

Studies of Viscosity and Thermodynamic Parameters of Substituted Benzimidazolyl Derivatives in Binary Solvent Mixture

A.W Wakode¹ and S. M. Bagade²

Department of Chemistry, Arts & Science College, Pulgaon, Wardha, Maharashtra, India¹

Department of Physics, Arts & Science College, Pulgaon, Wardha, Maharashtra, India²

ankushwakode@gmail.com

Abstract: Viscosity experimental data for binary solvent mixtures including substituted benzimidazolyl derivatives have been examined. The investigation was conducted for temperature variation as well as variations in solute concentration in binary solvents. Similar to other transport properties, viscosity measurement offers insight into the interactions between solutes and solvents. In a similar manner, thermodynamic parameters such as free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) have been assessed using relative viscosity and density at various temperatures. Viscosity and thermodynamic parameters have been determined to understand molecular interaction.

Keywords: Thermodynamic parameters, molecules interaction, viscosity, Enthalpy change, Entropy change

I. INTRODUCTION

In medicinal chemistry, substituted benzothiazolyl and benzimidazolyl derivatives are among the heterocyclic molecules with the greatest use. There are many biological applications for biological activities involving benzothiazolyl and benzimidazolyl substituted derivatives [1] widely used in bioorganic and medicinal chemistry. Literature survey reveals that, intension has been given to the synthesis of benzimidazole derivatives which is main focus of medicinal research recent observations suggest that substituted benzimidazoles and heterocycles, which are the structure isosters of nucleotides, owing fused heterocyclic nuclei structures that allow them to interact easily with the biopolymer, possess potential activity with lower toxicities in the chemotherapeutic approach in man[2-3]. In addition, the importance of benzimidazoles as inhibitors of p38MAP kinase, B-Rafkinase, anti-HIV[4], antimicrobial agents[5-6]. Viscosity and density, two thermophysical characteristics of liquid systems, are directly correlated with molecular interactions occurring in System[7]. These interactions determine how the drug acts, such as how far it can travel through the bloodstream, how it binds to receptors, and how it causes physiological effects. There are various kinds of contacts, including charge transfer, ionic or covalent bonds, hydrogen bonding, ion-dipole, and hydrophobic interactions. A number of studies have recently been published that analyze solute-solvent interactions and obtain thermodynamic characteristics of biological molecules using the viscometric approach[8-10].

Numerous researchers examine the thermodynamics and molecular interactions of binary and ternary liquid mixtures at varying temperatures[11-14]. The viscosity and a few thermodynamic characteristics in various substituted 1,3 propanedione are determined by P.B. Agrawal et al.[15]. Using toluene at 303.15, 308.15, and 313.15 K, M V Rathnam et al.[16] examines the density, viscosities, and Ultrasonic velocity of n-butyl acetate. The thermodynamic properties of 1, 3-diaryl carbamides in binary mixture were investigated by S.S. Ubarhande et al [17]. Jheng-Yu Wu, Yan-Ping Chen, and Chie-Shaan Su.[18] investigate the density and viscosity of an ionic binary combination containing acetonitrile, N, N-dimethylacetamide, methanol, and N-methyl-2-pyrrolidone in 1-n-Butyl-3-methylimidazolium tetrafluoroborate. M.R. Aware investigate the impact of butanol addition to binary liquid system of non-polar solvents[19]. The volumetric and viscosimetric characteristics of the binary mixture of triethylene glycol monomethyl ether + water at T= (293.3, 303.15, 313.15, 323.15, 333.15) K under atmospheric pressure are determined by Xin-Xue-Li et al. (2010)[20]. Sharma Sangita and B. Pragnesh Patel Binary mixtures of 1, 8 cineole with hydrocarbons (o-xylene, m-xylene, and toluene) at 303.15, 308.15, and 313.15 K were studied for density and viscosity using 11

measurers[21]. Viscometric study on binary liquid mixtures of propiophenone with aniline and n-alkyl substituted anilines, at 303.15 to 318.15 K was determined by Nanduri Gayatri Devi et. al[22]. Therefore, we make the decision to investigate the thermodynamic characteristics and viscosity of benzimidazolyl derivatives in binary solvent.

II. METHODOLOGY

The solvents Dimethyl Sulphoxide (DMSO), 1, 4-Dioxane and Acetone of AR grade (purity 99.9%) were used and binary solvent mixtures prepare in doubly distilled water. Weighing was made on one pan digital Balance (Wensar) with an accuracy of ±0.001 g. The densities of pure solvent and solutions of various concentrations were measured at different temperature using a precalibrated bicapillary pycnometer. The viscosities were measured by means of Ostwald’s Viscometer thoroughly cleaned and dried. The viscometer was kept in suite thermostatic water bath and temperature variation was maintained within ±0.1 °C. Each measurement, sufficient time was allowed to attain thermal equilibrium between viscometer and water bath. The accuracy of viscosity measurement was within ± 0.11 % Kg⁻¹s⁻¹. From the observations, relative and specific viscosities were calculated. From the temperature variations study, values of enthalpy change (ΔH) Entropy change (ΔS) & free energy change (ΔG) were evaluated.

