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STUDIES OF VISCOSITYAND THERMODYNAMIC PARAMETERS OF SUBSTITUTED BENZOTHIAZOLYL DERIVATIVES IN BINARY SOLVENT MIXTURE

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ABSTRACT

Experimental data on viscosity have been studied for the binary solvent mixtures of substituted benzothiazolyl derivatives. The study was implemented for variation in concentration of solute in binary solvents as well as variation in temperatures. Viscosity measurement like other transport properties provides information about solute-solute and solute-solvent interaction similarly from relative viscosity and density at different temperature, thermodynamic parameters like fee energy change (ΔG) enthalpy change (ΔH) and entropy change (ΔS) have been evaluated. Thermodynamic parameters and viscosity have been calculated to interpret molecular interaction.

Keywords: Viscosity, molecular interaction, thermodynamic parameters.

INTRODUCTION

Benzothiazolyl and benzimidazolyl substituted derivatives are the heterocyclic compounds with wide application in pharmaceutical chemistry. Activities in biological field through antimicrobial of Benzothiazolyl and benzimidazolyl substituted derivatives have wide range of biological applicability[1]. Benzothiazolyl derivatives are widely found in bioorganic and medicinal chemistry with applications in drug discovery and development for treatment of autoimmune and inflammatory diseases in the prevention of solid organ transplant rejection, epilepsy, antitumor, antiviral, anticonvulsant, neuroprotective and immunosuppressive properties[2].The thermophysical properties of liquid Systems like viscosity and density are strictly related to the molecular interactions taking place in the System[3]. These interactions decides the drug actions i.e. drug reaching to the blood stream its extent of distribution, it's binding to receptors and producing physiological actions. The interactions are of different types such as ionic or covalent, charge transfer, hydrogen bonding, ion-dipole and hydrophobic interactions. There are various papers appeared recently which use viscometric method to access thermodynamic parameters of biological molecule and interpreted the solute-solvent interactions[4-6]. Many workers studies molecular interactions and thermodynamic study of ternary liquid mixture at different temperatures[7-8]. P.B. Agrawal et al.[9] determine the viscosity and some thermodynamic parameters in some substituted 1, 3 propanedione. Xin-Xue-Li et al.[10] determine the volumetric and viscosimetric properties 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. Sangita Sharma and Pragnesh B. Patel [11] measurers density and viscosity study of binary mixtures of 1, 8 cineole with hydrocarbons (o-xylene, m-xylene and toluene) at 303.15, 308.15, 313.15K.). M V Rathnam et al.[12]measures the density, viscosities and speed of sound of n-butyl acetate with toluene at 303.15, 308.15, and 313.15K. S.S.Ubarhande et al. studied the thermodynamic parameters of 1, 3-diaryl carbamidesin binary solvent mixtures[13]. M.R. Aware, study the effect of addition of butanol tobinary liquid System of non-polar solvents [14]. Jheng-Yu Wu, Yan-Ping Chen, Chie-Shaan Su.[15] study the density and viscosity of ionic binary mixture of 1-n-Butyl-3-methylimidazolium Tetrafluoroborate with Acetonitrile, N, N- Dimenthylacetamide, Methanol, and N-Methylk-2-pyrrolidone. Hence we decide to study the viscosity and thermodynamic parameters of benzothiazolyl derivatives in binary solvent.

EXPERIMENTAL

Material and Methods

The solvents Dimethyl Sulphoxide, Acetone, 1, 4-Dioxanof AR grade (purity 99.9%) were used and binary solvent mixtures prepare in doubly distilled water. Weighing was made on one pan digital Balance 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 bicapilary 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 % $Kg^{-1}s^{-1}$.From the observations, relative and specific viscosities were calculated. From the temperature variations study, values of enthalpy change (H) entropy change (S) & free energy change (G) were evaluated.
The thermodynamic parameters were calculated by using following expressions –

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

$$\text{Log}\ \eta_{r1} - \text{Log}\ \eta_{r2} = \frac{\Delta H}{2.303}\left(\frac{1}{T1} - \frac{1}{T2}\right) \qquad (2)$$

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

RESULTS AND DISCUSSION

Different concentrations of benzothiazolyl derivatives were prepared in 75 % solvent-water mixture. Densities were measured with Pyknometer calibrated with conductivity water (0.996×10^{3} Kgm^{-3}at 303K).The viscosity of solutions were measured by clean dried Ostwald's viscometer. The viscosities determined for ternary mixtures of benzothiazolyl derivatives + DMSO + water, benzothiazolyl derivatives + Acetone + water and benzothiazolyl derivatives + 1, 4-Dioxan + water, at different concentrations with the variation in temperature have been prepared in Table-1.
It would be observed from Table.1 relative viscosities decreases with decrease in concentration of benzothiazolyl derivatives. This shows the simultaneous decrease in interaction between solute-solvent. Viscosity study was carried out at 298.15, 303.15 and 308.15 K. It reflects that with increase in temperature, relative viscosity decreases due to decrease in solute-solvent interaction.

