Physical Chemistry: An Indian Journal

Research | Vol 12 Iss 3

Studies in Thermo-Physical Parameters of N-Benzothiazol-2-Yl-3, 5-Disubstituted Pyrazolines in Binary Liquid Mixtures at Different Temperatures

Gotmare AG*, Burghate AS and Wadhal SA

Department of Chemistry, Shri Shivaji Science College, Amravati-444603 Maharashtra, India

***Corresponding author:** Gotmare AG, Department of Chemistry, Shri Shivaji Science College, Amravati-444603 Maharashtra, India, Tel: 07212660855; E-mail: gotmare.anuja@gmail.com

Received: July 18, 2017; **Accepted:** August 31, 2017; **Published:** September 04, 2017

Abstract

Viscosity (η) measurements were carried out for N-Benzothiazol-2-yl-3, 5-disubstituted pyrazolines viz. (BHPMPP), (BHPPP), (BHPCPP), (BHMPMPP), (BHMPPP), (BHMPCPP) in binary solvents at 295.15 K, 300.15 K and 305.15 K. With the help of above data molar volume (V_m), Enthalpy (ΔH), Entropy (ΔS) and Gibb's energy (ΔG) of activation were calculated. The above study has been extended in determination of excess parameters. Results used to establish the intermolecular interaction between molecules.

Keywords:* *Viscosity; N-Benzothiazol-2-yl-3;5-disubstituted pyrazoline; Enthalpy; Entropy; Gibb's energy

Introduction

Information on intermolecular force is obtained by macroscopic measurements of properties like viscosity which point the existence and action of forces at a molecular level [1-7]. Viscosity is one of the unique physical property [8-10], generally taken into consideration for study of liquids or liquid mixtures [11,12]. The viscosity of a system is determined by how molecules constituting the system interact.

Interaction between molecules played a major part in determining the properties of matter. Molecular interactions are of key importance in diverse fields of protein folding, drug design, separation technologies etc.

The system that has been taken for the further investigation is a binary system in which molecular recognition is studied between the N-Benzothiazol-2-yl-3, 5-disubstituted pyrazolines with three different solvents i.e. DMSO, dioxan and acetone. The solvent have versatile and wide applications. It is therefore, not surprising that it has been the subject of extensive investigation resulting in the accumulation of an immense literature.

Citation: Gotmare AG, Burghate AS, Wadhal SA. Studies in Thermo-Physical Parameters of N-Benzothiazol-2-Yl-3, 5-Disubstituted Pyrazolines in Binary Liquid Mixtures at Different Temperatures. Phys Chem Ind J. 2017;12(3):114

As we know heterocyclic compounds have special appearance in terms of properties. Every heterocyclic compounds are best known for their applications in pharmacy, industry, medicine, agriculture etc. as they have tremendous variety of applications [13]. Pyrazolines are one of them and known from long time. The molecular interactions of pyrazolines are best known for antimicrobial [14], analgesics [15], antidepressant [16], antitumor [17,18], anti-HIV [19], antifungal, antibacterial [20,21], anti-cancer [22] etc. Some other activities are also shown by pyrazolines [23,24].

For this, measurement of density, viscosity, molar volume of the binary mixtures are performed over the entire range of composition in the temperature range of (295.15 K to 305.15 K) at intervals of 5 K. In present investigation, we report viscosities *(η)* and molar volume *(V_m)* of the binary mixtures of N-Benzothiazol-2-yl-3, 5-disubstituted pyrazolines can be discussed in terms of solute-solute, solute-solvent, solvent-solvent types of interactions.

Experimental Section

Materials

The compounds N-Benzothiazol-2-yl-3, 5-disubstituted pyrazolines was a discovered compound and further used to investigate physical properties [25]. The distilled deionised water with a conductivity approximately 1×10^{-4} S·m^{-1} was used in experimentation. Solutions were prepared on the basis of stoichiometry. The balance Contech balance (± 0.001 g) used for weighing purpose.

Apparatus and procedure

The densities of solutions were measured by densitometer DMA 35 (Anton Paar) by calibrate and taking proper care of it. The accuracy of densitometer was $\pm 5 \times 10^{-4}$ g·cm^3. For the determination of viscosity Ostwald's viscometer was used and calibrated it by using double distilled deionized water and benzene. The viscosity measurement was done for pure solvents and their mixture at atmospheric pressure and T/K=(295.15 to 305.15). For the determination of viscosity temperature was maintained at temperature control thermostat by Bio technics India (Model BTI-05) which required approximately 30 mins. for thermal stability and which has accuracy of about ± 0.01 K. Flow time was measured by using electronic digital stopwatch which shows uncertainty of about ± 0.01 S.

The viscosity (η) was calculated by using following relationship

$$\eta/\eta_w = \rho t/(\rho_w t_w) \quad \text{(A.1)}$$

Where, η and η_w (Kg·m^{-1}·s^{-1}), ρ and ρ_w(Kg·m^{-3}) and t and t_w (s) are the viscosity, density and flow time of mixtures and pure water respectively.

Results and Discussion

The viscosities of pure solvents i.e. DMSO, dioxan and acetone are shown in TABLE 1 and calculated viscosities of N-Benzothiazol-2-yl-3, 5-disubstituted pyrazolines in binary mixture i.e. DMSO-water, dioxan-water and acetone-water at temperature T/K=(295.15 to 305.15) are listed in TABLE 2. With this calculated molar volume (V_m) are also shown in TABLE 2, by using following formula:

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho} \quad \text{(A.2)}$$

Where, x_1, x_2 are mole fraction of solvent (DMSO, dioxan and acetone) and distilled water.