The thermodynamic parameters were calculated by using following expressions –

$$\Delta G = -2.303 R \times \text{slope} \dots\dots\dots (1)$$

$$\text{Log } \eta_1, \text{Log } \eta_2 = \frac{\Delta H}{2.303} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \dots\dots\dots (2)$$

$$\Delta S = \left(\frac{\Delta G - \Delta H}{T} \right) \dots\dots\dots (3)$$

III. RESULTS AND DISCUSSION

Benzimidazolyl derivatives were produced in a 75% solvent-water combination at varying concentrations. Pycnometers calibrated with conductivity water (0.996x10³ Kg m⁻³ at 303K) were used to measure densities. A clean, dried Ostwald’s viscometer was used to measure the viscosity of the solutions. Table-1 presents the viscosities measured at various concentrations and temperature variations for ternary mixes containing benzimidazolyl derivatives + DMSO + water, benzimidazolyl derivatives + Acetone + water, and benzimidazolyl derivatives + 1, 4-Dioxane + water.

One could observe it from the table that the Relative viscosities decrease when benzimidazolyl derivative concentration increases. This demonstrates the increase in solute-solvent interaction. A study on viscosity was conducted at 298.15, 303.15, and 308.15 K. It illustrates how relative viscosity decreases as temperature rises because solvent-solvent interaction decreases.

Table-1: Determination of relative viscosities of different temperature.

System:2a		Temp:298K	
Relative Viscosity ((η _r))			
Conc. (M)	DMSO- Water	Acetone-Water	1,4 Dioxane-Water
6.25x10 ⁻⁴	2.358	1.626	1.949
1.25x10 ⁻³	2.053	1.573	1.806
2.50x10 ⁻³	2.048	1.447	1.733
5.00x10 ⁻³	2.037	1.508	1.741
1.00x10 ⁻²	2.032	1.441	1.727

System:2a		Temp:303K	
Relative Viscosity ((η _r))			
Conc. (M)	DMSO- Water	Acetone-Water	1,4 Dioxane-Water
6.25x10 ⁻⁴	2.229	1.549	1.927

1.25x10 ⁻³	2.198	1.544	1.776
2.50x10 ⁻³	2.093	1.432	1.728
5.00x10 ⁻³	2.069	1.448	1.716
1.00x10 ⁻²	2.033	1.443	1.634

System:2a Temp:308K

Relative Viscosity (η_r)

Conc. (M)	DMSO- Water	Acetone-Water	1,4 Dioxane-Water
6.25x10 ⁻⁴	2.207	1.536	1.864
1.25x10 ⁻³	2.151	1.488	1.745
2.50x10 ⁻³	2.085	1.359	1.791
5.00x10 ⁻³	2.028	1.399	1.723
1.00x10 ⁻²	2.014	1.372	1.621

System:2b Temp:298K

Relative Viscosity (η_r)

Conc. (M)	DMSO- Water	Acetone-Water	1,4 Dioxane-Water
6.25x10 ⁻⁴	2.259	1.551	2.016
1.25x10 ⁻³	2.211	1.443	1.919
2.50x10 ⁻³	2.091	1.417	1.883
5.00x10 ⁻³	2.064	1.397	1.832
1.00x10 ⁻²	2.051	1.378	1.809

System:2b Temp:303K

Relative Viscosity (η_r)

Conc. (M)	DMSO- Water	Acetone-Water	1,4 Dioxane-Water
6.25x10 ⁻⁴	2.208	1.548	1.908
1.25x10 ⁻³	2.172	1.517	1.855
2.50x10 ⁻³	2.072	1.434	1.835
5.00x10 ⁻³	2.039	1.418	1.806
1.00x10 ⁻²	2.047	1.376	1.795

System:2b Temp:308K

Relative Viscosity (η_r)

Conc. (M)	DMSO- Water	Acetone-Water	1,4 Dioxane-Water
6.25x10 ⁻⁴	2.263	1.544	1.811
1.25x10 ⁻³	2.176	1.537	1.804

2.50×10^{-3}	2.038	1.461	1.738
5.00×10^{-3}	2.023	1.406	1.705
1.00×10^{-2}	2.035	1.355	1.672

