Viscometric Study of Substituted 1-Phenyl-3-Aryl-1H-Pyrazol-4-Carboxylic Acid in 70% DMF- Water at Different Temperature

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Abstract

Density and viscometric measurements of Substituted 1-phenyl-3-aryl-1H-pyrazol-4-carboxylic acid derivatives in binary mixture of 70% DMF-water are performed. Jones-Dole empirical equation analyzed the obtained data .Thermodynamic parameters enthalpy change(ΔH) , entropy change (ΔS) and Gibbs free energy change(ΔG) is determined. The interactions between solute-solute, solute-solvent and solvent–solvent interactions are studied.

KEYWORDS: Substituted 1-phenyl-3-aryl-1H-pyrazol-4-carboxylic acid derivatives, Jones-Dole empirical equation and thermodynamic parameters.

Introduction

To predict solute–solvent interactions in the solution, volumetric and viscometric properties are helpful. This interactions also helpful in predicting the absorption of drugs and transport of drugs across the biological membranes. To understand drug action, the drug–water molecular interaction and their temperature dependence play an important role. The interaction of β-cyclodextrin with the amphiphilic drug promazine hydrochloride by using viscometric technique is reported.[1] The average free energy of activation of the pure solvent can be calculated at all the temperatures according to Eyring's model.[2] Many industrial chemical processes or laboratory works need experimental data of viscosity at any given temperature and composition for binary liquid mixtures.[3] Effect of temperature and chain length on the viscosity and surface tension of binary systems of N, N-dimethylformamide with 1-octanol, 1-nonanol and 1-decanol are studied.[4] The literature survey shows the viscosity at different concentration of magnesium sulphate in mixture of formamide and ethylene glycol at room temperature is studied.[5] Effect of temperature on viscosity of substituted aminopyrimidine in 60% DMF-water Mixture is reported.[6] Influence of the temperature on the viscosity of magnetic ionic liquids is studied.[7] Gibbs free energy change, entropy change and enthalpy change in aqueous binary mixture of isomeric diols is reported at different temperature.[8] The volumetric and viscometric study of glycine at different temperatures are done.[9] Viscometric study at different temperatures of schiff-based resin of 2-methoxy-1-napthaldehyde is reported.[10] Viscometric study of substituted 2-oxo-2-H-chromene-3carbohydrazide derivatives in 70% DMF- water at different temperatures are reported.[11] Volumetric and viscometric study of thiamine hydrochloride, pyridoxine hydrochloride and sodium ascorbate at T = (275.15, 277.15 and 279.15) K in dilute aqueous solutions is reported.[12]

Density and viscosity measurements for 4-aminobutyric acid in various composition in aqueous metformin hydrochloride at different temperature are reported.[13] Density and viscosity of drug paracetamol in various aqueous mixtures of ethanol is determined.[14] Density and viscosity of sodium ibuprofen in water at various temperature is studied.[15] Density and viscosity are studied at various temperature and composition of fatty acid and methyl esters from soyabean, castor and Jatrophacurcas oils.[16] Densities and viscosities are studied at different temperatures for aqueous binary mixtures of glycol-ether at various concentration range.[17-18] Thermodynamic properties of sodium dodecyl sulfate in aqueous mixtures of methanol, ethanol, n-propanol and iso-propanol at different temperatures are investigated.[19] Thermodynamic parameters of substituted azomethine drugs is done by viscometrically.[20] Thermodynamic parameters of various drugs like substituted pyrazolin,[21-22]substituted thiopyrimidine,[23] nicotinic acid,[24] amino acids,[25] niacin,[26] dodecyltrimethylammoniumbromide,[27] 1,3-diaryl carbamides, [28] curcumin mixture[29] are determined. Thermodynamic study of polyvinyl pyrrolidone in water/dimethyl sulfoxide solutions is reported by viscometrically.[30] Studies of volumetric, viscometric and molar properties of diisopropyl amine with 1-alkanols (C_6–C_{10}) at different temperatureis reported.[31]

