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Thermodynamic study of different substituted imidazolinone drugs at different concentration in 70% (DMF+water) solvent by viscometrically

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ABSTRACT

In the present work we investigate the densities, specific viscosities of different substituted 5-oxo imidazolinone drugs of different concentration in the range ($1x10^{-2}$ M to $6x10^{-4}$ M) in 70% (DMF+water) solvent at 303K.. The experimental data study the effect of concentration of solute on viscosity in DMF-water mixtures. From the viscometric data, the molecular interactions present in different solutions were studied. Appreciable molecular interactions have been observed between solute substituted 5-oxo imidazolinone and solvent 70%(DMF-water) mixture. The themodynamic properties such as free energy change(ΔG), enthalpy change(ΔH) and entropy change (ΔS) of different substituted oxoimidazolinone drugs have been investigated in 70% (DMF+water) solvent by the measurement of densities and viscosities at different temperature such as 305K, 307K and 309K. The experimental data study gives the idea about effect of temperature on the molecular interaction and nature of reaction.

Key words: specific viscosity, Density, thermodynamic parameters, substituted 5-oxo oxoimidazolinone.

INTRODUCTION

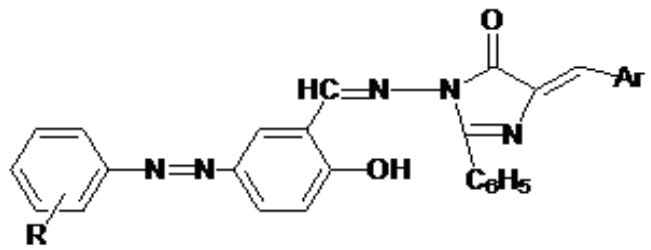
Viscosity is one of the important physical property owned by the liquid. Shearing effect in the liquid is responsible for the viscous nature of the liquid which is nothing but the movement of liquid layers over each other. Viscometric study reveals the important information regarding solute-solute and solute-solvent interaction in an aqueous and in nonaqueous solution.

Solute-solvent interactions play an crucial role in a variety of phenomenon. Mehrotra et al[1], Das et al[2] and Kapadi et al[3] collectively studied the molecular interaction of an electrolyte in binary mixture of liquids. Berry and Irvings[4] has done the viscometric study of concentrated aqueous electrolyte solution at various concentrations. Dhondge et al[5] has been done the viscometric studies of some drugs including Metform in hydrochloride (MH), Ranitidine hydrochloride (RH), and Tramadol hydrochloride (TH) in aqueous solutions at different temperatures. Pandey et al.[6] has done the viscosity measurement of aqueous binary electrolyte having different molar concentrations. A report on viscometric studies on N,N-dimethyl acetamide and ethanol binary mixtures at different temperatures was also presented by Peshwe et al[7]. The Jones-Doles equation[8] helps to evaluate the observed viscosity concentration dependence of dilute electrolyte solutions. The density and viscosity of thiamine hydrochloride + water and pyridoxine hydrochloride +water at different temperatures were measured by Dhondge et al[9]. The dependence of concentration of viscosity in concentrated electrolyte solution was reported by Breslau Miler[10] and Vand[11]. Rajagopal et al[12] also reported density and viscosity measurements for 4-aminobutyric acid in various composition in aqueous metformin hydrochloride at different temperature.

