Viscometric Studies of Molecular Interactions in Binary Mixtures of Formamide with Alkanol at 298.15 and 308.15 K

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Abstract – Viscosity data were measured at 298.15 K and 308.15 K for formamide + 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol or 2-methyl-2-propanol mixtures. For an equimolar mixture, deviation in viscosity follows the sequence: 2-methyl-2-propanol >2-methyl-1-propanol>1-butanol>2-propanol>1-propanol. The viscosity data were further analyzed in terms of graph theory. Free energy of activation was also calculated from experimental viscosity data along with previously reported excess volume data. The deviation in viscosity and free energy of activation were fitted to Redlich-Kister polynomial equation. The viscosity data were also correlated by correlations like Grunberg-Nissan, Tamura-Kurata, Hind-McLaughlin-Ubbelohde, and Katti-Chaudhari relation. Various adjustable parameters, G_{12}, T_{12}, H_{12}, and W_{vis}/RT, of various correlations were used to predict viscosity deviation of binary mixtures. Positive value of G_{12} indicates strong interaction in the studied systems. Grunberg-Nissan relation has lowest deviation among the four correlations for formamide + 1-propanol or 2-propanol mixtures; and for mixtures of formamide with 1-butanol or 2-methyl-1-propanol, Tamura-Kurata has lowest deviation. Grunberg-Nissan gives lowest deviation for formamide + 2-methyl-2-propanol mixtures.

Key words: Viscosity, Graph theoretical approach, Formamide, Butanol, Propanol, Intermolecular interactions

1. Introduction

Viscosity of various binary mixtures was measured extensively to correlate and derive its relation with other physical properties to get significant knowledge about the various types of molecular interactions taking place in the binary mixtures. This is very important for the solutions of many engineering problems concerning heat, mass transport and fluid flow [1,2]. Viscosity data on various liquids and liquid mixtures at varying temperature and pressures have been reported from time to time [3-8]. Formamide was selected for this study, as it is the simplest amide that contains a peptide linkage, the fundamental building block of proteins. Formamide molecules are highly polar [9] and are strongly self-associated through extensive three-dimensional network of hydrogen bonds, through its three hydrogen bond donors (3 H-atoms) and three acceptors (two lone pairs of electrons at oxygen and one on nitrogen atom). Alcohols are self-associated organic compounds through hydrogen bonding of their hydroxyl groups. These are biologically and industrially important amphiphilic materials.

Amide-alkanol mixtures have been widely studied as both are biologically interesting compounds. The excess and deviation of a thermodynamic property of their binary mixture as function of composition, temperature and pressure could be a very effective tool to get information about molecular structure and intermolecular forces in liquid mixtures.

Ultrasonic and viscosity measurements of formamide with ethanol, 1-propanol, 1,2-ethanediol and 1,2-propanediol at temperatures of 293.15 to 318.15 K were performed by Nain [10]. Densities and viscosities of formamide with polar 2-alkanol (C1-C7) were reported by Almasi as a function of composition and temperatures and interpreted the data in terms of the statistical associating fluid theory and perturbed chain statistical associating fluid theory [2]. Kondaiah et al. measured the volumetric and viscometric properties of propanoic acid in equimolar mixtures of N,N-dimethyl formamide + alkanols [5]. Negative and positive values of various excess and deviation parameters were attributed to the existence of strong interactions, like dipole-dipole interactions, H-bonding between the carbonyl group of acid molecules and hydroxyl group of alcohol groups. The viscosity of formamide with 2-methoxyethanol and 2-ethoxyethanol was discussed in terms of molecular interactions due to physical, chemical and structural effects between the unlike molecules [8]. Gracia et al. and Gomez Marigliano and Solimo also studied formamide with alkanol (C1-C3) and observed the sigmoid behavior in viscosity deviation versus mole fraction of formamide curves [11,12].

We have reported excess volume, enthalpy and ultrasonic velocity data for formamide + alkanol in our previous publications [13-19]. In the present paper, viscosity data at 298.15 K and 308.15 K for formamide + 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol or 2-methyl-2-propanol mixtures are reported. The viscosity data were correlated by using various correlations like Grunberg-Nissan, Tamura-Kurata, Hind-McLaughlin-Ubbelohde, Katti-Chaudhari relation. The measured

data were further analyzed in terms of graph theory and free energy of activation was also calculated from experimental viscosity data employing excess volume data [17].

2. Experimental

Formamide, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol or 2-methyl-2-propanol mixtures (Merck or Sigma) were purified by standard procedures [14,19,20]. Refractive indices were measured with a thermostatically controlled Abbe refractometer (OSAW, India) using sodium D-line with an accuracy of ±0.001 unit. The temperature of water thermostat was controlled to ±0.01 K by a mercury-in-toluene regulator. The binary mixtures were prepared by weight using a weighing balance (Shimadzu UniBloc 321-62900-64, AUX 120), which can measure with an accuracy of ±0.00001 g and accuracy in mole fraction is ±0.0001. Viscosities in the pure liquids and their binary mixtures were measured by using a modified suspended level Ubbelodhe viscometer. The viscometer was calibrated at working temperatures beforehand. A freshly distilled liquid was filled in the reservoir of the viscometer through the side tube. Then it was clamped gently at the top in a vertical position after immersing it to an appropriate depth in the water thermostat to maintain the required temperature. To avoid the change in the effective length of capillary from one reading to another, the viscometer was hung exactly vertical. After remaining in bath for about 30 minutes, the liquid was drawn up through the capillary tube into bulb. The time of flow of each liquid was measured at least 3~4 times until reproducible timing was attained. The characteristic constants A and B of viscometer were then determined from the measured times of flow of two liquids of known viscosities at desired temperatures using following equation:

$$\upsilon_i = \eta_i / \rho_i = At_i - B/t_i$$

where υ_i, η_i and ρ_i are the kinematic viscosity, absolute viscosity and density of pure liquids respectively and t_i is the time of flow in seconds. The dynamic viscosity, η, is deduced with an uncertainty of ±0.003×10⁻³ Ns m⁻². For viscometer, the values of con-

stants at 298.15 K, A=4.2673×10⁻⁹ m² S⁻², B=1.984×10⁻⁶ m² and at 308.15 K are A=4.32×10⁻⁹ m² s⁻², B=8.6×10⁻⁸ m², respectively.

The purities of purified samples were checked by measuring viscosities and refractive indices of the pure compounds and these agree well with their respective literature values as shown in Table 1. The purified samples were also analyzed by gas chromatography for their purity and found to have better than 99.6 wt%.