TABLE 1. **Experimental viscosities (η) of solvents (DMSO, dioxan, acetone) at T/K=(295.15 to 303.15).**

Sr. No.	**Solvents**	**10^3·η/kg·m^{-1}·s^{-1}**		
--	--	295.15 K	300.15 K	305.15 K
1	DMSO	1.86	1.63	1.54
2	Dioxan	1.15	1.06	0.993
3	Acetone	0.451	0.393	0.344

TABLE 2. **Experimental viscosities (η)[a] and molar volume (V_m) of solvent (DMSO, dioxan, acetone)+water binary mixture from T/K=(295.15 to 303.15).**

X_1	**X_2**	**10^3·η/kg·m^{-1}·s^{-1}**	**V_m/m^3·mol^{-1}**	**10^3·η/kg·m^{-1}·s^{-1}**	**V_m/m^3·mol^{-1}**	**10^3·η/kg·m^{-1}·s^{-1}**	**V_m/m^3·mol^{-1}**
--	--	**295 K**	--	**300 K**	--	**305 K**	--
				DMSO+Water			
				BHPMPP			
0.479578587	0.5204094	2.91	0.0425272	2.76	0.042728	2.65	0.0427028
0.479572777	0.5204031	2.92	0.0427853	2.79	0.043145	2.71	0.0427276
0.479567004	0.5203968	3.01	0.0427561	2.91	0.0427362	2.8	0.0426158
0.479561195	0.5203905	3.05	0.0430566	2.96	0.0427262	2.89	0.0425131
0.479555386	0.5303842	3.12	0.0428672	3.04	0.0428069	2.98	0.0424922
				BHMPMPP			
0.47958161	0.5204089	2.71	0.0428942	2.56	0.0427767	2.47	0.0424948
0.479571962	0.5204022	2.77	0.0428818	2.62	0.0427406	2.54	0.04274
0.479565764	0.5203955	2.84	0.0427348	2.7	0.0428073	2.62	0.0428087
0.479559565	0.5203887	2.93	0.0426872	2.79	0.042795	2.74	0.0427167
0.479553329	0.520382	3.02	0.0430489	2.87	0.0428868	2.83	0.0425696
				Dioxane+Water			
				BHPMPP			
0.449685113	0.5503022	1.41	0.0488167	1.33	0.048519	1.23	0.0487991
0.44679353	0.5502951	1.49	0.0479245	1.38	0.0485996	1.32	0.048415
0.449673629	0.5502881	1.56	0.0481522	1.45	0.0486855	1.38	0.0487732
0.449667869	0.5502811	1.63	0.0485117	1.54	0.048636	1.47	0.0484761
0.449662109	0.550274	1.72	0.0484288	1.63	0.0482754	1.56	0.0482352

--	--	--	--	BHMPMPP	--	--	--
0.449684691	0.5503016	1.5	0.0485856	1.36	0.0482534	1.27	0.0482515
0.449678545	0.5502941	1.55	0.0485032	1.44	0.0482832	1.32	0.0483356
0.449672398	0.5502866	1.62	0.0488447	1.51	0.0494189	1.43	0.048943
0.449666252	0.5502791	1.68	0.0487651	1.62	0.0483965	1.54	0.0487106
0.44966007	0.5502715	1.74	0.0487127	1.67	0.0485104	1.61	0.0484347
				Acetone+Water			
				BHPMPP			
0.553499818	0.4464899	6.74	0.0476726	6.35	0.046023	5.76	0.0466358
0.553494066	0.4464852	7.22	0.0474799	6.61	0.0473873	6.18	0.046852
0.55348849	0.4464806	7.58	0.0480707	7.05	0.0473821	6.54	0.0474031
0.553482597	0.446476	8.13	0.0474927	7.48	0.0475042	7.04	0.0470054
0.553476845	0.4464713	8.4	0.0485239	7.95	0.0472825	7.69	0.0470576
--	--	--	--	BHMPMPP	--	--	--
0.553499397	0.4464895	7.22	0.0475219	6.59	0.0475504	5.85	0.0477466
0.553493259	0.4464846	7.69	0.0473869	7.06	0.0473512	6.41	0.048413
0.553487121	0.4464796	8.13	0.047449	7.44	0.0477109	6.98	0.047438
0.553480983	0.4464747	8.79	0.0475584	8.15	0.0474037	7.7	0.0470092
0.553474808	0.4464697	9.32	0.0471442	8.96	0.0466266	8.39	0.0468179

[a] Standard Uncertainty (u) is $u(\eta)=0.0171$ kg·m^{-1}·s^{-1} and the combined expanded uncertainty U_c is $U_c(\eta)=0.0484$ kg·m^{-1}·s^{-1} with 0.95 level of confidence (k=2)

From the data listed in TABLE 2, with increase in temperature for the selected systems in binary solvent mixtures, there is decrease in the viscosity as well as molar volume. The reverse trend is observed, as there is increase in concentration, the viscosity and molar volume values are also increases.

The above results are obtained since the existence of liquids depends on intermolecular forces, we might expect that studies of the liquid state would provide much information about molecular interactions. In liquid, each molecule surrounded by a substantial number of relatively near neighbors and feels their attractive intermolecular interactions while in isolated molecules intermolecular energy is very small in comparison with the kinetic energy of the molecules. Hence in above case, increase in temperature, increases the kinetic or thermal energy which in turn increases the mobility of ions.

Values of molar volume are observed to decrease with increasing temperature. This is because the interaction of molecules of N-Benzothiazol-2-yl-3, 5-disubstituted pyrazolines between molecules of solvent decreases with increasing temperature. The molecular thermal motion intensified with increasing temperature and the interaction between molecules correspondingly weakened so the difference of solution structure and solvent structure decreases gradually.

Thermodynamic properties give more emphasis on interactions between the hetero molecules and solute-solvent interactions. Hence parameters like Gibb's energy of activation of viscous flow (ΔG), enthalpy (ΔH) and entropy (ΔS) are also calculated and listed in TABLE 3, and shown in FIG. 1, these values are determined by using following relationship.

$$\Delta G = -2.303 \times \text{slope} \times R \times T \qquad (A.3)$$

$$\log\eta_{r_1} - \log\eta_{r_2} = \frac{\Delta H}{2.303}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (A.4)$$

$$\Delta S = \frac{\Delta G - \Delta H}{T} \qquad (A.5)$$

Where, R is gas constant and T is absolute temperature. η_{r_1}, η_{r_2} are difference of the viscosities of two temperatures, T_1 and T_2 are temperatures at two different range. ΔH is change in enthalpy and ΔG change in Gibb's energy of activation.