Viscometric studies on substituted-2, 3Dihydroquinazolin- 4 (1H) ones in 70%DMF-water is done.[32] Viscosity of ammonium salts in water and ethanol-water systems is studied.[33] Viscometric properties of binary mixtures of 1,3,4-oxadiazole derivative with chloroform, N,N-dimethyl formamide at 303, 308 and 313 K and atmospheric pressure is done.[34] The metal complexes of Cu(II), Co(II), Ni(II) and Zn(II) withchromone schiff base are reported.[35] Viscosity for different molar concentration of L-Cerine, L-Proline and L-Histidine in dioxane-water mixture have investigated.[36] The viscometric studies of methyl cellulose-sodium dodecyl sulphate complex in aqueous solution is reported.[37]

In the present work, viscometric study of substituted1-phenyl-3-aryl-1H-pyrazol-4-carboxylic acid is carried out at different temperatures by using their solutions of different concentrations. Following substituted1-phenyl-3-aryl-1H-pyrazol-4-carboxylic acid are used.

i) Ligand A (L_A)= 1- phenyl-3-(4’- methyl) phenyl-1H- pyrazol-4-carboxylic acid
ii) Ligand B (L_B)= 1- phenyl-3-(4’- bromo) phenyl-1H- pyrazol-4-carboxylic acid
iii) Ligand C (L_C)= 1- phenyl-3-(4’- ethyl) phenyl-1H- pyrazol-4-carboxylic acid
iv) Ligand D (L_D)= 1, 3-diphenyl-1H- pyrazol-4-carboxylic acid

The solutions of ligands are prepared in the 70% solvent-water at different temperature (T= 300K, 305K, 310K and 315K) and at different concentration.

Experimental

The ligands of which physical parameters are to be explored are synthesized by using reported protocol.[38] The A. R. grade solvents and freshly prepared doubly distilled water are used. The densities of pure solvent and solutions of various concentrations are measured at different temperatures using a specific gravity bottle. All the weights are taken on one pan digital balance (petit balance AD-50B) with an accuracy of ± 0.001 gm. Viscosities of the solutions are determined with the help of calibrated Ostwald viscometer (± 0.11% $Kgm^{-1}s^{-1}$). The flow time of solutions are measured by using digital clock (Racer Company) having an accuracy up to ±0.01Sec.

Results and Discussion

To calculate the relative and specific viscosity the following empirical equations are useful. [39-41]

$$\eta_r = \frac{\eta}{\eta_0} = \frac{d_s \times t_s}{d_0 \times t_0} \qquad (1)$$

$$\eta_{sp} = (\eta_r - 1) \qquad (2)$$

Where,

η_r	Relative viscosity
η_{sp}	Specific viscosity
d_s	Density of solution
η	Viscocity of solution
η_o	Viscosity of solvent
d_o	Density of solvent
t_o	Flow time for solvent
t_s	Flow time for solution

The viscosity data can be analyzed by Jones-Dole empirical equation.[42-43]

$$\frac{\eta_r - 1}{\sqrt{c}} = \frac{\eta_{sp}}{\sqrt{c}} = A + B\sqrt{c} \qquad (3)$$

Where,

A =Falkenhagen coefficient

B = Jones-Dole coefficient

C = Concentration of solutions

The Falkenhagen coefficient (*A*) reflects the solute-solute interactions while Jones-Dole coefficient (*B*) reflects the solute-solvent interactions.[44]

The thermodynamic parameters can be calculated by using following equations.[45]

$$\Delta G = - 2.303 \text{ R x Slope} \qquad (4)$$

$$\log\frac{\eta_{r1}}{\eta_{r2}} = \left(\frac{\Delta H}{2.303}\right)\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (5)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad (6)$$

In present study with increase in concentration, the relative viscosity and density of the compounds increases. The increase in viscosity with increase in concentration credited to the increase in the solute-solvent interactions. The viscosity and density data for different ligands at different concentration is given in table no.1

Table1: Densities(d) and viscosities(η_r) of substituted1-phenyl-3-aryl-1H-pyrazol-4-carboxylic acid derivatives of different concentration in 70% (DMF+ water) solvent at 300K.