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

System:1a		Temp:298K	
Relative Viscosity (η_r)			
Conc. (M)	DMSO- Water	Acetone-Water	1,4 Dioxan-Water
0.01	2.898	1.076	1.739
0.005	2.593	1.023	1.596
0.0025	2.648	0.897	1.523
0.00125	2.627	0.958	1.531
0.000625	2.772	0.891	1.667

System:1a		Temp:303K	
Relative Viscosity (η_r)			
Conc. (M)	DMSO- Water	Acetone-Water	1,4 Dioxan-Water
0.01	2.709		1.717
0.005	2.638	0.994	1.566

0.0025	2.643	0.882	1.518
0.00125	2.659	0.898	1.506
0.000625	2.803	0.893	1.424

System:1a		Temp:308K	
Relative Viscosity (ɳr)			
Conc. (M)	DMSO- Water	Acetone-Water	1,4 Dioxan-Water
0.01	2.747	1.071	1.654
0.005	2.611	0.938	1.535
0.0025	2.685	0.809	1.581
0.00125	2.538	0.849	1.513
0.000625	2.814	0.892	1.411

System:1c		Temp:298K	
Relative Viscosity (ɳr)			
Conc. (M)	DMSO- Water	Acetone-Water	1,4 Dioxan-Water
0.01	2.719	1.001	1.806
0.005	2.631	0.893	1.709
0.0025	2.463	0.837	1.673
0.00125	2.734	0.867	1.992
0.000625	2.734	0.828	1.559

System:1c		Temp:303K	
Relative Viscosity (ɳr)			
Conc. (M)	DMSO- Water	Acetone-Water	1,4 Dioxan-Water
0.01	2.748	1.004	1.698
0.005	2.599	0.867	1.614
0.0025	2.333	0.771	1.692
0.00125	2.781	0.868	1.757
0.000625	2.787	0.826	1.585

System:1c		Temp:308K	
Relative Viscosity (ɳr)			
Conc. (M)	DMSO- Water	Acetone-Water	1,4 Dioxan-Water
0.01	2.803	1.004	1.601
0.005	2.616	0.817	1.494
0.0025	2.138	0.739	1.598
0.00125	2.613	0.819	1.475

0.000625	2.665	0.805	1.462

System:1b		Temp:298K	
Relative Viscosity (ƞr)			
Conc. (M)	DMSO- Water	Acetone-Water	1,4 Dioxan-Water
0.01	2.819	1.024	1.898
0.005	2.728	0.949	1.96
0.0025	2.904	0.892	1.613
0.00125	2.949	0.833	1.705
0.000625	3.182	0.884	1.783

System:1b		Temp:303K	
Relative Viscosity (ƞr)			
Conc. (M)	DMSO- Water	Acetone-Water	1,4 Dioxan-Water
0.01	2.864	0.983	1.793
0.005	2.794	0.916	1.731
0.0025	2.83	0.886	1.612
0.00125	2.949	0.853	1.65
0.000625	2.83	0.889	1.772

System:1b		Temp:308K	
Relative Viscosity (ƞr)			
Conc. (M)	DMSO- Water	Acetone-Water	1,4 Dioxan-Water
0.005	2.797	0.921	1.773
0.005	2.484	0.854	1.693
0.0025	2.494	0.828	1.577
0.00125	2.612	0.870	1.559
0.000625	2.831	0.838	1.597

Table-2: Determination of thermodynamic parameters

System-1a in 75% DMSO-Water			
Conc. (M)	ΔG(J/mol)	ΔS ($JK^{-1}mol^{-1}$)	ΔH(J/mol)
0.01	-32014.02	-119.29	4131.00
0.005	-38390.02	-143.48	5085.26
0.0025	-62228.21	-227.89	6822.96
0.00125	-45263.84	-162.14	3865.79
0.000625	-41836.51	-150.53	3773.87

System-1a in 75% Dioxan-Water

Conc. (M)	ΔG(J/mol)	ΔS (JK^{-1}mol^{-1})	ΔH(J/mol)
0.01	-58532.81	-216.71	7131.52
0.005	-61002.79	-224.22	6935.50
0.0025	-45378.73	-163.25	4087.31
0.00125	-90125.60	-329.79	9800.23
0.000625	-48576.30	-173.09	3869.23