3. Results and Discussion

Experimental values of viscosities of binary mixture of formamide with 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol or 2-methyl-2-propanol over the entire composition range at 298.15 and 308.15 K were reported in Table 2. Viscosity deviation ($\Delta\eta$) of various binary mixtures was calculated using Eq. (1)

$$\Delta\eta = \eta - x_1\eta_1 - x_2\eta_2 \tag{1}$$

In the above equation, η represents the measured viscosity of binary mixture; the symbols η_1 and η_2 refer to the viscosity of pure components of the mixture. The $\Delta\eta$ data were also fitted to the following Redlich-Kister equation [37]:

$$\Delta\eta = x_1(1 - x_1)\left[\sum_{n=1}^{4} \eta^{(n)}(1 - 2x_1)^n\right] \tag{2}$$

where $\eta^{(n)}$ are the adjustable parameters, and x_1 is the mole fraction of formamide in formamide (1) + alkanol (2) mixture. These parameters were evaluated by fitting measured $\Delta\eta$ data to Eq. (2) by the least squares method and reported in Table 3 along with the standard deviations $\sigma(\Delta\eta)$ of $\Delta\eta$.

$$\sigma(\Delta\eta) = \left\{\left[\sum(\Delta\eta_{exptl.} - \Delta\eta_{calcd.(Eq.(2))})^2\right] / (m - n)\right\}^{1/2} \tag{3}$$

where m is the number of experimental values, and n is the number of adjustable parameters in Eq. (2). The choice of n to have 1~4 values was dictated by the consideration that the maximum deviation $\sigma_{max}(\Delta\eta)$ of $\Delta\eta$ (as calculated from Eq. (2) from the

Table 1. Comparison of experimental values of refractive index, n_D and viscosity, η(m Ns m⁻²) of pure liquids with the corresponding literature values

| Compound | T/K | n_D | | η | |
		Exptl.	Literature	Exptl.	Literature
Formamide	298.15	1.446	1.44597 [21]	3.125	3.322[22], 3.34[23], 3.302[24]
	308.15	1.428	1.4280 [25]	2.518	2.6531[22], 2.5[23], 2.542[24]
1-Propanol	298.15	1.384	1.3833[26], 1.3832 [27]	1.863	1.9165[28], 1.95[23], 2.0767[29]
	308.15	1.379	1.3791 [27]	1.505	1.5542[28], 1.4[23], 1.5947[29]
2-Propanol	298.15	1.375	1.3751[26], 1.3765 [30]	2.032	2.0763[29]
	308.15	1.372	1.3716 [30]	1.515	1.5317[29]
1-Butanol	298.15	1.397	1.39741[31], 1.3972 [27]	2.546	2.5416[22], 2.560[32], 2.5868[29]
	308.15	1.394	1.3933 [27]	2.018	1.9978[22], 1.991[32], 1.9882[29]
2-Methyl-1-propanol	298.15	1.394	1.3939[33], 1.3932 [30]	3.354	3.404[34], 3.435[32], 3.0968[29]
	308.15	1.390	1.3896 [30]	2.474	2.188[34], 2.508[32] 2.2492[29]
2-Methyl-2-propanol	298.15	1.385	1.3852 [33]	4.448	4.433[32], 4.3898[35]
	308.15	1.380	1.37947 [36]	2.663	2.611[32], 2.6427[35]

Table 2. Experimental viscosity and viscosity deviation ($\times 10^{-3}$ Ns M^{-2}) data for various (1+2) binary mixtures as functions of mole fractions of formamide

x_1	η	$\Delta\eta$	x_1	η	$\Delta\eta$
Formamide (1) + 1-propanol (2); T = 298.15 K					
0.0684	1.882	−0.068	0.5306	2.685	0.152
0.1116	1.922	−0.082	0.6374	2.879	0.211
0.1582	1.976	−0.087	0.6532	2.920	0.233
0.2120	2.054	−0.077	0.7166	3.010	0.242
0.2624	2.139	−0.055	0.7584	3.070	0.250
0.3030	2.211	−0.034	0.8496	3.148	0.213
0.4082	2.421	0.043	0.8958	3.166	0.172
0.4613	2.531	0.086	0.9658	3.155	0.072
0.4958	2.599	0.110			
Formamide (1) + 1-propanol (2); T = 308.15 K					
0.0684	1.547	−0.028	0.5306	2.102	0.059
0.1116	1.556	−0.063	0.6374	2.258	0.107
0.1582	1.602	−0.063	0.6532	2.284	0.117
0.2120	1.661	−0.060	0.7166	2.363	0.131
0.2624	1.716	−0.055	0.7584	2.395	0.121
0.3030	1.773	−0.040	0.8496	2.460	0.094
0.4082	1.920	0.001	0.8958	2.481	0.068
0.4613	1.999	0.026	0.9658	2.507	0.023
0.4958	2.054	0.046			
Formamide (1) + 2-propanol (2); T = 298.15 K					
0.0699	2.027	−0.082	0.5364	2.798	0.179
0.1139	2.029	−0.128	0.6585	3.015	0.263
0.1821	2.108	−0.124	0.7627	3.199	0.332
0.216	2.167	−0.102	0.8147	3.231	0.308
0.2685	2.293	−0.033	0.8526	3.209	0.245
0.308	2.385	0.016	0.8837	3.204	0.205
0.3604	2.472	0.046	0.9237	3.186	0.144
0.4178	2.571	0.082	0.9666	3.140	0.051
Formamide (1) + 2-propanol (2); T = 308.15 K					
0.0699	1.580	−0.006	0.5364	2.130	0.077
0.1139	1.512	−0.118	0.6585	2.301	0.125
0.1821	1.589	−0.110	0.7627	2.467	0.186
0.216	1.650	−0.083	0.8147	2.535	0.202
0.2685	1.726	−0.060	0.8526	2.550	0.179
0.308	1.775	−0.049	0.8837	2.552	0.150
0.3604	1.857	−0.021	0.9237	2.553	0.111
0.4178	1.937	0.003	0.9666	2.554	0.069
Formamide (1) + 1-butanol(2); T = 298.15 K					
0.0824	2.449	-0.146	0.6422	3.234	0.316
0.1332	2.413	-0.211	0.6975	3.262	0.311
0.2478	2.531	-0.160	0.7399	3.289	0.314
0.3473	2.648	-0.100	0.7935	3.311	0.305
0.3833	2.744	-0.025	0.8318	3.305	0.277
0.4346	2.874	0.076	0.8737	3.272	0.220
0.4697	2.953	0.134	0.9066	3.243	0.172
0.5271	3.071	0.220	0.9719	3.175	0.065
0.5804	3.173	0.290			

Table 2. Continued

x_1	η	$\Delta\eta$	x_1	η	$\Delta\eta$
Formamide (1) + 1-butanol(2); 308.15 K					
0.0824	1.887	−0.173	0.6422	2.558	0.218
0.1332	1.913	−0.172	0.6975	2.616	0.249
0.2478	1.990	−0.153	0.7399	2.611	0.223
0.3473	2.109	−0.083	0.7935	2.596	0.180
0.3833	2.163	−0.047	0.8318	2.608	0.173
0.4346	2.243	0.008	0.8737	2.610	0.154
0.4697	2.297	0.044	0.9066	2.610	0.138
0.5271	2.381	0.099	0.9719	2.522	0.017
0.5804	2.467	0.158			
Formamide (1) + 2-methyl-1-propanol (2); T = 298.15 K					
0.0832	3.210	−0.125	0.6422	3.788	0.581
0.1344	3.170	−0.154	0.6997	3.797	0.603
0.1821	3.188	−0.125	0.7457	3.763	0.579
0.2497	3.226	−0.071	0.7952	3.681	0.508
0.3496	3.352	0.078	0.8263	3.623	0.457
0.4371	3.476	0.222	0.8748	3.481	0.327
0.5042	3.598	0.359	0.9066	3.410	0.263
0.5829	3.726	0.505	0.9722	3.199	0.067
Formamide (1) + 2-methyl-1-propanol (2); T = 308.15 K					
0.0832	2.413	−0.065	0.6422	2.858	0.355
0.1344	2.392	−0.088	0.6997	2.879	0.373
0.1821	2.420	−0.062	0.7457	2.839	0.331
0.2497	2.483	−0.002	0.7952	2.813	0.303
0.3496	2.565	0.075	0.8263	2.785	0.274
0.4371	2.648	0.154	0.8748	2.756	0.243
0.5042	2.723	0.226	0.9066	2.676	0.161
0.5829	2.808	0.308	0.9722	2.523	0.005
Formamide (1) + 2-methyl-2-propanol (2); T = 298.15 K					
0.0843	4.472	0.135	0.6482	5.086	1.497
0.1361	4.933	0.665	0.7026	4.766	1.249
0.1879	5.171	0.972	0.7515	4.554	1.102
0.2524	5.387	1.273	0.7975	4.297	0.906
0.3529	5.353	1.373	0.8492	4.176	0.854
0.4406	5.346	1.482	0.8764	4.012	0.726
0.5155	5.339	1.574	0.9182	3.718	0.487
0.5864	5.269	1.599	0.9726	3.310	0.151
Formamide (1) + 2-methyl-2-propanol (2); T = 308.15 K					
0.0843	2.923	0.272	0.6482	3.555	0.986
0.1361	3.097	0.453	0.7026	3.495	0.934
0.1879	3.249	0.612	0.7515	3.344	0.789
0.2524	3.512	0.885	0.7975	3.210	0.662
0.3529	3.646	1.033	0.8492	3.043	0.503
0.4406	3.651	1.051	0.8764	2.947	0.410
0.5155	3.602	1.013	0.9182	2.791	0.261
0.5864	3.575	0.996	0.9726	2.586	0.063