TABLE 3. **Experimental enthalpies (ΔH), Gibb's energy of activation (ΔG) and entropies (ΔS) of solvent (DMSO, Dioxan, Acetone)+water binary mixture.**

X_1	X_2	Δ*H*/kJ·Mol^{-1}	Δ*G*/kJ·Mol^{-1}	Δ*S*/J·K^{-1}·Mol^{-1}
		DMSO+Water		
		BHPMPP		
0.4795786	0.5204094	840.655	-46.942827	-2.95866
0.4795728	0.5204031	669.368	-35.683901	-2.35017
0.479567	0.5203968	651.715	-35.55944	-2.29092
0.4795612	0.5203905	484.15	-27.572879	-1.70574
0.4795554	0.5303842	412.355	-25.529806	-1.45962
		BHPPP		
0.4795776	0.5204083	784.961	-41.167841	-2.75376
0.4795709	0.520401	691.005	-30.316764	-2.40441
0.4795642	0.5203937	611.898	-31.331599	-2.1441
0.4795574	0.5203864	532.338	-22.773995	-1.85105
0.4795507	0.5203791	544.449	-43.400478	-1.9595

		BHPCPP		
0.4795787	0.5204095	777.372	-40.118539	-2.72497
0.4795731	0.5204034	684.534	-29.679141	-2.38071
0.4795674	0.5203973	671.651	-38.295666	-2.36649
0.4795618	0.5203911	661.28	-34.305257	-2.31862
0.4795562	0.520385	622.633	-39.253057	-2.20629
		BHMPMPP		
0.4795816	0.5204089	831.551	-42.85285	-2.91468
0.479572	0.5204022	776.59	-38.295666	-2.71628
0.4795658	0.5203955	722.727	-36.166427	-2.52964
0.4795596	0.5203887	598.877	-33.508708	-2.10795
0.4795533	0.520382	579.389	-32.976398	-2.04122
		BHMPPP		
0.4795771	0.5204078	890.485	-45.954799	-3.12147
0.4795699	0.5203999	789.176	-38.295666	-2.75824
0.4795626	0.520392	700.689	-32.24878	-2.44313
0.4795554	0.5203842	648.241	-33.508708	-2.2725
0.4795481	0.5203763	632.245	-34.812675	-2.22352
		BHMPCPP		
0.4795784	0.5204091	975.432	-46.500512	-3.40644
0.4795723	0.5204026	949.75	-47.364079	-3.32371
0.4795663	0.520396	917.241	-49.380346	-

				3.22207
0.4795602	0.5203895	824.768	-45.954799	-2.90241
0.4795542	0.5203829	728.711	-39.89068	-2.56201
		Dioxan+Water		
		BHPMPP		
0.4496851	0.5503022	1232.36	-29.104706	-4.2049
0.4496794	0.5502951	1085.66	-28.036257	-3.71232
0.4496736	0.5502881	1100.07	-34.305257	-3.78126
0.4496679	0.5502811	928.484	-28.338793	-3.18941
0.4496621	0.550274	877.427	-26.806966	-3.01411
		BHPPP		
0.4496842	0.550301	955.45	-27.764358	-3.27738
0.4496775	0.5502928	985.05	-29.225337	-3.38092
0.4496708	0.5502847	1056.08	-33.072137	-3.6305
0.4496642	0.5502765	1103.31	-37.424439	-3.80244
0.4496575	0.5502683	1137.37	-43.082624	-3.93486
		BHPCPP		
0.4496853	0.5503023	1515.38	-44.677639	-5.2002
0.4496796	0.5502955	1446.3	-41.941413	-4.96081
0.4496741	0.5502886	1156.26	-35.232013	-3.97163
0.4496685	0.5502818	1099.68	-34.466099	-3.78049
0.4496629	0.5502749	960.65	-32.823215	-3.31158
		BHMPMPP		

0.4496847	0.5503016	1493.88	-39.768134	-5.11215
0.4496785	0.5502941	1447.88	-42.125232	-4.96668
0.4496724	0.5502866	1120.59	-34.263132	-3.84949
0.4496663	0.5502791	785.385	-23.402481	-2.69596
0.4496601	0.5502715	698.313	-22.337862	-2.40217
		BHMPPP		
0.4496837	0.5503004	717.955	-21.062616	-2.46339
0.4496765	0.5502916	914.615	-28.721749	-3.14446
0.4496693	0.5502828	939.939	-28.721749	-3.22887
0.4496621	0.550274	1005.5	-34.812675	-3.4677
0.4496549	0.5502652	1177.86	-40.036204	-4.05965
		BHMPCPP		
0.4496849	0.5503019	868.072	-24.892183	-2.97655
0.4496789	0.5502945	1221.21	-35.423491	-4.18878
0.4496729	0.5502872	1421.74	-46.127129	-4.8929
0.4496669	0.5502799	1520.67	-49.784366	-5.23485
0.4496609	0.5502726	1598.97	-54.571324	-5.51181
		Acetone+Water		
		BHPMPP		
0.5534998	0.4464899	1420.04	-172.3305	-5.30792
0.5534941	0.4464852	1396.93	-183.8192	-5.26917
0.5534885	0.4464806	1328.81	-169.59427	-4.9947
0.5534826	0.446476	1292.4	-181.39891	-

				4.91267
0.5534768	0.4464713	791.67	-118.71656	-3.03462
		BHPPP		
0.5534989	0.4464891	1822.14	-199.98763	-6.74044
0.5534922	0.4464837	1407.21	-169.59427	-5.25601
0.5534855	0.4464783	1278.29	-167.10697	-4.81798
0.5534789	0.446473	1168.21	-159.07254	-4.42427
0.5534722	0.4464676	989.904	-153.18266	-3.81029
		BHPCPP		
0.5535	0.44649	2187.83	-260.41053	-8.16081
0.5534944	0.4464854	2187.38	-255.24061	-8.14207
0.5534888	0.4464809	1913.15	-268.06966	-7.27072
0.5534832	0.4464764	1715.11	-265.51534	-6.60207
0.5534776	0.4464719	1579.74	-255.3038	-6.11682
		BHMPMPP		
0.5534994	0.4464895	1898.23	-229.77399	-7.09336
0.5534933	0.4464846	1640.52	-212.73242	-6.17749
0.5534871	0.4464796	1369.12	-199.13746	-5.22754
0.553481	0.4464747	1188.94	-191.47833	-4.60141
0.5534748	0.4464697	950.221	-153.18266	-3.67801
		BHMPPP		
0.5534984	0.4464887	1585.95	-183.8192	-5.89923

0.5534912	0.4464829	1503.91	-191.47833	-5.65129
0.553484	0.4464771	1286.95	-194.42327	-4.93792
0.5534768	0.4464713	1075.55	-172.3305	-4.15959
0.5534696	0.4464655	1069.62	-183.8192	-4.17811
		BHMPCPP		
0.5534996	0.4464897	2567.22	-295.42234	-9.54214
0.5534936	0.4464848	2147.24	-160.8418	-7.69362
0.5534876	0.44648	1765.7	-222.71034	-6.62605
0.5534816	0.4464752	1448.24	-226.71034	-5.58318
0.5534757	0.4464704	1372.28	-222.11486	-5.31466