Recently, X. Meng et al. reported the study of viscosity of 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) in the temperature of 243K to 363K from saturated pressures up to 30 MPa, which offers a remarkably low global warming potential. João C.F. Diogo[13] et al reported measurements of the viscosity of the ionic liquids 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl] imide ([C6mim][NTf2]), 1-ethyl-3-methylimidazolium ethyl sulfate ([C2mim][EtSO4]) and 1-ethyl-3-methylpyridinium ethyl sulfate [C2mpy][EtSO4], by means of a vibrating wire viscometer. The study of of the (LiF + NaF + KF(eut.)+Na7Zr6F31) fluoride system has been investigated by Peter Barborík et al[14]. Lee et al [15] has been reported the Estimation of micro structure of titania particulate dispersion through viscosity measurement. Jo et al[16] has done the viscosity measurements of multi-walled carbon nanotubes-based high temperature nano-fluids. Effects of concentration and temperature on viscosity in (l-alanine/l-threonine/glycylglycine + aqueous d-glucose/aqueous sucrose) systems has been reported by Riyazuddeen et al[17]. Comuñas et al[18] studied the viscosity measurements for squalane at high pressures to 350 MPa from T= 293.15K to 363.15K. The density and viscosity of binary (1-hexene + 1-decene) mixtures have been simultaneously measured over the temperature range from 298K to 470 K and at pressures up to 196 MPa have been investigated by Sagdeev et al[19]. Freitas et al[20] measured and predicted the high-pressure viscosities of biodiesel fuels. Measurement of viscosity of highly viscous non-Newtonian fluids by means of ultrasonic guided waves has been reported by Kazys et al[21]. Ghatee et al[22] has investigated measurement and study of density, surface tension, and viscosity of quaternary ammonium-based ionic liquids ($[N_{222(n)}]$Tf2N). High-throughput viscosity measurement of protein formulation using capillary electrophoresis instrumentation have been investigated by Allmendinger et al[23].

In the present work viscometric study of substituted 5-oxoimidazolidone was carried out at different temperature by preparing the solutions of different concentrations in 70% (DMF+water) solvent .

Different substituted oxoimidazolinone used are-



L_A: R = -3-Chloro

L_B: R = -H

L_C: R = -4-Bromo

L_D: R = -2-Bromo

L_E: R = -4-methoxy

L_A =1-[2-hydroxy-5-(phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene- 5- oxoimidazoline
L_B =1-[2-hydroxy-5-(4-bromo phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene-5-oxoimidazoline
L_C =1-[2-hydroxy-5-(4-methoxy phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene- 5-oxoimidazoline
L_D =1-[2-hydroxy-5-(2- bromo phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene- 5-oxoimidazoline
L_E =1-[2-hydroxy-5-(3-chloro phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene- 5-oxoimidazoline

MATERIALS AND METHODS

The ligands of which physical parameters is to be explore are synthesized by using reported protocol[24]. The DMF of AR grade was used. Freshly prepared doubly distilled water was used. The densities of pure solvent and solutions of various concentrations were measured at different temperature using a calibrated pycnometer. All the weighings were made on one pan digital balance (petit balance AD_50B) with an accuracy of + 0.001 gm. Viscosities of the solutions were determined with the help of calibrated Ostwald viscometer (± 0.11% Kgm-1s-1). The flow time of solutions were measured by using digital clock of racer company having error (±0.01Sec).

CALCULATION

To determine the relative and specific viscosity, in the different concentration of the substituted oxoimidazolidone solution were prepared and there viscosities are measured with help of the following mathematical relation

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

Where
η_r = Relative viscosity
η_w = Viscosityof 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 (ŋr) and the temperature (T),the graph between log (ŋr) 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[25]

$(\eta_r - 1) /\sqrt{C} = \eta_{sp}/\sqrt{C} = A + B\sqrt{C}$ ---------- (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 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…… (4)

$\log \eta_{r1} - \log \eta_{r2} = (\Delta H/2.303) \times (1/T1 - 1/T2)$ …… (5)

$\Delta S = (\Delta G - \Delta H)/T$…… (6)

Table 1 Densites (d) gm/cc and specific viscosities (ŋsp) of substituted oxoimidazolinone of different concentration in 70% (DMF+ water) solvent at 303K