corresponding experimental $\Delta\eta$ values) satisfied the relation σ_{max} $(\Delta\eta) \leq 2\sigma(\Delta\eta)$. Comparison of experimental $\Delta\eta$ values for the studied systems together with smoothing curves from Eq. (2) are shown in Fig. 1 and adjustable parameters $\eta^{(n)}$ along with standard

deviations $\sigma(\Delta\eta)$ are recorded in Table 3.

It has been observed from Fig. 1 that $\Delta\eta$ is negative at lower mole fraction ($x_1 \leq 0.4$) for all the studied binary mixtures except for formamide (1) + 2-methyl-2-propanol (2), for which $\Delta\eta$ is positive over the entire composition range. Positive value of $\Delta\eta$ indicates the presence of strong specific interaction among unlike molecules. Large positive deviation in the formamide (1) + 2-methyl-2-propanol (2)

Table 3. Adjustable parameters, $\eta^{(n)}$, of Redlich-Kister Eq. (2) along with standard deviation, $\sigma(\Delta\eta)$

System	T/K	$\eta^{(1)}$	$\eta^{(2)}$	$\eta^{(3)}$	$\eta^{(4)}$	$\sigma(\Delta\eta)$
Formamide (1) + 1-propanol (2)	298.15	0.482	1.632	0.034	0.124	0.005
	308.15	0.198	1.065	−0.125	−0.408	0.006
Formamide (1) + 2-propanol (2)	298.15	0.697	1.805	−0.323	0.521	0.025
	308.15	0.218	1.280	0.230	0.331	0.025
Formamide (1) + 1-butanol (2)	298.15	0.668	2.849	−1.051	−0.598	0.018
	308.15	0.346	2.134	−0.855	−0.226	0.019
Formamide (1) + 2-methyl-1-propanol (2)	298.15	1.488	3.934	−0.928	−1.793	0.017
	308.15	0.958	2.168	−0.543	−0.821	0.022
Formamide (1) + 2-methyl-1-propanol (2)	298.15	6.392	−0.761	−1.177	2.934	0.103
	308.15	4.344	−0.240	−0.643	0.314	0.046
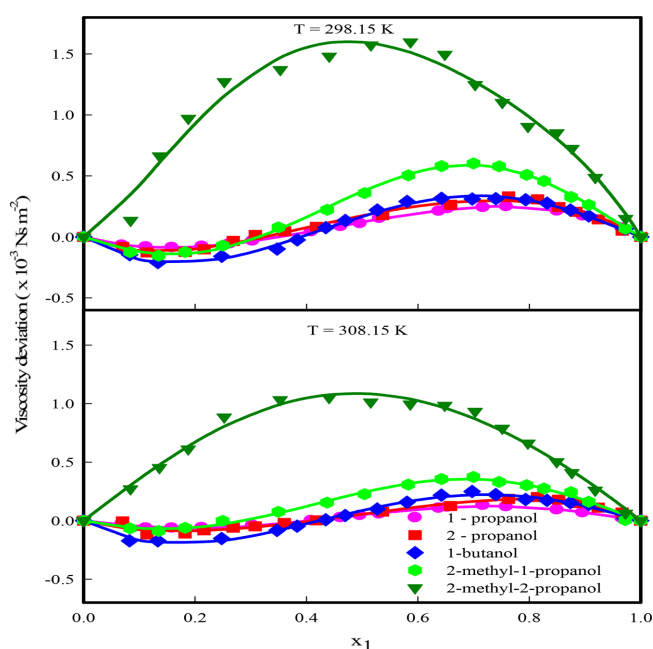
Fig. 1. Viscosity deviation of binary mixture of formamide (1) + alkanol (2). Solid line represents values calculated from Eq. ( ) and symbol represents experimental value.

mixture seems reasonable in view of weak intermolecular hydrogen bonding and van der Waals interactions due to bulkiness of tertiary alcohol in pure 2-methyl-2-propanol; while on mixing 2-methyl-2-propanol to formamide there is an increase in ability of alcoholic oxygen of 2-methyl-2-propanol (due to presence of three methyl group substituent on its carbon atom) to form hydrogen bond with formamide, which leads to strong interaction between unlike molecules. For the systems containing other alkanols, the $\Delta\eta$ value is negative for $x_1 \leq 0.4$. This may be due to breaking of intermolecular hydrogen bonding, and dipole-dipole interaction between monomer and polymer of like molecule. These effects overweigh the intermolecular hydrogen bonding between formamide and butanol due to lesser number of formamide molecules available for hydrogen bonding. As the concentration of formamide increases beyond $x_1 > 0.4$, $\Delta\eta$ becomes positive due to increase in specific interactions between unlike molecules. The sigmoid behavior was also confirmed by Gracia et al. as well as by Gomez Marigliano and Solimo for viscosity

deviation of binary mixtures of formamide + 1-alkanol (C1-C3) [11, 12].

$\Delta\eta$ values at equimolar composition for these systems follow the order: 2-methyl-2-propanol>2-methyl-1-propanol>1-butanol>2-propanol>1-propanol. The higher positive viscosity for 2-methyl-2-propanol over 2-methyl-1-propanol is due to branching of alkyl group and van der Waals interactions due to bulkiness of tertiary alcohol in 2-methyl-2-propanol. Thus, addition of formamide to 2-methyl-2-propanol favors the formation of intermolecular hydrogen bonding between unlike molecules resulting in more viscous solution than pure component [38]. While 1-butanol (due to greater hydrogen bonding and van der Waals dispersion forces in comparison to 2-methyl-1-propanol) has weak intermolecular hydrogen bonding with formamide. So 2-methyl-1-propanol has larger $\Delta\eta$ value than 1-butanol. Same behavior was observed for the isomers of propanol as 2-propanol has higher value of $\Delta\eta$ than 1-propanol. This is also due to presence of two methyl groups as substituent on carbon atom in 2-propanol.