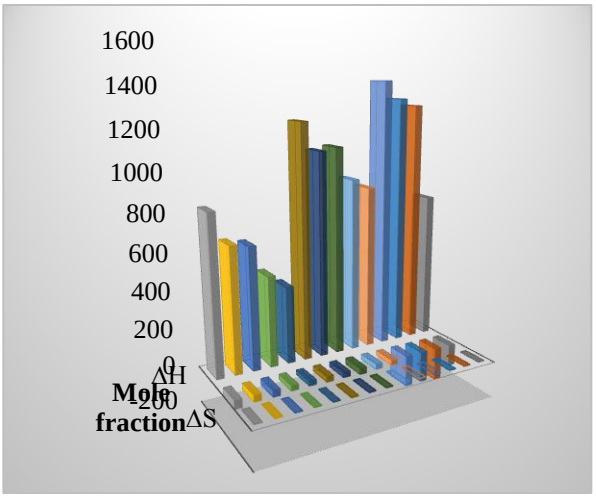

FIG. 1. **Comparison of enthalpies (ΔH), Gibb's energy of activation (ΔG) and entropies (ΔS) of solvent (DMSO, Dioxan, Acetone)+water binary mixture with mole fraction.**

From the observed data, Gibb's energy values at various concentrations are negative consequently change in enthalpy is positive and entropy change is negative. The results are discussed on the basis of solution formation. When the enthalpy of pure components are determined, the values indicates $\Delta H_{sol}>0$. Intermolecular forces between unlike molecules leading to a non-ideal solution and depends on adhesive and cohesive forces. If adhesive forces are less than cohesive forces, $\Delta H_{sol}>0$. At the limit these solutions are heterogeneous. Whenever there is a tendency for the solvent to solvate with the solute i.e. whenever there are strong specific forces between the dissimilar molecules, the observed solubility may well be larger than the ideal solubility. Enhanced solubility is observed whenever there are negative deviations from Raoult's law in the liquid solution, such deviations frequently occur in polar systems, especially in systems where hydrogen bonding between solute and solvent is strong. However, even in nonpolar systems, specific solvation forces may be sufficiently strong to result in solubility's above the ideal. Mixing liquids of different degrees of order usually brings about a net decrease of order and hence positive contributions to the enthalpy ΔH_{mix} of mixing.

From the investigations of the solvation of ions and dipolar molecules in binary solvent mixtures it has been found that the ratio of solvent components in the solvent shell can be different from that in the bulk solution. As expected, the solute is surrounded preferably by the component of the mixture which leads to the more negative Gibb's energy of solvation (ΔG_{solv}) while Gibb's energy values found to be reversed because of dissolution of selected systems in binary solvent mixtures are exothermic.

Measured values of density and viscosity are used to calculate excess parameters like excess molar volume (V_m^E), excess viscosity (η^E), excess Gibb's energy of activation of viscous flow (G^{*E}) are listed in TABLE 4 and shown in FIG. 2-4, for the same following relationships are used

$$V_m^E = \frac{[x_1M_1+x_2M_2]}{\rho} - [\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}] \quad \text{(A.6)}$$

$$\eta^E = \eta - [x_1\eta_1 + x_2\eta_2] \quad \text{(A.7)}$$

$$G^{*E} = RT\,[ln\eta V - (x_1 ln\eta_1 V_1 + x_2 ln\eta_2 V_2)] \quad \text{(A.8)}$$

Where, for each equation, ρ, η and V_m are density, viscosity and molar volume of the mixtures and x_i, V_{m_i}, M_i and η_i (i=1,2) are the mole fraction, molar volume, molar mass and viscosity of the compounds DMSO, dioxan and acetone (1) and water (2) respectively, *R* is gas constant and *T* is absolute temperature.

The excess parameters of the selected systems in binary solvent mixtures are presented in TABLE 4 and shown in FIG. 2-4. The excess parameters V_m^E, η^E, G^{*E} values increases with increase in temperature as well as in concentration.

TABLE 4. **Experimental excess viscosities (η^E), excess molar volume (V_m^E) and excess Gibb's energy of activation (G^{*E}) of solvent (DMSO, dioxan, acetone)+water binary mixture from T/K=(295.15 to 303.15).**

X_1	X_2		$10^3 \cdot \eta^E$			$10^{-3} \cdot V_m^E$			G^{*E}	
		295.15 K	300.15 K	305.15 K	295.15 K	300.15 K	305.15 K	295.15 K	300.15 K	305.15 K
						DMSO+Water				
						BHPMPP				
0.4795786	0.5204094	1.23	1.29	1.29	-1.0049	-1.24	-1.8	-8604.8723	-8731.0127	-8878.8118
0.4795728	0.5204031	1.24	1.32	1.32	-0.64637	-0.6489	-1.7677	-8590.0581	-8706.7928	-8877.5439
0.479567	0.5203968	1.33	1.44	1.44	-0.69336	-1.2314	-1.9312	-8591.7361	-8730.5386	-8884.2142
0.4795612	0.5203905	1.37	1.49	1.49	-0.27507	-1.2511	-2.0819	-8574.5549	-8731.1178	-8890.3334
0.4795554	0.5303842	1.44	1.57	1.57	-0.54803	-1.1431	-2.1171	-8585.3674	-8726.4119	-8891.5803
						BHPPP				
0.4795776	0.5204083	0.94	0.995	1.01	-1.1808	-1.0356	-1.8632	-8612.0876	-8722.9102	-8881.8105
0.4795709	0.520401	1.01	1.08	1.1	-0.68586	-1.4981	-1.9973	-8591.6276	-8741.7988	-8887.2092
0.4795642	0.5203937	1.04	1.12	1.15	-0.76625	-1.0866	-1.9072	-8594.6536	-8724.5089	-8883.1533
0.4795574	0.5203864	1.09	1.19	1.22	-0.48372	-0.86129	-1.5648	-8582.9316	-8714.9725	-8868.5015
0.4795507	0.5203791	1.22	1.35	1.34	-0.20485	-1.2048	-1.7034	-8571.41	-8728.8835	-8874.0592
						BHPCPP				
0.4795787	0.5204095	0.98	1.08	1.05	-0.08793	-1.5935	-2.2214	-8567.7116	-8746.0397	-8896.9634
0.4795731	0.5204034	1.03	1.09	1.12	-0.5045	-1.1499	-1.8046	-8584.3065	-8727.4084	-8879.1222
0.4795674	0.5203973	1.08	1.14	1.16	-0.32194	-0.39784	-0.80729	-8576.6888	-8696.2998	-8837.2565
0.4795618	0.5203911	1.14	1.24	1.23	-0.38452	-1.2837	-1.7786	-8578.9882	-8732.4741	-8877.5563
0.4795562	0.520385	1.19	1.36	1.29	-0.79064	-1.3519	-1.877	-8595.2415	-8735.0667	-8881.4588
						BHMPMPP				
0.4795816	0.5204089	1.03	1.09	1.08	-0.48713	-1.1629	-2.0907	-8583.8236	-8728.1711	-8891.4236
0.479572	0.5204022	1.09	1.15	1.15	-0.51062	-1.2198	-1.7506	-8584.5356	-8730.2818	-8876.8329
0.4795658	0.5203955	1.16	1.23	1.23	-0.72392	-1.1315	-1.6595	-8592.9573	-8726.3878	-8872.7593
0.4795596	0.5203887	1.25	1.32	1.35	-0.797	-1.1548	-1.7953	-8595.6925	-8727.1049	-8878.2172
0.4795533	0.520382	1.34	1.4	1.44	-0.29266	-1.0312	-2.0087	-8574.9964	-8721.7593	-8886.9635
						BHMPPP				
0.4795771	0.5204078	0.96	0.995	1	-0.28699	-0.94014	-1.6466	-8575.7034	-8718.9668	-8872.6961
0.4795699	0.5203999	1.04	1.08	1.1	-0.16937	-0.98418	-1.9043	-8570.7087	-8720.5191	-8883.2686
0.4795626	0.520392	1.11	1.18	1.19	-0.31882	-1.1977	-2.1054	-8576.4831	-8729.0702	-8891.4942
0.4795554	0.5203842	1.19	1.28	1.28	-0.15677	-1.0133	-1.6382	-8569.688	-8721.198	-8871.546
0.4795547	0.5203764	1.26	1.35	1.35	0.080272	-0.52262	-1.2652	-8559.897	-8700.7937	-8855.6746
						BHMPCPP				
0.4795184	0.5204091	0.93	0.935	0.954	-0.2163	-0.97787	-2.5331	-8572.8782	-8720.5408	-8910.2016
0.4795723	0.5204026	1	1.02	1.02	-0.61113	-0.72961	-1.3336	-8588.6195	-8710.094	-8859.3646