Table-2: Determination of thermodynamic parameters

System-2a in 75% DMSO-Water			
Conc. (M)	$\Delta G(\text{J/mol})$	$\Delta S (\text{JK}^{-1}\text{mol}^{-1})$	$\Delta H(\text{J/mol})$
6.25×10^{-4}	-44677.23	165.55	4409.93
1.25×10^{-3}	-59707.73	214.03	4068.90
2.50×10^{-3}	-69989.75	254.83	6147.31
5.00×10^{-3}	-64551.96	233.29	5061.35
1.00×10^{-2}	-64034.99	247.71	9945.48
System-2a in 75% Dioxane-Water			
Conc. (M)	$\Delta G(\text{J/mol})$	$\Delta S (\text{JK}^{-1}\text{mol}^{-1})$	$\Delta H(\text{J/mol})$
6.25×10^{-4}	-68532.81	241.71	7631.52
1.25×10^{-3}	-63002.79	225.22	7435.50
2.50×10^{-3}	-62378.73	213.25	6587.31
5.00×10^{-3}	-55125.60	204.79	5290.23
1.00×10^{-2}	-54576.30	198.09	4969.23
System-2a in 75% Acetone-Water			
Conc. (M)	$\Delta G(\text{J/mol})$	$\Delta S (\text{JK}^{-1}\text{mol}^{-1})$	$\Delta H(\text{J/mol})$
6.25×10^{-4}	-38800.81	161.09	6933.93
1.25×10^{-3}	-44903.55	181.73	6295.37
2.50×10^{-3}	-52298.70	197.13	5805.80
5.00×10^{-3}	-54293.44	199.92	5494.39
1.00×10^{-2}	-55200.30	209.63	5151.78
System-2b in 75% DMSO-Water			
Conc. (M)	$\Delta G(\text{J/mol})$	$\Delta S (\text{JK}^{-1}\text{mol}^{-1})$	$\Delta H(\text{J/mol})$
6.25×10^{-4}	-42833.91	175.90	7873.54

1.25×10^{-3}	-48111.51	185.89	6952.33
2.50×10^{-3}	-54962.68	196.72	6145.15
5.00×10^{-3}	-55387.42	201.60	5262.70
1.00×10^{-2}	-56713.77	215.09	4596.82

System-2b in 75% Dioxane-Water

Conc. (M)	ΔG (J/mol)	ΔS (JK ⁻¹ mol ⁻¹)	ΔH (J/mol)
6.25×10^{-4}	-54163.76	194.22	6110.44
1.25×10^{-3}	-52172.46	188.47	5860.19
2.50×10^{-3}	-48846.05	172.33	5705.12
5.00×10^{-3}	-46404.82	162.34	5240.62
1.00×10^{-2}	-44823.53	152.22	5115.11

System-2b in 75% Acetone-Water

Conc. (M)	ΔG (J/mol)	ΔS (JK ⁻¹ mol ⁻¹)	ΔH (J/mol)
6.25×10^{-4}	-44294.28	166.97	6221.33
1.25×10^{-3}	-52558.90	187.53	6176.98
2.50×10^{-3}	-54469.27	205.54	5895.62
5.00×10^{-3}	-55705.14	212.74	5670.53
1.00×10^{-2}	-58145.46	225.34	5268.50

Where, 1,2-Dihydro-benzo[4,5]imidazo[2,1-c][1,2,4]triazin-3-one (2a) and (1,2-Dihydro-benz[4,5]imidazo[2,1-c][1,2,4]triazin-3-ylidene)-(4-phenyl-thiazole-2-yl)-amine (2b).

A liquid's viscosity usually decreases as temperature rises. In many circumstances, the drop is noticeable, averaging two percent for every degree that the temperature rises. This has been described in terms of liquid "hole theory." This hypothesis states that a liquid has holes or voids. The liquid molecules must constantly enter these holes in order for the liquid to flow; otherwise, they would stop moving altogether. On the other hand, this procedure uses energy. Therefore, for a liquid molecule to enter a hole, some energy is required. A liquid can flow more easily at a higher temperature because energy becomes more available as the temperature rises.

The thermodynamic parameters enthalpy change (ΔH), entropy change (ΔS), and free energy change (ΔG) shown in Table 2 were calculated using the viscosities measured at various temperatures. Enthalpy change decreases but entropy change increases with increase in concentration for DMSO-water and Acetone-water, but enthalpy and entropy change decreases with concentration increase for the 1,4-Dioxane-water system. The polarity of the liquids may provide an explanation for these discrepancies. Because acetone and DMSO are polar substances, their results are similar; however, because 1, 4-Dioxane is a somewhat non-polar substance, its results may differ. When ΔG is negative, it indicates that energy is released with favourable interactions.

IV. CONCLUSION

It may be concluded that due to variable solvent-solvent and solute-solvent interactions variable trends are observed in viscosity and other physical properties values.

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