Conc. X 10^{-3} mole/lit	L_A		L_B		L_C		L_D		L_E	
	Density (d) gm/cc	Rel. Viscosity η_r	Density (d) gm/cc	Rel. Viscosity η_r	Density (d) gm/cc	Rel. Viscosity η_r	Density (d) gm/cc	Rel. Viscosity η_r	Density (d) gm/cc	Rel. Viscosity η_r
10	1.0168	1.2086	1.0229	1.4927	1.0138	1.1659	1.0225	1.6601	1.0215	1.2635
5	1.0144	1.1862	1.0214	1.4806	1.0128	1.1452	1.0218	1.6096	1.0208	1.2134
2.5	1.0128	1.1549	1.0209	1.4602	1.0119	1.1148	1.0211	1.5796	1.0201	1.1633
1.25	1.0114	1.1240	1.0198	1.3896	1.0112	1.0847	1.0206	1.4499	1.0194	1.1231
0.625	1.0105	1.0937	1.0174	1.3077	1.0104	1.0643	1.0199	1.3503	1.0188	1.0929

The value of A = Falkenhagen coefficient, B= Jones-Dole coefficient is calculated by ploting the graph between of $\sqrt{C}$ Vs ŋsp/$\sqrt{C}$ of all substituted oxoimidazolinone.

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

Ligand + 70%DMF-Water	A	B (Lit/mol)
A	4.269	-22.33
B	14.45	-99.75
C	2.856	-11.77
D	16.01	-98.75
E	4.001	-13.86