3-1. Graph Theory on Viscosity Deviation

An analysis of excess molar volume, V^E, and excess molar enthalpy, H^E, data of formamide (1) + alkanol (2) mixtures have revealed that formamide exists as dimer in propanol [14] and as trimer in butanol, and the mixture formation involves: (a) a mixing of 1_n with 2_n to establish 1_n-2_n; (b) these 1_n-2_n contacts between formamide and butanol would then cause rupture of intermolecular association in formamide and alkanol to yield monomer; (c) the monomers of formamide then interact with butanol to give 1-2 molecular entity. The change in viscosity due to mixing processes (a), (b) and (c) is then expressed [39-42] by

$$\Delta\eta = \left[\frac{x_1 x_2 V_2}{\sum x_i V_i}\right][\chi_{12} + (2x_1 + x_2)\chi^*] \qquad (4)$$

According to Graph theory [43], if the atoms in a structural formula of a molecule are represented by vertices and bonds joining them by edges, then the resulting graph describes the totality of information contained in that molecule [44-47]. Consequently, if δ_m^v, δ_n^v … represents the degrees of mth and n^{th} vertices of the graph of a molecule, then connectivity parameters of third degree, ξ_i, are

defined [47] by Eq. (5):

$$^3\xi_i = \sum_{m<n<o<p} (\delta_m^v \delta_n^v \delta_o^v \delta_p^v)^{-0.5} \tag{5}$$

where δ_m^v … reflects explicitly the valency of mth vertex in molecular graph of i (i=1 or 2) and is related [47] to maximum valency, Z_m, and number of H-atoms, h_m, attached to m^{th}... vertex by the relation:

$$\delta_m^v = Z_m - h_m \tag{6}$$

The $^3\xi_i$ values for the compound selected for the present mixtures are reported elsewhere [14]. Further, Kier [44] has suggested that the information regarding the effect of branching in the molecules can be obtained by evaluation of $^3\xi_i$ of molecules. It has been found that $^3\xi_i$ for various isomers of heptane follow the order: n-heptane < 3-methyl hexane < 2,3-dimethylpentane, and the sequence for their molar volume is the reverse of this [14]. The $^3\xi_i$ values for the pure compounds are recorded in Table 4.

Thus $V_2/V_1 = (^3\xi_1/^3\xi_2)$, and Eq. (4) then reduces to:

$$\Delta\eta = \left[\frac{x_1 x_2 (^3\xi_1/^3\xi_2)}{x_1 + x_2 (^3\xi_1/^3\xi_2)}\right][\chi_{12} + (2x_1 + x_2)\chi^*] \tag{7}$$

The derivation of Eq. (7) and assumptions made therein were discussed earlier [15,17]. Calculation of $\Delta\eta$ from Eq. (7) requires the knowledge of two unknown interaction parameters χ_{12} and χ^*. These parameters are calculated using η^E data at two compositions (x_1=0.4 and 0.5) for various binary mixtures, and parameters χ_{12} and χ^* along with ($^3\xi_i$) values calculated from Graph theoretical approach [14] are recorded in Table 4. These were subsequently used to evaluate $\Delta\eta$ at other mole fraction (x_1). Such values of $\Delta\eta$ are recorded in Table 5. As the calculated $\Delta\eta$ was found to compare well with their corresponding experimental data (Fig. 2), this lends further support to the assumptions made in the derivation of Eq. (7).

Gibbs free energy of activation is calculated using Eyring viscosity equation

$$G^{*E} = RT\left(\ln(V\eta) - \sum_{i=1}^{2} x_i \ln(V_i \eta_i)\right) \tag{8}$$
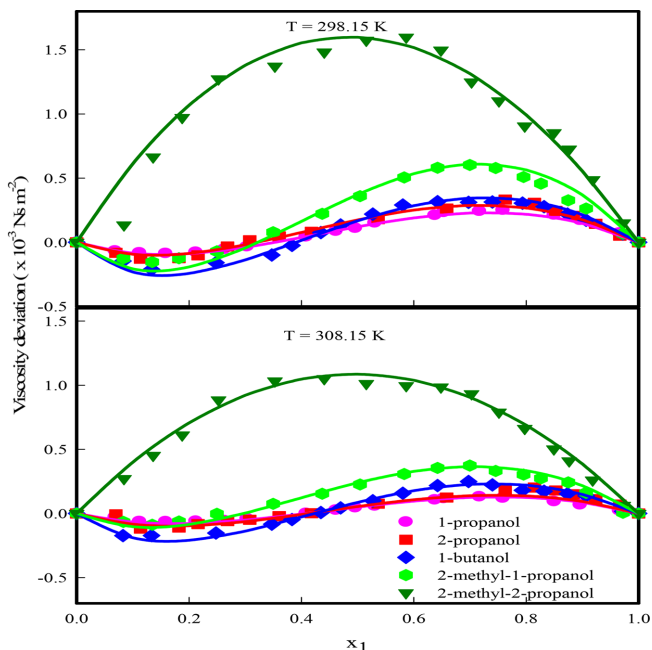

Fig. 2. Comparison of experimental viscosity deviation with the values predicted using graph theory. Solid line represents graph theory and symbol represents experimental value.

where G^{*E} is the free energy of activation, R is the gas constant, T is temperature, η is viscosity of binary mixture, V_i and η_i are the molar volumes and molar viscosities of pure components, respectively. The G^{*E} data were also fitted to Redlich-Kister Eq. (2). Adjustable parameters $G^{*(n)}$ and standard deviations $\sigma(G^{*E})$ were recorded in Table 6 and compared with smoothing curves from Redlich-Kister equation in Fig. 3, and G^{*E} values are tabulated in Table 7.

Excess Gibbs free energy of activation is negative at lower mole fraction for all the studied binary mixtures. Positive value of excess Gibbs free energy of activation indicates the presence of specific interaction among unlike molecules. Negative value of excess Gibbs free energy of activation indicates the presence of weak interaction among unlike molecules and strong interaction among like molecules. Excess Gibbs free energy of activation follows the order: 2-methyl-2-propanol>2-methyl-1-propanol>1-butanol>2-propanol>1-propanol.

Table 4. Values of the various ($^3\xi_i$) parameters, χ_{12} and χ^* involved in Graph theoretical approach

System	Temp.	$^3\xi_1$	$^3\xi_2$	χ_{12}	χ^*
Formamide (1) + 1-propanol (2)	298.15	0.312	0.4082	−5.161	3.811
	308.15	0.312	0.4082	−3.482	2.474
Formamide (1) + 2-propanol (2)	298.15	0.312	0.4714	−6.491	4.910
	308.15	0.312	0.4714	−4.400	3.115
Formamide (1) + 1-butanol (2)	298.15	0.312	0.7020	−13.825	9.940
	308.15	0.312	0.7020	−10.419	7.321
Formamide (1) + 2-methyl-1-propanol (2)	298.15	0.312	0.5000	−14.478	10.943
	308.15	0.312	0.5000	−7.972	6.146
Formamide (1) + 2-methyl-1-propanol (2)	298.15	0.312	0.6123	1.937	5.021
	308.15	0.312	0.6123	0.575	3.906