0.4795663	0.520396	1..09	1.11	1.11	-0.49098	-0.82948	-0.7838	-8583.5088	-8713.9532	-8836.2685
0.4795602	0.5203895	1.16	1.2	1.22	-0.25585	-0.99931	-2.2261	-8573.7626	-8720.7003	-8896.4222
0.4795542	0.5203829	1.26	1.31	1.32	-0.46209	-1.5121	-1.8499	-8581.8643	-8741.6813	-8880.2809
						Dioxan+Water				
						BHPMPP				
0.4496851	0.5503022	2.98	3.11	2.82	-0.8	-0.08	-1.86	-8389.1557	-8543.6915	-8667.5746
0.4496794	0.5502951	3.78	3.61	3.72	-2.1339	0.035844	-2.4403	-8434.603	-8539.5488	-8687.7243
0.4496736	0.5502881	4.48	4.31	4.32	-1.8	0.15747	-1.9113	-8422.9729	-8562.61	-8668.8425
0.4496679	0.5502811	5.18	5.21	5.22	-1.2694	0.076555	-2.3626	-8404.733	-8537.6823	-8684.5269
0.4496621	0.550274	6.08	6.11	6.12	-1.4002	-0.46957	-2.7296	-8408.9282	-8556.2478	-8697.161
						BHPPP				
0.4496842	0.550301	4.68	4.51	4.72	-1.4862	-0.40559	-2.446	-8412.7546	-8554.9629	-8688.1477
0.4496775	0.5502928	5.18	4.91	5	-0.99484	0.26008	-1.7419	-8395.8985	-8531.8343	-8663.3501
0.4496708	0.5502847	5.98	5.71	5.72	-0.89091	-0.021534	-2.3184	-8392.154	-8541.2368	-8683.173
0.4496642	0.5502765	7.08	6.91	6.62	-1.0385	-0.55218	-2.5093	-8396.8781	-8559.2773	-8689.601
0.4496575	0.5502683	8.28	8.11	7.62	-1.6788	-0.14991	-2.2468	-8418.3078	-8545.1487	-8680.1602
						BHPCPP				
0.4496853	0.5503023	4.38	4.11	3.62	-1.171	0.21213	-1.8314	-8402.1046	-8533.7449	-8666.733
0.4496796	0.5502955	5.08	4.91	4.32	-1.7332	0.2506	-1.7675	-8420.9337	-8532.195	-8664.2758
0.4496741	0.5502886	5.48	5.41	5.12	-1.2936	0.17503	-1.7294	-8405.7927	-8534.5502	-8662.7201
0.4496685	0.5502818	6.28	6.21	5.92	-1.1209	0.16014	-1.986	-8399.7289	-8534.827	-8671.3973
0.4496629	0.5502749	7.58	7.31	7.32	-1.0359	-0.20892	-2.2605	-8396.6355	-8547.2709	-8680.7338
						BHMPMPP				
0.4496847	0.5503016	3.88	3.41	3.22	-1.1384	-0.47537	-2.6782	-8400.996	-8557.3819	-8696.3031
0.4496724	0.5502866	5.08	4.91	4.82	-0.76518	1.2536	-1.6581	-8387.9541	-8497.8499	-8660.2189
0.4496663	0.5502791	5.68	6.01	5.92	-0.89118	-0.28235	-2.0127	-8391.951	-8549.99	-8672.2874
0.4496601	0.5502715	6.28	6.51	6.62	-0.97664	-0.11917	-2.4323	-8394.5878	-8544.1334	-8686.6902
						BHMPPP				
0.4496837	0.5503004	4.58	5.01	5.02	-0.82524	-0.29602	-2.4874	-8390.4316	-8551.1753	-8689.5919
0.4496765	0.5502916	5.48	5.71	5.52	-1.1672	-0.16149	-2.3888	-8401.6963	-8546.2827	-8685.8741
0.4496693	0.5502828	6.08	6.31	6.02	-1.2458	-0.36105	-2.4138	-8404.097	-8552.8998	-8686.6424
0.4496621	0.550274	6.88	6.91	6.62	-1.4802	-0.46398	-2.4489	-8411.7792	-8556.1959	-8687.4523
0.4496549	0.5502652	7.68	7.61	7.02	-1.2014	-0.084487	-2.1794	-8402.0897	-8542.8581	-8677.7664
						BHMPCPP				
0.4496849	0.5503019	4.08	4.21	4.32	-1.1416	-0.24907	-3.1803	-8401.1082	-8549.5773	-8714.0108
0.4496789	0.5502945	5.38	5.01	4.92	-0.6508	-0.50401	-2.298	-8384.3605	-8558.1364	-8682.7384
0.4496729	0.5502872	6.58	5.71	5.62	-1.416	0.090442	-1.5008	-8409.916	-8537.4291	-8654.7828
0.4496669	0.5502799	7.48	6.61	6.22	-0.63794	-0.44963	-1.8234	-8383.4588	-8555.7781	-8665.7162
0.4496609	0.5502726	8.48	7.41	6.92	-1.2024	-0.42783	-1.7681	-8402.2197	-8554.7859	-8663.5545
						Acetone+Water				