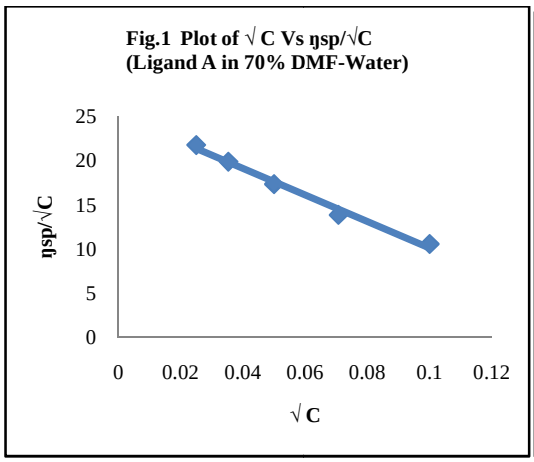


Fig.1 Plot of √ C Vs ŋsp/√C
(Ligand A in 70% DMF-Water)
ŋsp/√C
√ C

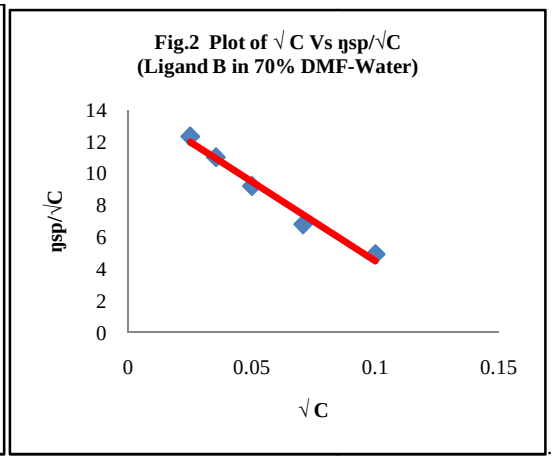


Fig.2 Plot of √ C Vs ŋsp/√C
(Ligand B in 70% DMF-Water)
ŋsp/√C
√ C

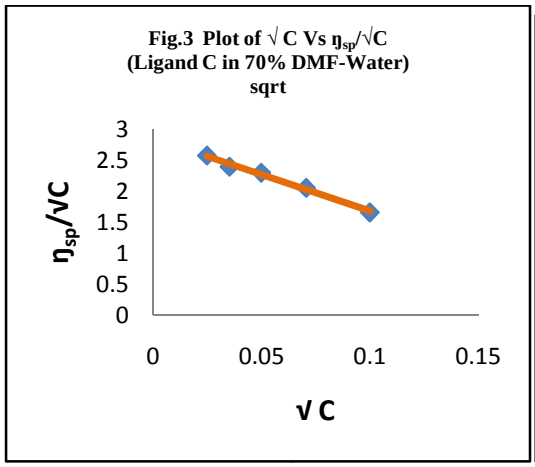


Fig.3 Plot of √ C Vs ηsp/√C
(Ligand C in 70% DMF-Water)
sqrt
ηsp/√C
√ C

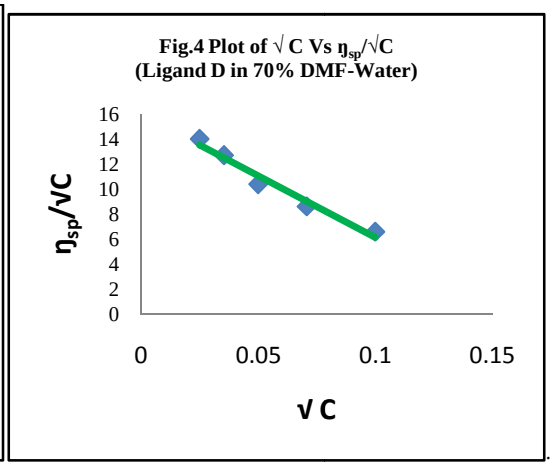


Fig.4 Plot of √ C Vs ηsp/√C
(Ligand D in 70% DMF-Water)
ηsp/√C
√ C

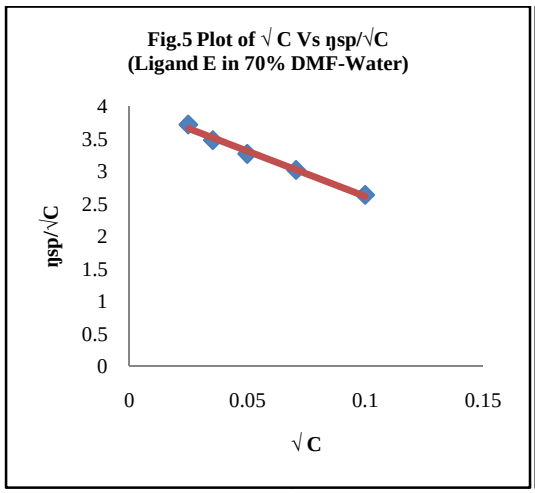


Fig.5 Plot of √ C Vs ŋsp/√C
(Ligand E in 70% DMF-Water)
ŋsp/√C
√ C

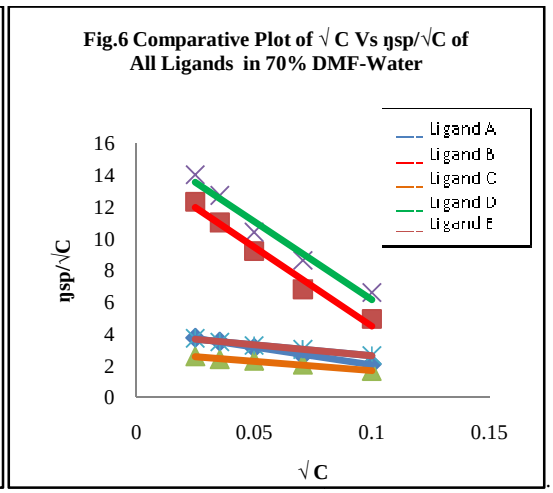


Fig.6 Comparative Plot of √ C Vs ŋsp/√C of
All Ligands in 70% DMF-Water
Ligand A
Ligand B
Ligand C
Ligand D
Ligand E
ŋsp/√C
√ C

Table 3 Densites (d) gm/cc Relative and relative viscosities (ŋr) of substituted oxoimidazolinone of 0.01M concentation in 70% (DMF+ water) solvent at different temperature (303, 305,307 and 309) K