Table 5. Viscosity deviation, $\Delta\eta(\times10^{-3}$ Ns M^{-2}), values calculated from Redlich Kister Eq. and Graph Theory

x_1	$\Delta\eta$			
	T = 298.15 K		T = 308.15 K	
	Exptl	Graph	Exptl	Graph
Formamide (1) + 1-propanol (2)				
0.1	−0.078	−0.085	−0.047	−0.066
0.2	−0.082	−0.089	−0.064	−0.077
0.3	−0.037	−0.040	−0.047	−0.051
0.4	0.037	0.037	−0.004	−0.004
0.5	0.120	0.120	0.050	0.050
0.6	0.195	0.190	0.097	0.096
0.7	0.241	0.228	0.121	0.125
0.8	0.240	0.218	0.113	0.125
0.9	0.169	0.147	0.069	0.086
Formamide (1) + 2-propanol (2)				
0.1	−0.110	−0.093	−0.075	−0.083
0.2	−0.098	−0.087	−0.086	−0.096
0.3	−0.023	−0.020	−0.059	−0.064
0.4	0.076	0.076	−0.008	−0.008
0.5	0.174	0.174	0.054	0.054
0.6	0.252	0.251	0.117	0.107
0.7	0.294	0.287	0.165	0.139
0.8	0.284	0.267	0.182	0.137
0.9	0.198	0.175	0.140	0.094
Formamide (1) + 1-butanol (2)				
0.1	−0.178	−0.231	−0.161	−0.189
0.2	−0.207	−0.243	−0.191	−0.209
0.3	−0.126	−0.138	−0.132	−0.138
0.4	0.015	0.015	−0.027	−0.027
0.5	0.167	0.167	0.087	0.087
0.6	0.286	0.285	0.177	0.178
0.7	0.336	0.344	0.220	0.227
0.8	0.299	0.325	0.203	0.220
0.9	0.177	0.214	0.125	0.148
Formamide (1) + 2-methyl-1-propanol (2)				
0.1	−0.120	−0.207	−0.063	−0.103
0.2	−0.131	−0.192	−0.058	−0.085
0.3	−0.025	−0.045	0.012	0.003
0.4	0.163	0.163	0.122	0.122
0.5	0.372	0.372	0.240	0.240
0.6	0.534	0.534	0.327	0.328
0.7	0.588	0.609	0.354	0.366
0.8	0.500	0.564	0.302	0.334
0.9	0.281	0.368	0.173	0.216
Formamide (1) + 2-methyl-2-propanol (2)				
0.1	0.427	0.612	0.357	0.400
0.2	0.927	1.068	0.670	0.706
0.3	1.327	1.379	0.907	0.921
0.4	1.554	1.554	1.047	1.047
0.5	1.598	1.598	1.086	1.086
0.6	1.492	1.517	1.026	1.038
0.7	1.278	1.314	0.875	0.905
0.8	0.983	0.992	0.646	0.688
0.9	0.588	0.554	0.351	0.386

Table 6. Value of Gibbs excess molar free energy of activation (J mol^{-1}) of binary mixture of formamide (1) + alkanol (2)

x_1	G^{*E}	x_1	G^{*E}	x_1	G^{*E}
Formamide (1) + 1-propanol (2); T=298.15 K					
0.0684	−36.86	0.4082	235.34	0.7166	372.61
0.1116	−24.71	0.4613	282.49	0.7584	359.71
0.1582	−1.03	0.4958	305.52	0.8496	279.99
0.2120	40.73	0.5306	342.24	0.8958	217.50
0.2624	90.23	0.6374	374.08	0.9658	86.14
0.3030	128.90	0.6532	387.99		
Formamide (1) + 1-propanol (2); T=308.15 K					
0.0684	5.93	0.4082	198.48	0.7166	315.36
0.1116	−20.55	0.4613	237.03	0.7584	286.20
0.1582	8.84	0.4958	262.01	0.8496	208.65
0.2120	45.55	0.5306	276.37	0.8958	152.05
0.2624	76.36	0.6374	314.83	0.9658	52.76
0.3030	114.89	0.6532	321.63		
Formamide (1) + 2-propanol (2); T=298.15 K					
0.0699	−53.76	0.3604	207.54	0.8526	290.27
0.1139	−82.00	0.4178	251.35	0.8837	241.34
0.1821	−38.00	0.5364	340.33	0.9237	167.78
0.216	3.57	0.6585	387.95	0.9666	65.38
0.2685	100.90	0.7627	404.47		
0.308	165.24	0.8147	360.02		
Formamide (1) + 2-propanol (2); T=308.15 K					
0.0699	43.42	0.3604	161.14	0.8526	291.84
0.1139	−109.89	0.4178	203.18	0.8837	242.14
0.1821	−48.42	0.5364	298.75	0.9237	173.76
0.216	14.29	0.6585	328.74	0.9666	97.82
0.2685	74.63	0.7627	351.49		
0.308	105.02	0.8147	339.15		
Formamide (1) + 1-butanol(2); 298.15 K					
0.0824	−86.61	0.4697	330.93	0.7935	407.82
0.1332	−119.52	0.5271	405.25	0.8318	364.19
0.2478	-3.68	0.5804	459.76	0.8737	291.68
0.3473	94.77	0.6422	471.09	0.9066	228.68
0.3833	175.08	0.6975	453.36	0.9719	83.23
0.4346	275.46	0.7399	440.13		
Formamide (1) + 1-butanol(2); 308.15 K					
0.0824	−164.00	0.4697	275.68	0.7935	361.48
0.1332	−127.67	0.5271	341.24	0.8318	331.00
0.2478	−33.76	0.5804	402.78	0.8737	281.35
0.3473	97.19	0.6422	455.50	0.9066	237.88
0.3833	152.05	0.6975	471.42	0.9719	50.53
0.4346	228.66	0.7399	429.70		
Formamide (1) + 2-methyl-1-propanol (2); 298.15 K					
0.0832	−40.90	0.5042	472.45	0.8263	478.54
0.1344	−33.29	0.5829	575.01	0.8748	357.56
0.1821	14.62	0.6422	620.60	0.9066	288.09
0.2497	88.07	0.6997	624.62	0.9722	81.92
0.3496	237.69	0.7457	595.72		
0.4371	365.45	0.7952	528.69		

Experimental values of viscosities of the present binary systems were also correlated using the following relations.

Grunberg and Nissan [48] suggested a logarithmic relation between

Table 6. Continued

x_1	G^{*E}	x_1	G^{*E}	x_1	G^{*E}
0.308	165.24	0.8147	360.02		
Formamide (1) + 2-methyl-1-propanol (2); 308.15 K					
0.0832	−13.02	0.5042	438.21	0.8263	411.26
0.1344	−6.39	0.5829	515.73	0.8748	350.64
0.1821	47.55	0.6422	552.33	0.9066	249.05
0.2497	143.02	0.6997	555.69	0.9722	35.32
0.3496	259.96	0.7457	502.54		
0.4371	360.15	0.7952	454.89		
Formamide (1) + 2-methyl-2-propanol (2); 298.15 K					
0.0843	143.76	0.5155	1123.24	0.8492	724.89
0.1361	463.58	0.5864	1154.39	0.8764	630.58
0.1879	654.49	0.6482	1114.58	0.9182	445.38
0.2524	843.39	0.7026	989.42	0.9726	151.89
0.3529	954.27	0.7515	903.64		
0.4406	1050.75	0.7975	779.60		
Formamide (1) + 2-methyl-2-propanol (2); 308.15 K					
0.0843	308.70	0.5155	1074.80	0.8492	603.93
0.1361	496.48	0.5864	1067.16	0.8764	505.66
0.1879	656.03	0.6482	1055.44	0.9182	337.80
0.2524	897.61	0.7026	1007.36	0.9726	95.33
0.3529	1047.72	0.7515	883.99		
0.4406	1087.62	0.7975	764.46		