Conc. (C) mol/lit	L_A		L_B		L_C		L_D	
	Density (d) gm/cc	Relative Viscosity (η_r)	Density (d) gm/cc	Relative Viscosity (η_r)	Density (d) gm/cc	Relative Viscosity (η_r)	Density (d) gm/cc	Relative Viscosity (η_r)
0.01	1.0639	2.4737	1.0728	2.4737	1.0437	2.3010	1.0722	2.3269
0.005	1.0616	2.3221	1.0706	2.3221	1.0415	2.1704	1.0695	2.2289
0.0025	1.0592	2.2256	1.0693	2.2256	1.0407	2.0791	1.0683	2.1528
0.00125	1.0589	2.0973	1.0680	2.0973	1.0395	1.9872	1.0671	2.0584
0.000625	1.0577	1.8946	1.0666	1.8946	1.0383	1.8419	1.0660	1.8176

The graphs are plotted between √C versus $\eta_{sp}/\sqrt{C}$. The graphs for each system show the validity of Jones-Dole equation. The values of *A* and *B* have determined from the intercept and slope of √C versus

$\eta_{sp}/\sqrt{C}$ respectively. The plots of $\sqrt{C}$ versus $\eta_{sp}/\sqrt{C}$ for all four systems are shown in Fig. no. 1 to 5. From the table no. 2 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 Falkenhagen coefficient-*A* is positive in all the systems and this coefficient reflects strong solute-solute interaction.

Table 2: *A* and *B* Coefficient values

Ligand + 70% DMF-Water	*A* (lit$^{3/2}$ mol$^{-1/2}$)	*B* (lit mol^{-1})
L_A	13.918	-48.379
L_B	26.365	-116.09
L_C	27.289	-129.89
L_D	40.091	-216.47