Temp K	L_A		L_B		L_C		L_D		L_E	
	Density (d) gm/cc	Rel. Viscosity η_r	Density (d) gm/cc	Rel. Viscosity η_r	Density (d) gm/cc	Rel. Viscosity η_r	Density (d) gm/cc	Rel. Viscosity η_r	Density (d) gm/cc	Rel. Viscosity η_r
303	1.0168	1.2086	1.0229	1.4927	1.0138	1.1659	1.0225	1.6601	1.0215	1.2636
305	1.0142	1.1922	1.0223	1.4767	1.0129	1.1504	1.0212	1.5871	1.0207	1.2406
307	1.0135	1.1871	1.0216	1.4672	1.0121	1.1443	1.0208	1.5388	1.0201	1.2156
309	1.0112	1.1688	1.0211	1.4542	1.0116	1.1379	1.0202	1.4950	1.0197	1.1681

Fig 7: Plot of log η_r Vs 1/T
Ligand A

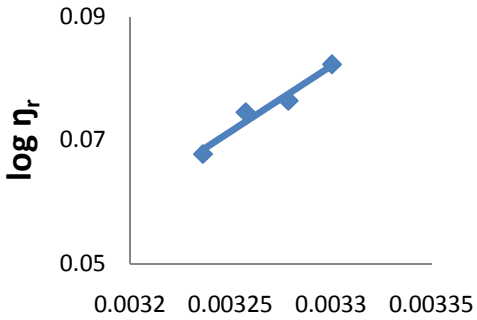


Fig 8: Plot of log η_r Vs 1/T
Ligand B

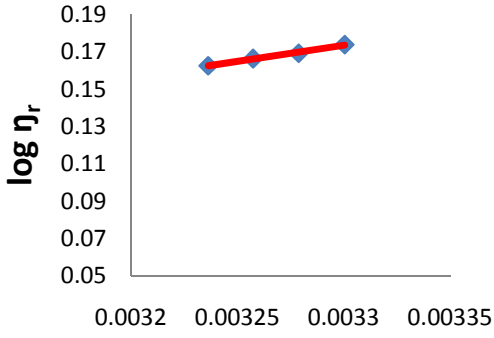


Fig 9: Plot of log η_r Vs 1/T
Ligand C

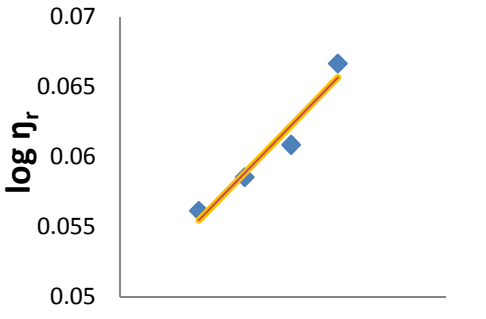
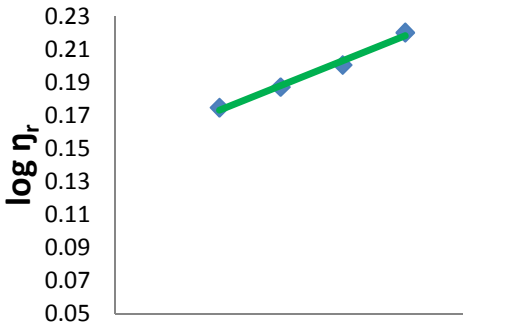
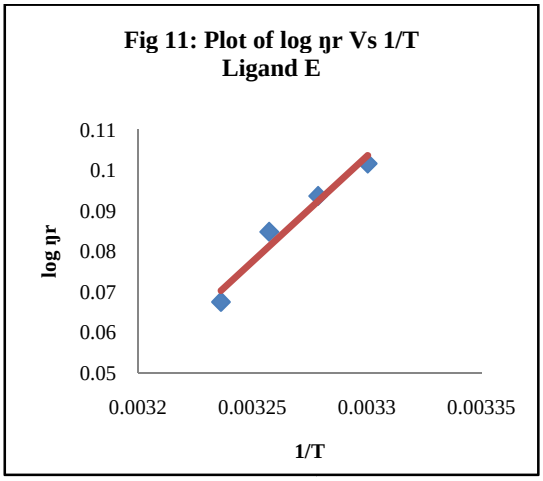