						BHPMPP				
0.5534998	0.4464899	1.22	1.5	1.47	-4.72	-7.73	-8.06	-8201.6453	-8423.2173	-8526.3271
0.5534941	0.4464852	1.7	1.76	1.89	-4.9584	-6.0337	-7.7905	-8211.8224	-8350.387	-8514.8187
0.5534885	0.4464806	2.06	2.2	2.25	-4.2282	-6.0459	-7.1097	-8181.4884	-8350.6623	-8485.1625
0.5534826	0.446476	2.61	2.63	2.75	-4.9538	-5.8996	-7.6107	-8450.0531	-8344.2433	-8506.5272
0.5534768	0.4464713	2.88	3.1	3.4	-3.6756	-6.1813	-7.5514	-8397.3719	-8355.9077	-8503.7154
						BHPPP				
0.5534989	0.4464891	1.48	1.57	1.43	-4.9716	-6.279	-7.6112	-8451.4831	-8360.9967	-8507.2686
0.5534922	0.4464837	1.93	1.98	2.08	-4.9624	-6.0455	-7.5223	-8450.8484	-8350.849	-8503.1559
0.5534855	0.4464783	2.21	2.46	2.42	-3.619	-6.3154	-6.6743	-8395.5043	-8362.0288	-8466.478
0.5534789	0.446473	2.68	3.1	2.92	-3.8744	-6.1534	-7.2153	-8405.63	-8354.9004	-8489.3909
0.5534722	0.4464676	3.3	3.45	3.61	-5.0821	-5.5124	-7.4822	-8455.0598	-8327.647	-8500.6377
						BHPCPP				
0.5535	0.44649	1.52	1.35	1.23	-5.3331	-6.3427	-7.8604	-8466.5478	-8363.7196	-8518.1043
0.5534944	0.4464854	2.05	1.96	1.65	-5.8761	-5.8708	-7.6397	-8489.0793	-8343.522	-8508.2775
0.5534888	0.4464809	2.62	2.42	2.29	-5.0868	-6.0426	-7.4535	-8455.8182	-8350.5311	-8499.9786
0.5534832	0.4464764	3.27	2.65	2.97	-4.8672	-6.0667	-7.6114	-8446.4721	-8351.3072	-8506.5665
0.5534776	0.4464719	3.73	3.26	3.47	-4.9483	-7.3485	-6.4318	-8449.6029	-8405.8639	-8455.7368
						BHMPMPP				
0.5534994	0.4464895	1.7	1.74	1.56	-4.9006	-5.825	-6.6706	-8448.5488	-8341.8175	-8466.8524
0.5534933	0.4464846	2.17	2.21	2.12	-5.0745	-6.0791	-5.8465	-8455.5224	-8352.2891	-8431.7066
0.5534871	0.4464796	2.61	2.59	2.69	-5.0031	-5.6369	-7.0668	-8452.3121	-8333.4089	-8483.2997
0.553481	0.4464747	3.27	3.3	3.41	-4.8728	-6.0254	-7.6067	-8446.6662	-8349.5247	-8506.3235
0.5534748	0.4464697	3.8	4.11	4.1	-5.3945	-6.999	-7.8508	-8468.1196	-8390.7506	-8516.666
						BHMPPP				
0.5534984	0.4464887	1.34	1.37	1.46	-5.7383	-6.4771	-7.8762	-8483.4886	-8369.4087	-8464.4806
0.5534912	0.4464829	1.83	1.94	1.93	-5.9555	-5.6778	-6.1349	-8492.3724	-8335.3421	-8443.8281
0.553484	0.4464771	2.17	2.13	2.37	-5.047	-5.4598	-6.249	-8454.082	-8325.9326	-8448.3847
0.5534768	0.4464713	2.62	2.4	2.92	-5.055	-4.0442	-3.6168	-8454.1518	-8267.1161	-8339.0607
0.5534696	0.4464655	2.97	2.87	3.24	-4.3757	-4.3657	-4.5758	-8425.8329	-8280.0288	-8377.9789
						BHMPCPP				
0.5534996	0.4464897	1.62	1.4	1.08	-4.2912	-4.6801	-3.7898	-8423.4369	-8294.071	-8346.9209
0.5534936	0.4464848	2.24	1.93	1.82	-3.8744	-3.6356	-2.959	-8406.1606	-8251.0465	-8313.1098
0.5534876	0.44648	2.82	2.56	2.56	-4.8371	-5.3878	-5.9926	-8445.4427	-8322.987	-8437.6179
0.5534816	0.4464752	3.17	2.89	3.1	-4.1561	-4.5537	-5.1615	-8417.1768	-8288.1152	-8402.574
0.5534757	0.4464704	3.81	3.77	3.72	-4.0206	-4.7232	-5.0451	-8411.3966	-8294.8665	-8397.4874

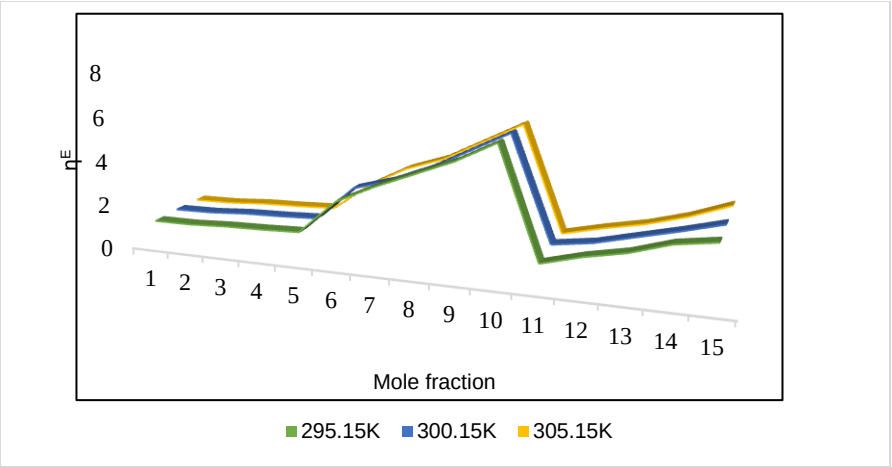

FIG. 2. **Variation of excess viscosity (η^E) with mole fraction of solvent (DMSO, dioxan, acetone)+water binary mixture.**

