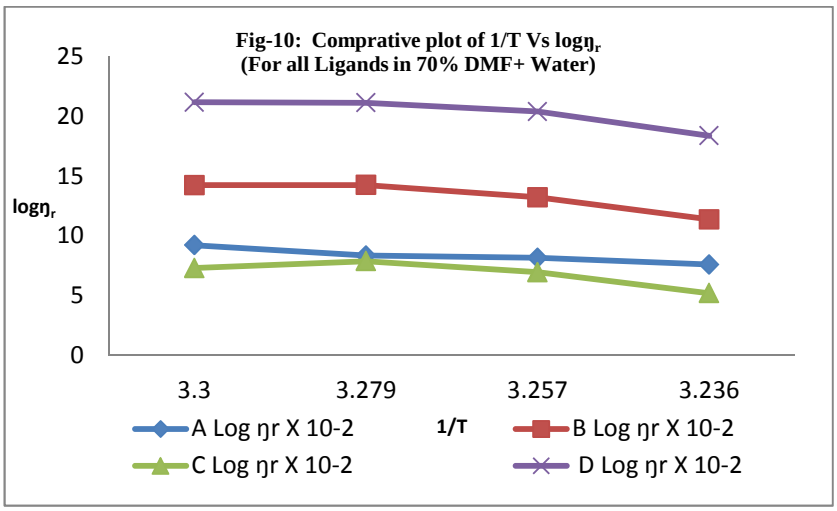
GRAPHICAL REPRESENTATION











CONCLUSION

The present study deals with the in viscometric measurements of N,N'bis(salicyliden)-arylmethanediamine derivatives at different temperatures by using their solutions of different concentrations. The relative viscosity of solution of synthesized ligands increases with increase in the concentration of solutions. The increase in viscosity with increase in concentration may be attributed to the increase in the solute-solvent interactions. The values of Falkenhagen coefficient (*A*-coefficient) are positive in all the systems, shows that there is strong solute-solute interaction in all the systems. The *B*-coefficient is found to be negative for all the systems and it is a measure of disorder introduced by the solute into the solvent in all the systems. The negative values of ΔG and ΔH indicate reactions are spontaneous and exothermic. The negative value of ΔS indicates that there is an association of solvent molecules around the ligand.

Acknowledgement
The authors appreciatively acknowledge The Director; Head, Department of Chemistry, Govt. Vidarbha Institute of Science and Humanities, Amravati for providing the necessary facilities and help during the work.

REFERENCES

[1] A. Solank, I. Thakur, *Ind. J. Chem*., **2006**, 45B, 517.
[2] K.M.Darji, D.R.Patel, G.D.Acharya, *Int. J. Adv. Pharma. Bio. Chem.*, **2014**, 3(3), 529.
[3] T.Kanabara ,Y.Kawai, K.Hasegawa, *J. Polym. Sci. A*, **2001** ,39(21), 3739.
[4] T.Kaliyappan, S.Rajagopan,P.Kannan, *J. Appl. Polym. Sci*., **2004** , 91(1), 494.
[5] T. S.Pitchumony, M.Palaniandava, *Inorganica Chimica Acta*, **2002**, 337, 420.
[6] M.Shaikha, M. Shafiqb, M. Farooquic, *J. Adv. Sci. Res*., **2011**, 2(2), 21.
[7] N. Sakamoto, *Polymer*., **1987**, 28(2), 288.
[8] P.Hormnirun, A.Sirivat, A.M.Jamieson, *Polymer*, **2000**, 41(6), 2127.
[9] E.Díaz, R.Valenciano, J.González, *Polymer Testing*, **2002**, 21(3), 247.
[10] M.S.Ali, M.A.Rub, K.Din, *J. Saudi Chem. Soc*., **2015**, 19(1), 83.
[11] Y.Sun , X. Li, S. Hirota, *Biophys. J*., **2003**, 85(2), 1223.
[12] N.G. Belnikevitch, *Polymer*, **1983**, 24(6), 719.
[13] Y.Li , Y.Li, B.Ren, *J. Chem. Thermodynamics*, **2013**, 66, 14.
[14] Y.Li, Y.H.Li, B.Z. Ren, *Thermochimica Acta*, **2013**, 568,189.
[15] S. J. Kharat, *Thermochimica Acta*, **2013**, 566, 124.
[16] M.A.Mughal, A.H.Mughal, H.Saleem, IOSR *J. Eng. (IOSRJEN)*, **2014**, 4(2), 20.
[17] Y. Li, Z.S.Yang, F.D.Wang, *Bioorg. Med. Chem*., **2003**, 11 , 4363.
[18] S.A.Matar, W.H.Talib, M.A.AlDamen, *Arabian J.Chem*., **2015**.
[19] M.S.Alam, J.H.Choi, D.U.Lee, *Bioorg.Med.Chem*., **2012**, 20(13), 4103.
[20] G.Saravanan, V.Alagarsamy, C.R.Prakash, *Drug Discoveries and Therap*., **2012**, 6, 78.
[21] M.B. Palkar , K.S. Jain, *Med. Chem. Res*., **2015**, 24(5), 1988.
[22]A.M.Alafeefy, M.A.Bakht, A.S.Awaad, *Bioorg. Med. Chem. Letters*, **2015**, 25(2), 179.
[23] S.N.Pandeya, D.Sriram, E.Declercq, *Pharmaceutica Acta Helvetiae*., **1999**, 74, 11.
[24] S.N.Pandeya , D.Sriram,EDeclercq, *Eur. J. Pharm. Sci*., **1999**, 9(1), 25.
[25] P.Kavitha, M.R.Chary, K.L. Reddy, *J. Saudi Chem. Soc*., **2013**, 1.
[26] P. Kavitha, K.L. Reddy, *Arabian J.Chem*., **2013**, 1.
[27] P. Kavitha, K.L.Reddy, *Arabian J.Chem*., **2012**, 1.
[28] J.Lu, Q.Sun, Li, S.P.Yan, *J. Inorg. Biochem.*, **2014**, 137, 46.
[29] H.Naeimi, K.Rabiei, F. Salimi , *Bull. Korean Chem. Soc*., **2008**, 29(12), 2445.
[30] G. Jones, M. Dole, *J. Am. Chem. Soc*., **1929**, 5(1), 2950.