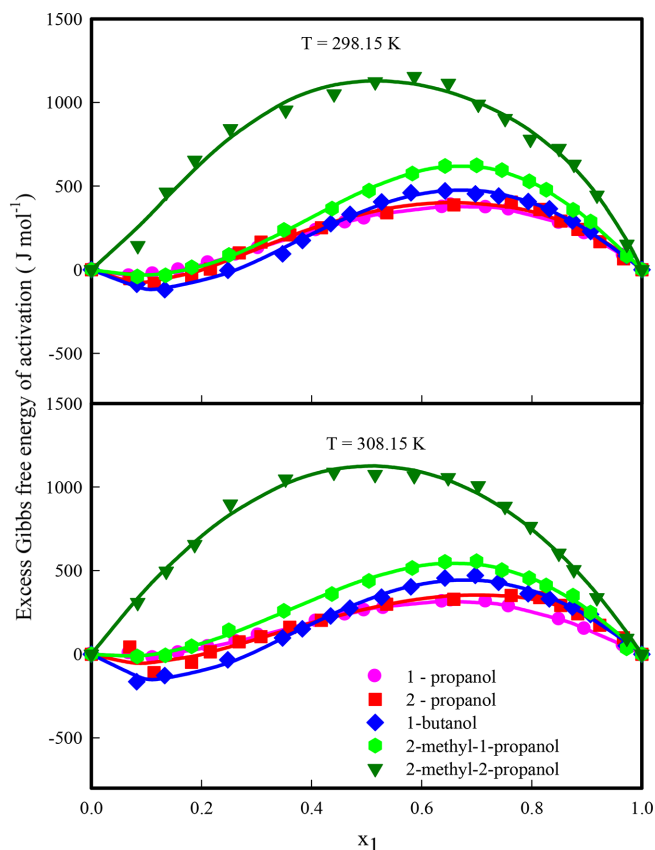**Fig. 3. Gibbs free energy of activation of binary mixture of formamide (1) + alkanol (2).**

the viscosity of a liquid mixture (η) and that of its pure components (η_i),

$$\eta = \exp\left[\sum_{i=1}^{2}(x_i\ln\eta_i) + G_{12}\prod_{i=1}^{2}x_i\right] \tag{9}$$

where G_{12} is a constant that is regarded as a measure of the strength of the molecular interactions between the mixing components and is proportional to the interchange energy.

Tamura and Kurata [49] developed the following one parameter equation to predict the viscosity of binary mixtures.

$$\eta = \left[\sum_{i=1}^{2}x_i\phi_i\eta_i + 2T_{12}\prod_{i=1}^{2}(x_i\phi_i)^{1/2}\right] \tag{10}$$

where ϕ_i is the volume fraction of ith component and T_{12} is an adjustable parameter.

Hind, McLaughlin and Ubbelohde [50] proposed the following

equation to predict the viscosity of binary liquid mixtures

$$\eta = \left[\sum_{i=1}^{2}x_i^2\eta_i + 2H_{12}\prod_{i=1}^{2}x_i\right] \tag{11}$$

where H_{12} is the interaction parameter.

Katti and Chaudhari [51, 52] derived the following equation

$$\ln\eta V_m = \sum_{i=1}^{2}x_i\ln(\eta_iV_i) + x_1x_2(W_{vis}/RT) \tag{12}$$

where W_{vis} is an interaction term and V_i is the molar volume of pure component i. To numerically compare the estimation capability of the various relations, percentage standard deviations were cal-

Table 7. Adjustable parameters, $G^{(n)}$, of Redlich-Kister Eq. along with standard deviation, $\sigma(G^{*E})$ of the viscosity deviation $\Delta\eta$ for the various (1+2) binary mixtures

System	T/K	$G^{(1)}$	$G^{(2)}$	$G^{(3)}$	$G^{(4)}$	$\sigma(G^{*E})$
Formamide (1) + 1-propanol (2)	298.15	1260.9	1447.8	−379.3	344.4	4.18
	308.15	1062.3	1279.1	−419.9	−317.6	7.66
Formamide (1) + 2-propanol (2)	298.15	1361.3	1492.4	−769.2	894.3	22.57
	308.15	1089.0	1468.2	−171.5	704.8	35.46
Formamide (1) + 1-butanol (2)	298.15	1436.3	2531.4	−1131.0	−207.6	16.18
	308.15	1300.8	2489.1	−1238.5	131.8	19.48
Formamide (1) + 2-methyl-1-propanol (2)	298.15	1914.0	2947.5	−607.3	−961.7	10.18
	308.15	1796.2	2182.8	−502.7	−431.6	20.06
Formamide (1) + 2-methyl-2-propanol (2)	298.15	4516.7	285.7	161.97	1901.16	53.13
	308.15	4536.18	163.9	124.91	207.99	35.17

Table 8. Adjustable parameters, G_{12}, T_{12}, H_{12}, W_{vis}/RT of various correlations used to predict viscosity deviation $\Delta\eta$ for the various (1+2) binary mixtures

System	T/K	G_{12}	T_{12}	H_{12}	W_{vis}/RT
Formamide (1) + 1-propanol (2)	298.15	0.2801	3.0651	2.7278	0.4697
	308.15	0.1879	2.3631	2.0938	0.3773
Formamide (1) + 2-propanol (2)	298.15	0.2581	3.1911	2.8587	0.4530
	308.15	0.2272	2.4322	2.1480	0.4001
Formamide (1) + 1-butanol (2)	298.15	0.2306	3.5631	3.1807	0.5768
	308.15	0.1463	2.7545	2.4413	0.4953
Formamide (1) + 2-Methyl-1-propanol (2)	298.15	0.4489	4.2639	4.0076	0.7991
	308.15	0.3671	3.2299	2.9853	0.7146
Formamide (1) + 2-Methyl-2-propanol (2)	298.15	1.4975	6.9545	6.8397	1.8626
	308.15	1.4002	4.9239	4.6706	1.7669

Table 9. Standard deviations of calculated values of viscosity using various correlations_Grunberg-Nissan, Tamura-Kurata, Hind-McLaughlin-Ubbelohde, and Katti-Chaudhari

System	T/K	G-N	T-K	H-Mc-U	W_{vis}/RT
Formamide (1) + 1-propanol (2)	298.15	4.457	4.619	5.040	4.692
	308.15	3.218	3.373	3.556	3.446
Formamide (1) + 2-propanol (2)	298.15	5.516	5.554	6.081	5.723
	308.15	5.015	5.455	5.783	5.375
Formamide (1) + 1-butanol (2)	298.15	6.317	5.907	6.551	6.914
	308.15	6.269	6.036	6.444	6.867
Formamide (1) + 2-Methyl-1-propanol (2)	298.15	8.087	5.982	7.256	7.976
	308.15	5.694	4.415	5.468	6.013
Formamide (1) + 2-Methyl-2-propanol (2)	298.15	3.230	4.400	2.372	3.754
	308.15	1.232	4.763	1.498	1.405

culated using following relation:

$$\sigma(\%) = \left[\frac{\sum\{100(\eta_{exptl.} - \eta_{theo.})/\eta_{exptl.}\}^2}{(n-1)} \right]^{1/2} \quad (13)$$

where n represents the number of experimental data points.

Adjustable parameters, G_{12}, T_{12}, H_{12}, W_{vis}/RT of various correlations used to predict viscosity deviation for the present binary mixtures are given in Table 8. Standard deviations of calculated values of viscosity using various correlations are given in Table 9.

Grunberg-Nissan relation has lowest deviation among the four correlations for formamide + 1-propanol or 2-propanol mixtures; and for mixtures of formamide with 1-butanol or 2-methyl-1-propanol, Tamura-Kurata has lowest deviation. Grunberg-Nissan gives lowest deviation for formamide + 2-methyl-2-propanol mixtures. Forte and Moore [53] and Ramamoorthy [54] reported that for a binary mixture, a positive value of G_{12} indicates the presence of the strongest interactions and a negative value means the presence of weak interaction between components. On the basis of generalization we can conclude that like viscosity deviation, G_{12} values are positive, which shows strong interaction for all studied binary mixtures.