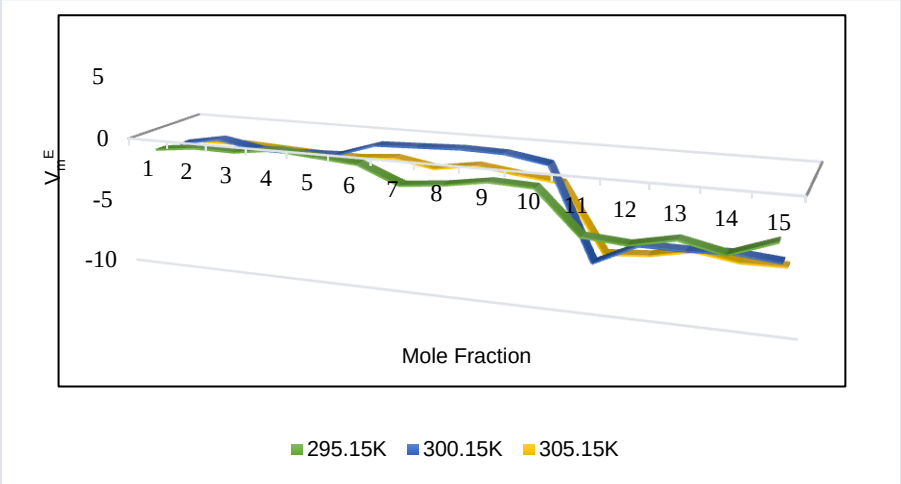

FIG. 3. **Variation of excess molar volume (V_m^E) with mole fraction of solvent (DMSO, dioxan, acetone)+water binary mixture.**

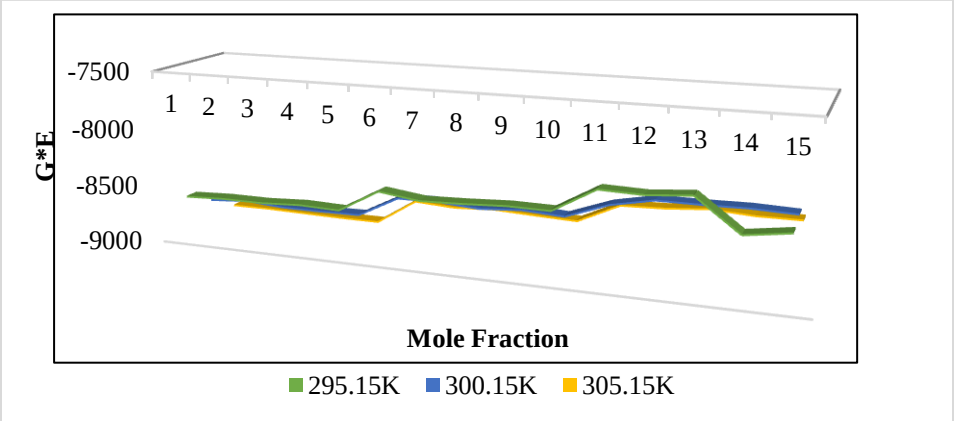

FIG. 4. **Variation of excess Gibb's energy of activation (G^{*E}) with mole fraction of solvent (DMSO, dioxan, acetone)+water binary mixture.**

The negative V_m^E values indicate the presence of strong molecular interactions between the components of the mixtures. The forces are responsible for the interactions are non-specific and specific forces which can be saturated and lead to stoichiometric molecular compounds. The structure and size of N-Benzothiazol-2-yl-3, 5-disubstituted pyrazolines lead to interstitial accommodation with binary solvent mixtures.

From the tabulated data, excess molar volume (V_m^E) of binary systems are negative over the entire composition range (295.15 to 305.15) K and at atmospheric pressure while exceptions observed because of the overlapping of solute-solvent interactions and hydrogen bonding between the molecules. The influence of temperature on V_m^E for the systems is slightly more negative with increasing temperature. This can be happened because of the relative orientations of molecules depend on the interplay of two factors : i) The presence of an electric field set up by the polar molecules tend to live up the dipoles whereas the kinetic energy of the molecules tends to toss them about in a random manner.

A correlation between the signs of η^E and V_m^E has been observed for a number of binary solvent systems [26,27] i.e. η^E is positive when V_m^E is negative and vice versa. V_m^E is negative because of dispersion forces and dipolar interactions. The excess viscosity values are explained in TABLE 4 and shown in FIG. 2.

The values of excess viscosity found to be positive because of hydrogen bonding which is responsible for the strong, temperature-dependent self and hetero-association of amphiprotic solvents. Cooperative solvent/solvent interactions such as chain wise association by intermolecular hydrogen bonding [28].

From the TABLE 4 and FIG. 4, it is clear that, the values of G^{*E} are found to be negative. By increasing temperature the values also increase. The results are obtained so because of the change in intermolecular free space. The changes occur because of ions as structure makers and structure breakers. If ions with high charge density are strongly coordinated, leading to well defined ion/water complexes i.e. structure makers and larger weakly interacting monovalent ions have only a small influence on the orientation of the surrounding water molecules and mainly disrupt the H-bond network of bulk water with structure breaking as net effect. According to Reed and Taylor [29] and Palepu et al. [30], G^{*E} may be considered as a reliable criterion to detect or exclude the presence of interaction between unlike molecules. According to these authors, the magnitude of the positive G^{*E} values is an excellent indicator of the strength of specific interactions.

Conclusion

The experimental viscosities (η) and molar volumes (V_m) are determined for N-Benzothiazol-2-yl-3, 5-disubstituted pyrazolines in binary mixture from (295.15 K to 305.15 K). From experimental measurements of viscosities (η), molar volumes (V_m), ΔG, ΔH, ΔS, excess parameters (η^E, V_m^E, G^{*E}) were calculated. The viscosities and molar volume decreases with increasing temperature and increase with increasing concentration. The study of change in molar volume with respect to change in temperature over the selected range reveals that introduction of solute molecules in binary solvent mixtures decreases with increase in temperature indicating structure breaking property of solute/selected system change in excess viscosity. Deviation of viscosity ($\Delta\eta$) increases with increase in molarity but decrease with increase in temperature. This supports the observation from thermodynamic parameters. That with increase in temperature thermal motion at particles of

system increases which results in weakening of solute solvent interaction which in turn causes solvation effect and structural effect.