System-1a in 75% Acetone-Water

Conc. (M)	ΔG(J/mol)	ΔS (JK^{-1}mol^{-1})	ΔH(J/mol)
0.01	-36800.81	-136.09	4433.93
0.005	-52903.55	-193.73	5795.37
0.0025	-59298.70	-222.13	8005.80
0.00125	-47293.44	-170.92	4494.39
0.000625	-42200.30	-154.63	4651.78

System-1b in 75% DMSO-Water

Conc. (M)	ΔG(J/mol)	ΔS (JK^{-1}mol^{-1})	ΔH(J/mol)
0.01	-46833.91	-178.90	7373.54
0.005	-36111.51	-131.89	3852.33
0.0025	-34962.68	-130.72	4645.15
0.00125	-43387.42	-156.60	4062.70
0.000625	-34713.77	-128.09	4096.82

System-1b in 75% Dioxan-Water

Conc. (M)	ΔG(J/mol)	ΔS (JK^{-1}mol^{-1})	ΔH(J/mol)
0.01	-46163.76	-169.22	5110.44
0.005	-44172.46	-163.47	5360.19
0.0025	-30846.05	-117.33	4705.12
0.00125	-39404.82	-147.34	5240.62
0.000625	-66823.53	-257.22	11115.11

System-1b in 75% Acetone-Water

Conc. (M)	ΔG(J/mol)	ΔS (JK^{-1}mol^{-1})	ΔH(J/mol)
0.01	-38294.28	-141.97	4721.33
0.005	-52558.90	-192.53	5776.98
0.0025	-55469.27	-200.54	5295.62
0.00125	-58705.14	-217.74	7270.53

0.000625	-37145.46	-137.34	4468.50

System-1c in 75% DMSO-Water

Conc. (M)	ΔG(J/mol)	ΔS (JK^{-1}mol^{-1})	ΔH(J/mol)
0.01	-38677.23	-140.55	3909.93
0.005	-53707.73	-189.03	3568.90
0.0025	-63989.75	-229.83	5647.31
0.00125	-58551.96	-208.29	4561.35
0.000625	-58034.99	-222.71	9445.48

System-1c in 75% Dioxan-Water

Conc. (M)	ΔG(J/mol)	ΔS (JK^{-1}mol^{-1})	ΔH(J/mol)
0.01	-49380.48	-185.91	6951.44
0.005	-63166.42	-240.55	9721.59
0.0025	-41262.09	-151.30	4580.51
0.00125	-53114.17	-194.91	5944.98
0.000625	-56637.25	-202.91	4845.43

System-1c in 75% Acetone-Water

Conc. (M)	ΔG(J/mol)	ΔS (JK^{-1}mol^{-1})	ΔH(J/mol)
0.01	-55967.10	-184.53	6254.83
0.005	-55794.77	-183.96	6027.32
0.0025	-50395.28	-166.15	4842.73
0.00125	-29792.95	-98.23	3566.00
0.000625	-46719.03	-154.03	4312.46

Where, 1a-1-Benzothiazole-2-yl-[1, 2] diazetidin-3-one, 1b-(1-Benzothiazol-2-yl-[1, 2] diazetidine-3-ylidene)-4(phenyl-thiazole-2-yl)-amine and 1c- (1-Benzothiazol-2-l-[1, 2] diazetidine-3-ylidene)-phenyl-amine.

The viscosity of a liquid generally decreases with rise in temperature. The decrease is appreciable being about two percent per degree rise of temperature in many cases. This has been explained in terms of 'hole theory' of liquids. According to this theory, there are vacancies or holes in a liquid. The liquid molecules keep on moving continuously into these vacancies also keep on moving around as otherwise the liquid will not be able to flow. This process however, requires energy. A liquid molecule, therefore, needs some energy to move into hole. As the energy becomes increasingly available at increasing temperature, a liquid can flow more easily at higher temperature.

The viscosities determined at different temperatures were used to evaluate thermodynamic parameters enthalpy change (ΔH), entropy change (ΔS), and free energy change (ΔG) presented in Table 2. For DMSO- water and Acetone -water with decrease in concentration, enthalpy change decreases but entropy change increases, but for the 1, 4-Dioxan-water System, with concentration decrease, enthalpy & entropy change decrease. These variations may be explained on the basis of polarity of solvents. Due to polar nature of Acetone and DMSO shows similar results and due to relatively non-polar nature of 1, 4-Dioxan results may show different nature. Negative value of ΔG represents release of energy with favourable interactions.

CONCLUSION

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

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