4. Conclusion

Viscosity data were measured at 298.15 K and 308.15 K for formamide + 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol or 2-propanol mixtures. For an equimolar mixture, vis-

cosity deviation follows the sequence: 2-methyl-2-propanol >2-methyl-1-propanol>1-butanol>2-propanol>1-propanol. The viscosity data were correlated by using various correlations like Grunberg-Nissan, Tamura-Kurata, Hind-McLaughlin-Ubbelohde, Katti-Chaudhari relations. Various adjustable parameters G_{12}, T_{12}, H_{12}, W_{vis}/RT of these correlations were used to predict viscosity deviation of binary mixtures. Positive value of G_{12} indicates strong interaction in the studied systems. For binary mixture of formamide with 1-propanol or 2-propanol, Grunberg-Nissan had lowest deviation. Tamura-Kurata showed lowest deviation for binary mixture of formamide with 1-butanol or 2-methyl-1-propanol, whereas for formamide and 2-methyl-2-propanol Grunberg-Nissan gave lowest deviation. The viscosity data were further analyzed in terms of graph theory. Free energy of activation was also calculated from experimental viscosity data employing previously reported excess volume data.

References

1. Iloukhani, H. and Mohammadlou, Z. B., "Densities, Viscosities, and Refractive Indices for Binary and Ternary Mixtures of Formamide (1) + N,N-dimethylacetamide (2) + 2-methyl-1-butanol

(3) at 298.15 K for the Liquid Region and at Ambient Pressure," *Arabian Journal of Chemistry*, In press. http://dx.doi.org/10.1016/j.arabjc.2016.12.004.

2. Almasi, M., "Densities and Viscosities of the Mixtures (formamide + 2-alkanol): Experimental and Theoretical Approaches," *The Journal of Chemical Thermodynamics*, **69**, 101-106(2014).

3. Almasi, M., "Densities and Viscosities of the Mixtures (formamide+2-alkanol): Experimental and Theoretical Approaches," *The Journal of Chemical Thermodynamics*, **69**, 106(2014).

4. Mohammad, A. A., Alkhaldi, K. H. A. E., Altuwaim, M. S. and Al-Jimaz, A. S., "Viscosity and Surface Tension of Binary Systems of N,N-dimethylformamide with Alkan-1-ols at Different temperatures," *The Journal of Chemical Thermodynamics*, **56**, 113(2013).

5. Kondaiah, M., Sreekanth, K., Sravana Kumar D. and Krishna Rao D., "Volumetric and Viscometric Properties of Propanoic acid in Equimolar Mixtures of N,N-dimethyl formamide + alkanols at T/K = 303.15, 313.15, and 323.15," *J. Solution Chem*, **42**, 494-515(2013).

6. Habibullah, M., Rahman, I. M. M., Uddin, M. A., Anowar, M., Alam, M. and Iwakabe, K., et al., "Densities, Viscosities, and Speeds of Sound of Binary Mixtures of Heptan-1-ol with 1,4-Dioxane at Temperatures from (298.15 to 323.15) K and Atmospheric Pressure," *Journal of Chemical & Engineering Data*, **58**, 2887-2897(2013).

7. Rajagopal, K., Chenthilnath, S. and Nain, A. K., "Volumetric and Viscometric Studies in Binary Liquid Mixtures of 2-methyl-2-propanol with Some ketones at Different Temperatures," *J. Solution Chem*, **41**, 1401-1411(2012).

8. Awasthi, A. and Awasthi, A., "Intermolecular Interactions in Formamide + 2-alkoxyethanols: Viscometric Study," *Thermochimica Acta*, **537**, 57-64(2012).

9. Marcus, Y., "Introduction to Liquid State Chemistry," New York, *Wiley Interscience*(1977).

10. Nain, A. K., "Molecular Interactions in Binary Mixtures of Formamide with 1-butanol, 2-butanol, 1,3-butanediol and 1,4-butanediol at Different Temperatures, An Ultrasonic and Viscometric Study," *Fluid Phase Equilibria*, **265**, 46-56(2008).

11. Garcia, B., Alcalde, R., Leal, J. M. and Matos, J. S., "Formamide-(C1-C5) Alkan-1-ols Solvent Systems," *J. of the Chemical Society Faraday Transactions*, **92**, 3347-3352(1996).

12. Gomez Marigliano, A. C. and Solimo, H., "Density, Viscosity, Excess Molar Volume, Viscosity Deviation, and Their Correlations for Formamide + Three Alkan-1-ols Binary Systems," *J. of Chemical & Engineering Data*, **47**, 796-800(2002).

13. Rani, M. and Maken, S., "Erratum to: Topological Studies of Molecular Interactions of Formamide with Propanol and Butanol at 298.15 K," *J. of Industrial and Engineering Chemistry*, **19**, 1760 (2013).

14. Rani, M. and Maken, S., "Topological Studies of Molecular Interactions of Formamide with Propanol and Butanol at 298.15 K," *J. of Industrial and Engineering Chemistry*, **18**, 1694-1704 (2012).

15. Rani, M., Agarwal, S., Lahot, P. and Maken, S., "Excess Molar Enthalpies of Binary Mixtures of Formamide with Butanol at 298.15 K Application of Prigogine-Flory-Patterson Theory and Treszczanowicz-Benson Association Model," *J. of Industrial and*

Engineering Chemistry, **19**, 1715-1720(2013).

16. Rani, M. and Maken, S., "Thermodynamics of Molecular Interactions in Binary Mixtures Containing Associated Liquids," *Korean J Chem Eng.*, **30**, 1636-1643(2013).

17. Rani, M. and Maken, S., "Excess Molar Enthalpies and Excess Molar Volumes of Formamide+1-propanol or 2-propanol and Thermodynamic Modeling by Prigogine-Flory-Patterson Theory and Treszczanowicz-Benson Association Model," *Thermochimica Acta*, **559**, 98-106(2013).

18. Rani, M., Gahlyan, S., Om, H., Verma, N. and Maken, S., "Ultrasonic Studies of Molecular Interactions in Binary Mixtures of Formamide with Some Isomers of Butanol at 298.15 K and 308.15 K," *J. of Molecular Liquids*, **194**, 100-109(2014).

19. Rani, M., Gahlyan, S., Gaur, A. and Maken, S., "Ultrasonic Study on Molecular Interactions in Binary Mixtures of Formamide with 1-propanol or 2-propanol," *Chinese J. of Chemical Engineering*, **23**, 689-698(2015).

20. Riddick, J. A., Bunger, W. B. and Sakano, T. K., "Organic Solvents," *Physical Properties and Methods of Purification*, fourth ed. New York, Wiley(1986).

21. Cases, A. M., Gómez Marigliano, A. C., Bonatti, C. M. and Sólimo, H. N., "Density, Viscosity, and Refractive Index of Formamide, Three Carboxylic Acids, and Formamide + carboxylic Acid Binary Mixtures," *J. of Chemical & Engineering Data*, **46**, 712-715(2001).

22. Nain, A. K., "Molecular Interactions in Binary Mixtures of Formamide with 1-butanol, 2-butanol, 1,3-butanediol and 1,4-Butanediol at Different Temperatures: An Ultrasonic and Viscometric Study," *Fluid Phase Equilibria*, **265**, 46-56(2008).

23. Gomez Marigliano, A. C. and Solimo, H. N., "Density, Viscosity, Excess Molar Volume, Viscosity Deviation, and Their Correlations for Formamide + Three Alkan-1-ols Binary Systems," *J. Chem Eng Data*, **47**, 796-800(2002).

24. Roy, M. N., Sarkar, B. K. and Chanda, R., "Viscosity, Density, and Speed of Sound for the Binary Mixtures of Formamide with 2-methoxyethanol, Acetophenone, Acetonitrile, 1,2-dimethoxyethane, and Dimethylsulfoxide at Different Temperatures," *J. of Chemical & Engineering Data*, **52**, 1630-1637(2007).