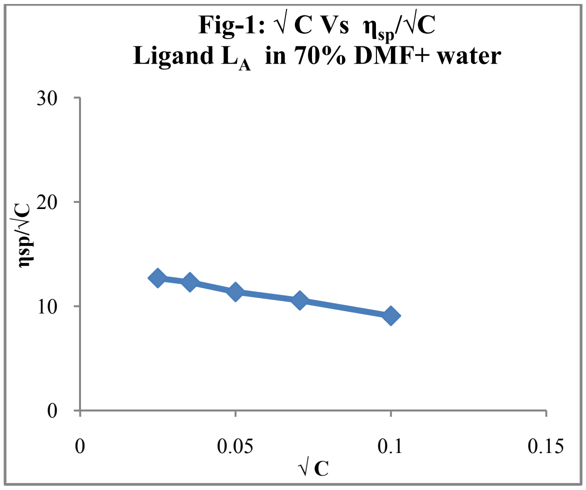


Fig-1: √ C Vs $\eta_{sp}/\sqrt{C}$
Ligand L_A in 70% DMF+ water

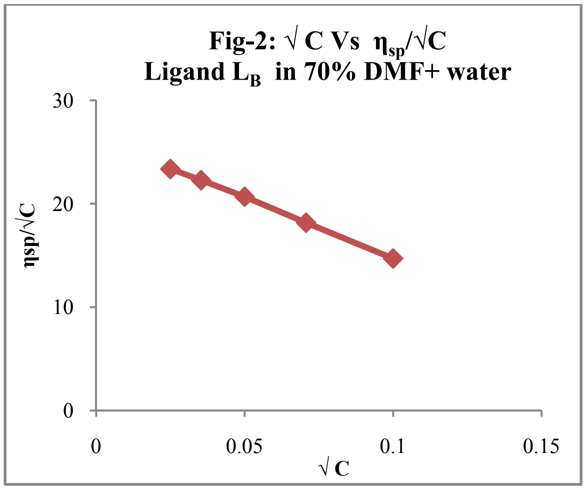


Fig-2: √ C Vs $\eta_{sp}/\sqrt{C}$
Ligand L_B in 70% DMF+ water

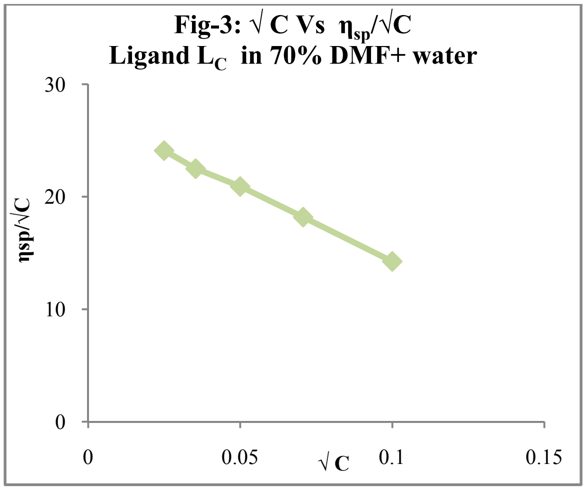


Fig-3: √ C Vs $\eta_{sp}/\sqrt{C}$
Ligand L_C in 70% DMF+ water

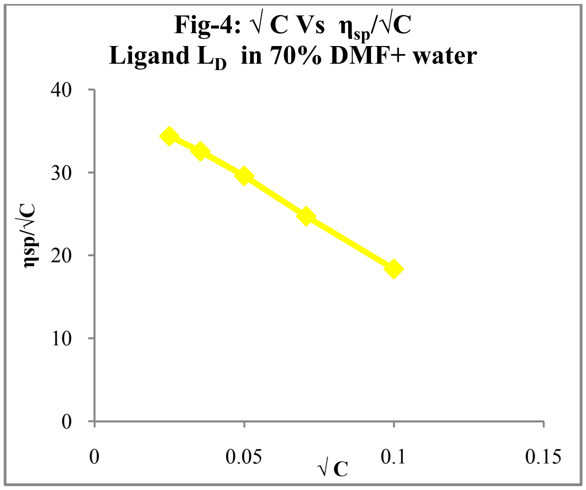


Fig-4: √ C Vs $\eta_{sp}/\sqrt{C}$
Ligand L_D in 70% DMF+ water

Viscometric study is performed for substituted1-phenyl-3-aryl-1H-pyrazol-4-carboxylic acid at following different temperatures 300, 305, 310 and 315K. The experimental data of different ligands is presented in table no. 3.

The thermodynamic parameter Gibbs free energy change (ΔG), enthalpy change(ΔH) and entropy change (ΔS) are studied for substituted 1-phenyl-3-aryl-1H-pyrazol-4-carboxylic acid at different temperatures. All these thermodynamic parameters are calculated by plotting graphs between 1/T versus logη_r. These are shown in the fig. no. 6 to 10. These thermodynamic parameters for solutions of different ligands at various concentrations are presented in table no. 4. The values of ΔG and ΔH are found to be negative. The negative values of ΔG and ΔH indicate the reactions are spontaneous and exothermic respectively. The negative value of ΔS indicates that there is an association of solvent molecules around the ligand.

Fig-5: √ C Vs ηsp/√C (All Ligands in 70% DMF+ water)