Acknowledgment

The authors are thankful to the Principal of Shri Shivaji Science College, Amravati for providing research laboratory and necessary things during the research work.

REFERENCES

1. Matkowska D, Hofman T. Volumetric properties of the {x1 [C4mim] [MeSO4]+(1− x1) MeOH} system at temperatures from (283.15 to 333.15) K and pressures from (0.1 to 35) MPa. J Solution Chem. 2013;42(5):979-90.
2. Bouzina Z, Negadi A, Dergal F, et al. Vapor-liquid equilibria of N, N, N′, N′ tetramethylethylenediamine (TMEDA), tetramethylpropylenediamine (TMPDA) and their aqueous solutions. J Mol Liq. 2015;201:83-9.
3. Wlazło M, Marciniak A, Letcher TM. Activity coefficients at infinite dilution and physicochemical properties for organic solutes and water in the ionic liquid 1-ethyl-3-methylimidazolium trifluorotris (perfluoroethyl) phosphate. J Solution Chem. 2015;44(3-4):413-30.
4. Stec M, Tatarczuk A, Śpiewak D, et al. Densities, excess molar volumes, and thermal expansion coefficients of aqueous aminoethylethanolamine solutions at temperatures from 283.15 K to 343.15 K. J Solution Chem. 2014;43(5):959-71.
5. Lewandowska K. Viscometric studies in dilute solution mixtures of chitosan and microcrystalline chitosan with poly (vinyl alcohol). J Solution Chem. 2013;42(8):1654-62.
6. Naik AB. Densities, viscosities, speed of sound and some acoustical parameter studies of substituted pyrazoline compounds at different temperatures. IJPAP. 2015;53:27-34.
7. Domańska U, Walczak K. Ternary liquid-liquid equilibria for mixtures of {ionic liquid+thiophene or benzothiophene+heptane} at T=308.15 K. J Solution Chem. 2015;44(3-4):382-94.
8. Laliberté M. Model for calculating the viscosity of aqueous solutions. J Chem Eng Data. 2007;52(2):321-35.
9. Gotmare AG, Burghate AS, Wadhal SA. Study of stability constants of complex of N-benzothiazol-2-yl-3, 5-disubstituted pyrazolines with some transition metal ions. J Chem Pharm Res. 2014;6(12):748-53.
10. Li Y, Li YH, Wang FA, et al. Volumetric and viscometric studies of cefepime hydrochloride in water and normal saline from (278.15 to 313.15) K. J Chem Thermodyn. 2013;66:14-21.
11. Ubharhande SS, Gotmare AG, Burghate AS, et al. Thermodynamic study of 1, 3-diaryl carbamides in binery solvent mixtures. Ras J Chem. 2012;5(3):360-4.
12. Rahul D, Sankar MG, Chand GP, et al. Studies of physical properties on molecular interactions in binary liquid mixtures of 3-chloroaniline with isomeric butanols at different temperatures. J Mol Liq. 2015;211:386-94.
13. Wakode AK, Burghate AS, Wadhal SA. Microwave assisted improved method for the synthesis, characterisation and antimicrobial studies of newly synhtesized benzothiazolyl and benzimidazolyl substituted derivatives. Indo Ame J Pharm Res. 2014;4(10):5010-6.
14. Samshuddin S, Narayana B, Sarojini BK, et al. Antimicrobial, analgesic, DPPH scavenging activities and molecular docking study of some 1, 3, 5-triaryl-2-pyrazolines. Med Chem Res. 2012;21(8).

15. Joshi RS, Mandhane PG, Diwakar SD, et al. Synthesis, analgesic and anti-inflammatory activities of some novel pyrazolines derivatives. Bioorg Med Chem Lett. 2010;20(12):3721-5.
16. Özdemir Z, Kandilci HB, Gümüşel B, et al. Synthesis and studies on antidepressant and anticonvulsant activities of some 3-(2-furyl)-pyrazoline derivatives. Eur J Med Chem. 2007;42(3):373-9.
17. Jainey PJ, Bhat IK. Antitumor, analgesie and anti-inflammatory activities of synthesized pyrazolines. J Young Pharm. 2012;4(2):82-7.
18. Acton QA. Central Nervous System Agents-Advances in Research and Application, Scholarly Editions, Atlanta, Georgia. 2013.
19. Rizvi SU, Siddiqui HL, Johns M, et al. Anti-HIV-1 and cytotoxicity studies of piperidyl-thienyl chalcones and their 2-pyrazoline derivatives. Med Chem Res. 2012;21(11):3741-9.
20. Hassan SY. Synthesis, antibacterial and antifungal activity of some new pyrazoline and pyrazole derivatives. Molecules. 2013;18(3):2683-711.
21. Rani M, Mohamad Y. Synthesis, studies and *in vitro* antibacterial activity of some 5-(thiophene-2-yl)-phenyl. J Saudi Chem Soc. 2014;18:411-7.
22. Banday AH, Mir BP, Lone IH, et al. Studies on novel D-ring substituted steroidal pyrazolines as potential anticancer agents. Steroids. 2010;75(12):805-9.
23. Jois VH, Kalluraya B, Girisha KS. Synthesis and antioxidant activity study of pyrazoline carrying arylfuran/thiophene moiety. J Serb Chem Soc. 2014;79(12):1469-75.
24. Hasan A, Abbas A, Akhtar MN. Synthesis, characterization and fluorescent property evaluation of 1, 3, 5-triaryl-2-pyrazolines. Molecules. 2011;16(9):7789-802.
25. Pande PS, Wadhal SA, Wadodkar KN. Indian J Chem. 2004;55-8.
26. Gill DS, Cheema JS. Preferential solvation of ions in mixed solvents. Z Phys Chem. 1983;134(2):205-14.
27. Marcus Y. Thermodynamics of solvation of ions. Part 5. -Gibbs free energy of hydration at 298.15 K. J Chem Soc Faraday Trans. 1991;87(18):2995-9.
28. Reichardt C, Welton T. Solvents and solvent effects in organic chemistry. John Wiley & Sons; 2011.
29. Reed III TM, Taylor TE. Viscosities of liquid mixtures. J Phys Chem. 1959;63(1):58-67.
30. Palepu R, Oliver J, MacKinnon B. Viscosities and densities of binary liquid mixtures of m-cresol with substituted anilines. Part 3. Can J Chem. 1985;63(5):1024-30.