25. Shukla, R. K., Kumar, A., Awasthi, N., Srivastava, U. and Gangwar, V. S., "Density, Viscosity and Refractive Index of Binary Liquid Mixtures at 293.15, 298.15, 303.15, 308.15 and 313.15 K," *Experimental Thermal and Fluid Science*, **37**, 1-11(2012).

26. Zarei, H. A., Asadi, S. and Iloukhani, H., "Temperature Dependence of the Volumetric Properties of Binary Mixtures of (1-propanol, 2-propanol and 1,2-propanediol) at Ambient Pressure (81.5 kPa)," *J. of Molecular Liquids*, **141**, 25-30(2008).

27. Jimenez, E., Cabanas, M., Segade, L., Garcia-Garabal, S. and Casas, H., "Excess Volume, Changes of Refractive Index and Surface Tension of Binary 1,2-ethanediol + 1-propanol or 1-butanol Mixtures at Several Temperatures," *Fluid Phase Equilibria*, **180**, 151-164(2001).

28. Nain, A. K., "Ultrasonic and Viscometric Studies of Molecular Interactions in Binary Mixtures of Formamide with Ethanol, 1-propanol, 1,2-ethanediol and 1,2-propanediol at Different Temperatures," *J. of Molecular Liquids*, **140**, 108-116(2008).

29. Aralaguppi, M. I. and Baragi, J. G, "Physico-chemical and Excess Properties of the Binary Mixtures of Methylcyclohexane + ethanol,

+ propan-1-ol, + propan-2-ol, + butan-1-ol, + 2-methyl-1-propa-nol, or 3-methyl-1-butanol at T=(298.15, 303.15, and 308.15) K," *J. Chem. Thermodyn*, **38**, 434-42(2006).

30. Bhardwaj, U., Maken, S. and Singh, K. C., "Excess Volumes of 1-Butanol, 2-Butanol, 2-Methylpropan-1-ol, and 2-Methylpropan-2-ol with Xylenes at 308.15 K," *J. Chem. Eng. Data.*, **41**, 1043-1045(1996).

31. Riddick, J. A., Bunger, W. B. and Sakano, T. K., "Organic Solvents Physical Properties and Methods of Purification," Wiley, New York, 1(1986).

32. Anson, A., Garriga, R., Martinez, S., Perez, P. and Gracia, M., "Densities and Viscosities of Binary Mixtures of 1-Chlorobutane with Butanol Isomers at Several Temperatures," *J. Chem. Eng. Data*, **50**, 677-682(2005).

33. Vittal Prasad, T. E., Sravani, Y., Sri Ranjita, V. and Prasad, D. H. L., "Excess Gibbss' Energies of Selected Binary Mixtures Formed by N,N-dimethyl Formamide at 95.5 kPa," *Fluid Phase Equilibria*, **249**, 49-54(2006).

34. Dubey, G. P., Sharma, M. and Oswal, S., "Volumetric, Transport, and Acoustic Properties of Binary Mixtures of 2-methyl-1-propanol with Hexadecane and Squalane at T=(298.15, 303.15, and 308.15)K, Experimental Results, Correlation, and Prediction by the ERAS Model," *The J. of Chemical Thermodynamics*, **41**, 849-858(2009).

35. Rajagopal, K. and Chenthilnath, S., "Excess Thermodynamic Studies in Binary Liquid Mixtures of 2-methyl-2-propanol with Ketones at 298.15, 303.15 and 308.15 K," *J. Mol. Liq.*, **155**, 20-28(2010).

36. Kijevcanin, M. L., Radovic, I. R., Djordjevic, B. D., Tasic, A. Z. and Serbanovic, S. P., "Experimental Determination and Modeling of Densities and Refractive Indices of the Binary Systems Alcohol + dicyclohexylamine at T=(288.15-323.15) K," *Thermochimica Acta*, **525**, 114-128(2011).

37. Redlich, O. and Kister, A. T., "Algebraic Representation of Thermodynamic Properties and the Classification of Solutions," *Industrial & Engineering Chemistry* **40**, 345-348(1948).

38. Nain, A. K., "Ultrasonic and Viscometric Study of Molecular Interactions in Binary Mixtures of Aniline with 1-propanol, 2-propanol, 2-methyl-1-propanol, and 2-methyl-2-propanol at Different Temperatures," *Fluid Phase Equilibria* **259**, 218-227(2007).

39. Maken, S., Deshwal, B. R., Chadha, R., Anu, Singh, K. C. and Kim, H., "Topological and Thermodynamic Investigations of Molecular Interactions in Binary Mixtures; Molar Excess Volumes

and Molar Excess Enthalpies," *Fluid Phase Equilibria* **235**, 42-49(2005).

40. Huggins, M. L., "The Thermodynamic Properties of Liquids, Including Solutions. I. Intermolecular Energies in Monotonic Liquids and Their Mixtures," *J. Phys. Chem.*, **74**, 371-378(1970).

41. Huggins, M. L., "The Thermodynamic Properties of Liquids, Including Solutions: Part 2. Polymer Solutions Considered as Ditonic Systems," *Polymer* **12**, 389-99(1971).

42. Singh, P. P. and Maken, S., "Topological Aspects of Molecular Interactions in Liquid Mixtures of Electrolytes," *Pure Appl Chem.*, **66**, 449-454(1994).

43. Harary, F., *Graph theory Reading*, M A Addison Wesley (1969).

44. Kier, L. B., *Physical chemical properties of drugs*. In: S. H. Yalkowaski AAS, S.C. Valvani (Eds.) editor. New York, Bessel, Marcel Dekker Inc., p. 295-297(1980).

45. Balaban, A. T., *Chemical Applications of Graph Theory*. London: Academic Press(1976).

46. Rouvray, D. H., "Graph Theory in Chemistry," *Royal Institute of Chemistry, Reviews*, **4**, 173-195(1971).

47. Kier, L. B. and Hall, L. H., *Molecular Connectivity in Chemistry and Drug Research*, New York: Academic Press(1976).

48. Grunberg, L. and Nissan, A. H., "Mixture Law for Viscosity," *Nature*, **164**, 799-800(1949).

49. Tamura, M. and Kurata, M., "On the Viscosity of Binary Mixture of Liquids," *Bulletin of the Chemical Society of Japan*, **25**, 32-38 (1952).

50. Hind, R. K. and McLaughlin, E., "Ubbelohde AR. Structure and Viscosity of Liquids. Camphor + Pyrene Mixtures," *Transactions of the Faraday Society*, **56**, 328-30(1960).

51. Katti, P. K. and Chaudhri, M. M., "Viscosities of Binary Mixtures of Benzyl Acetate with Dioxane, Aniline, and m-cresol," *J. of Chemical & Engineering Data*, **9**, 442-443(1964).

52. Katti, P. K., Chaudhri, M. M. and Prakash, O., "Viscosities of Binary Mixtures Involving Benzene, Carbon Tetrachloride, and Cyclohexane," *J. of Chemical & Engineering Data* **11**, 593-594 (1966).

53. Fort, R. J. and Moore, W. R., "Viscosities of Binary Liquid Mixtures," *Transactions of the Faraday Society*, **62**, 1112-1119(1966).

54. Ramamoorthy, K., "Excess Free-energy of Mixing (ΔF_m) and Strength of Interaction in Binary Liquid Mixtures from Viscosity Studies," *Indian J. of Pure and Applied Physsics*, **11**, 554-555 (1973).