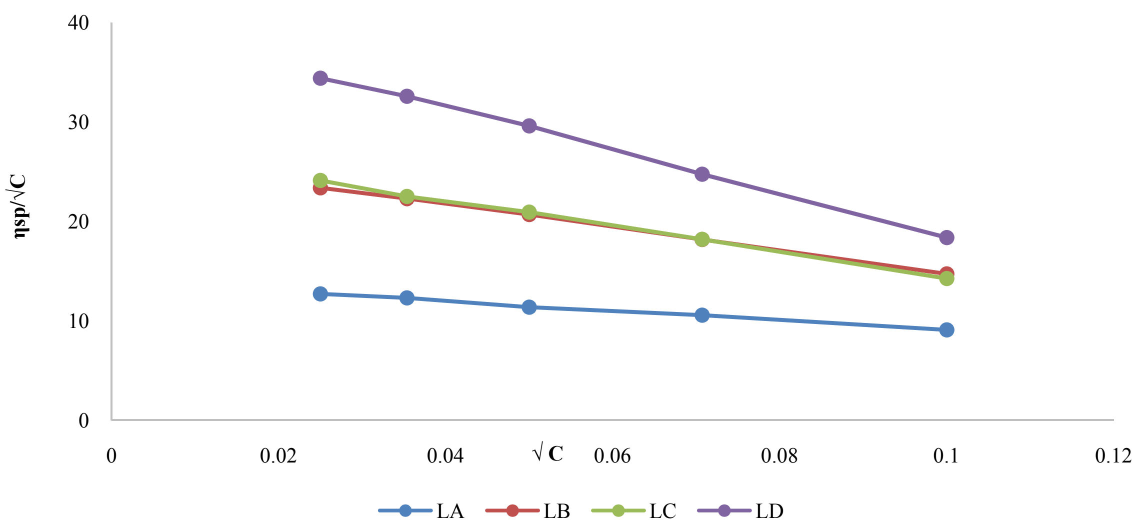


Table 3 Densites (d) and relative viscosities (η_r) of Substituted 1-phenyl-3-aryl-1H-pyrazol-4-carboxylic acid derivatives of 0.01M concentration in 70% (DMF+ Water) solvent at different temperature (*T*= 300, 305, 310 and 315K).

Temp. (K)	**L_A**		**L_B**		**L_C**		**L_D**	
	Density (d) gm/cc	**Relative Viscosity (η_r)**	**Density (d) gm/cc**	**Relative Viscosity (η_r)**	**Density (d) gm/cc**	**Relative Viscosity (η_r)**	**Density (d) gm/cc**	**Relative Viscosity (η_r)**
300	1.0639	2.1072	1.0728	2.3835	1.0437	1.0437	1.0722	2.3268
305	1.0621	2.0100	1.0715	2.2209	1.1437	1.1437	1.0635	2.2043
310	1.0614	1.9057	1.0701	2.0831	1.2032	1.2032	1.0512	2.0264
315	1.0605	1.7687	1.0695	1.9936	1.1973	1.1973	1.0411	1.8793

Table 4: Values of thermodynamic parameters for temperature difference(300 to 315K)

Ligands	ΔG **(J mol^{-1})**	ΔH **(J mol^{-1})**	ΔS **(J mol^{-1} K^{-1})**
L_A	-1327.1	-4432.4	-99.23
L_B	-1055.2	-3246.5	-70.25
L_C	-1085.3	-3381.8	-74.26
L_D	-1787.5	1483.5	-42.13