Fig 10: Plot of log η_r Vs 1/T
Ligand D





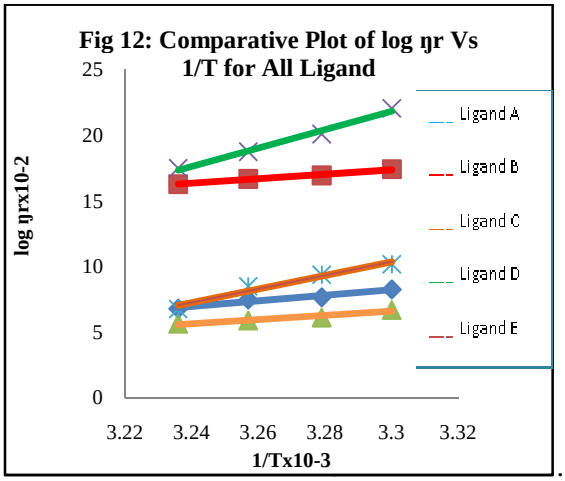


Table 4 Values of Thermodynamic Parameters for temperature difference 309K – 305°K

System	ΔG (J mol-1 K-1)	ΔH (J mol-1 K-1)	ΔS (J mol-1 K-1)
L_A	-4082.17	-3896.41	+0.6011
L_B	-3304.80	-3017.61	+0.9294
L_C	-3046.31	-2132.04	+2.9589
L_D	-13439.4	-11707.3	+5.6055
L_E	-9956.57	-11798.4	-5.9608

RESULTS AND DISCUSSION

In the present investigation, the relative viscosity of solution of substituted oxoimidazolinone ligands decreases with decrease in concentration of solutions. The decrease in viscosity with decrease in concentration is may be ascribed to the increase in the interactions of solute-solvent. The relation between viscosity (ηsp/√ C) and concentration of solution (√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. The values of Jones-Dole coefficients especially B-coefficients are the slope of graph (ηsp/√C) Vs (√C) while the values of Falkenhagen coefficient i.e. A-Coefficient are the intercept of graph of (ηsp/√C) Vs (√C). The order or disorder introduced by solute in solvent is measured by the values of B coefficient which shows either positive or negative values. B coefficient is in turn measures the effective hydrodynamic volume of solute, which accounts for the ion-solvent interaction.

In this work, the values of B-coefficients for all systems are negative. It is apparent from table 2 that B-coefficient is found to be negative for all system and is measure the effective thermodynamic volume of solute which accounts for solute-solvent interaction, it is known as a measure of disorder introduced by a solute in to the solvent. From data of table 1 and 2, it is conclude that, the value of Falkenhagen coefficient (A) and relative viscosity of ligand A, C and E is less than ligand B and D. this is because in a structure of ligand A, C and E have electron donation effect of the substituet by +R effect. But in case of ligand B and D there is also –I effect is strong. The decrease in relative viscosity of solutions with decrease in concentration measures the increase in interaction of solute and solvent. This is represented by the value of Jones-Dole coefficient (B) in table 2.

As the temperature increases the value of relative viscosity and density decreases shown in table 3. Due to increase in temperature the interaction between solute-solute and solute-solvent decreases. The themodynamic parameter such as free energy change(ΔG), enthalpy change(ΔH) and entropy change (ΔS) of different substituted 5-oxo imidazolinone drugs are calculated by plotting graph between 1/T Vrs log ŋr are shown in (fig 7-12). Thermodynamic parameter mentioned in table 4. The negative value free energy change(ΔG), enthalpy change(ΔH) interpreted that reaction of solute and solvent are spontaneous and exothermic and positive value of entropy change (ΔS) interpreted that, randomness of solute molecule in solvent increases.

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