Fig-6: Plot of 1/*T* Vs logη_r Ligand L_A in 70% DMF+ water

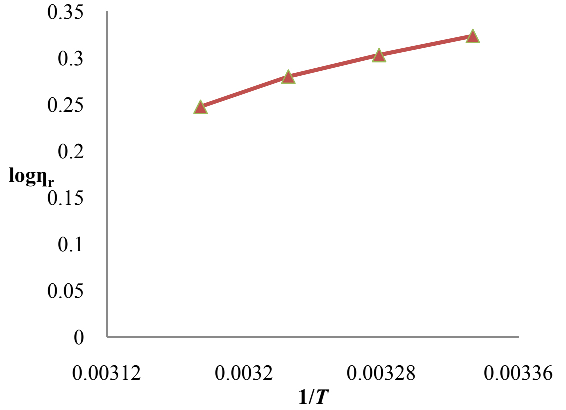


Fig-7: Plot of 1/*T* Vs logη_r Ligand L_B in 70% DMF+ Water

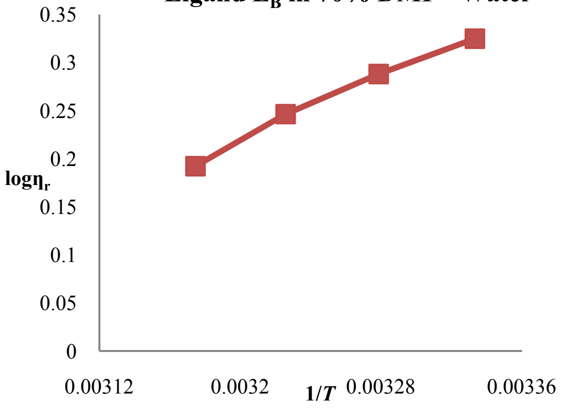


Fig-8: Plot of 1/*T* Vs logη_r Ligand L_c in 70% DMF+ Water

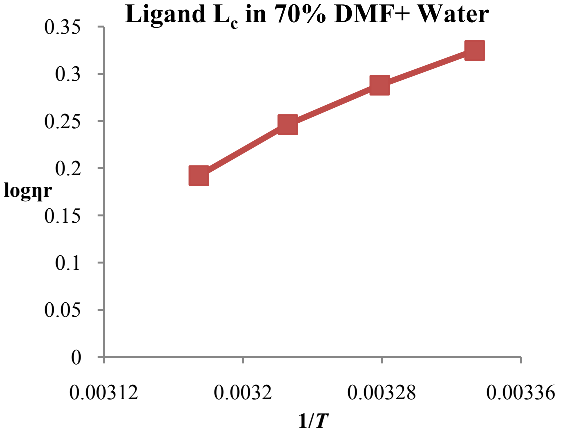
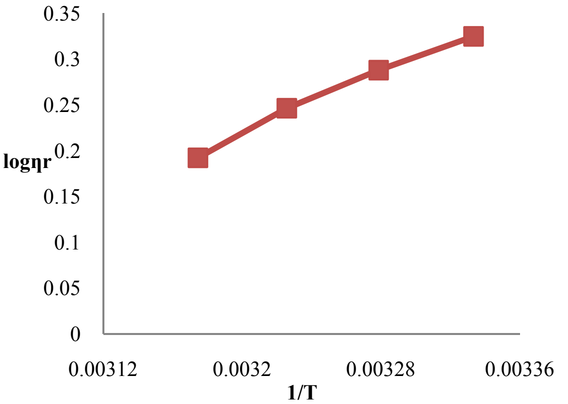


Fig-9: Plot of 1/T Vs logηr Ligand L_D in 70% DMF+ Water



Conclusions

In the present work, viscometric study is performed at different temperatures for substituted 1-phenyl-3-aryl-1H-pyrazol-4-carboxylic acid. It is found that the density and relative viscosity increases as the concentration increases. And it is attributed to the concentration increases the increase in the solute-solvent interaction. *B*-coefficient is found to be negative for all the systems and it measures the disorder introduced by solute into the solvent. The Falkenhagen coefficient-*A* is positive in all the systems and this coefficient reflects strong solute-solute interaction in systems. The negative values of ΔG and ΔH indicates the reactions are spontaneous and exothermic. The negative values of ΔS indicate that there is an association of solvent molecules around the ligand.

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References

[1]. M. S.Ali, M.A.Rub, K.Din, J. Saudi Chem. Soc., 2015,19(1),83.
[2]. T. S. Banipal,H. Singh, P.K.Banipal, V.Singh, Thermochim. Acta., 2013, 553, 31.
[3]. A. Awasthi, Thermochim. Acta, 2012, 537, 57.
[4]. A.M. Abubaker, M.S.Alkhaldi, A.S. Al-Tuwaim, J. Chem. Thermo., 2014, 74, 7.
[5]. A. Ali, M.Ibrahim, Pro. Ind. Acad. Sci., 2002, 114(5), 495.
[6]. M.M.Kalaskar, H.S.Chandak,M.P.Wadekar, J. Chem, Bio. And Phy. Sci.,2015, 5(4), 3868.
[7]. C. I. Daniela,J. Albo, E. Santos, A. Irabien, Fluid Phase Equa., 2013, 360, 29.
[8]. B. Hawrylak, S. Reecyk,C. Gabriel, Kim Gracie, J. Sol.Chem., 1998, 27(9), 827.
[9]. A. Pal, S.Kumar, Indian J. Chem., 2005, 44(A), 469.
[10]. M.A.Mughal, A.H.Mughal, H.Saleem, IOSR J. Eng., 2014, 4(2), 20.
[11]. P.P.Choudhari, D.S.Hedaoo, M.P.Wadekar, J. Chem, Bio. And Phy. Sci., 2016, 6(4), 1262.
[12]. S.S.Dhondge, P.N.Dahasahasra, L.J.Paliwal,V.M.Tangde, D.W.Deshmukh, J. Chem. Thermo., 2017, 107, 189.
[13]. K. Rajagopal, S.Jayabalakrishnan, J. Serb.Chem.Soc., 2011,76(1),129.
[14]. M.Shaikha, M.Shafiqb, M.Farooquic, J. Adv. Sci. Res., 2011, 2, 2.
[15]. S.J.Kharat, Thermochim. Acta, 2013, 566, 124.
[16]. K.U.Mara, R.F.Juliana, L.Marcos, J. Chem. Thermo., 2013, 58, 460.
[17]. C.Joao, Diogo, A.William, Fluid Phase Equilibria, 2013, 353, 76.
[18]. S.S.Dhondge, D.W.Deshmukh, J. Chem. Thermo., 2011, 43, 1961.
[19]. M.A.Motin, M.A.H.Mia, A.K.M.N. Islam, J. Saudi. Chem. Soc., 2015, 19, 172.
[20]. A.V.Kawalkar, D.S.Hedaoo, M.P.Wadekar, J. Chem, Bio. And Phy. Sci., 2015, 5(4), 3751.
[21]. V.G.Raut, P.B.Raghuwanshi, A.G.Doshi, Asian J. Chem., 2000, 12(3), 896.
[22]. P.B.Ragghuwanshi, M.L.Narwade, A.G.Doshi, Asian J. Chem.,2000,12(4), 973.
[23]. M.P.Wadekar, A.S.Shrirao, R.R.Tayade, Der Pharmacia Lettre, 2014, 6(6), 158.
[24]. T.A.Salman, K.A.Abd, Baghdad Sci. J., 2013, 10(2), 432.
[25]. R. Srivastava, A.R.Saksena, A. Gupta, Asian J. App. Sci., 2010, 3(1),13.
[26]. M.L.Narwade, R.Jumle, U. Wasnik, Asian J. Chem., 2002, 14(3), 1436.
[27]. M.F.Hossain, T.K.Biswas, M.N.Islam, M.E.Huque, Monatsh Chem., 2010, 141, 1297.
[28]. S.S.Ubarhande, A.G.Gotmare, A.S.Burghate, B.N. Berad, Rasayan J. Chem.,2012, 5(3), 360.
[29]. A.Pandey, A.K.Shukla, A.R.Saksena, R. Srivastava, World App. Sci J., 2011,1 3(4),725.
[30]. A.Mehrdad, J. Solution. Chem., 2012, 41(5), 766.
[31]. Gyan Prakashdubey, J.krishankumar, J. Mol. Liq., 2017, 229, 255.
[32]. D.S.Hedaoo, M.M.Kalaskar, M.P.Wadekar, J. Chem. Bio. And Phy. Sci., 2015, 5(3), 1719.
[33]. R. Saeed ,F. Uddin ,S. Masood,N. Asif , J.Mol.Liq., 2009,146(3), 112.
[34]. D.R.Godhani,P.B.Dobariya,A.M.Sanghani,J.P.Mehta,Arabian J.Chem.,2017,10(1), S422.
[35]. P. Kavitha, K.L.Reddy, Arabian J.Chem., 2012,1.
[36]. R. Palani, V. Shanbag, RasayanJ.Chem., 2008,1(3),495.
[37]. N. Sakamoto, Polymer, 1987, 28(2), 288.
[38]. M.A.Kira, M.O.Abdal-Raeman ,K.Z. Gadalla, Tetrahydron letter,2,1969,109.
[39]. B.S.Bhal ,G.D. Tuli,ABahl , Essentials of Phy.Chem.,24th Edition, S.Chand, New Delhi,1999, 356.
[40]. K.Kaur,H. Kumar, J. Mol. Liq., 2013,177,49.
[41]. P.B.Raghuwanshi,M.L.Narwade,A.G.Doshi, Asian J. Chem.,2000 12(4), 973.
[42]. G. Jones , M. Dole, J. Am. Chem. Soc., 1929, 5(1),2950.

[43]. R. Gupta ,M. Singh, J. Chem. Sci., 2005, 117(3), 275.
[44]. T.S. Banipal ,H. Singh ,P.K. Banipal, J. Chem. Eng. Data,2010,55, 3872.
[45]. R.R. Tayade,M.M. Kalaskar,M.P. Wadekar, Arch. Appl. Sci. Res.,2014,6(5).