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COMPARATIVE ANALYSIS OF MOLECULAR INTERACTIONS BETWEEN DRUGS OF AQUEOUS PROPYLENE GLYCOL WITH CERTAIN ALCOHOLS AT 308.15K: AN INSIGHT FROM DENSITY AND VISCOSITY STUDIES

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ABSTRACT: Density, ρ and viscosity, η of drug of aqueous solution of propylene glycol (PG) (3 m and 7 m) with *tert*-butanol/2-propanol have been measured over the entire composition range of alkanols at 308.15 K. From this experimental data, excess molar volume, V_m^E, deviation in viscosity, $\Delta\eta$, and excess Gibbs free energy of activation of viscous flow, ΔG^{*E} have been determined. Positive values of $\Delta\eta$, ΔG^{*E} and negative values of V_m^E have been observed over the entire composition range in the mixtures studied. The observed positive and negative values of various excess/deviation properties have been attributed to the existence of strong interactions such as geometrical fitting of smaller molecules into the voids created by larger molecules in the liquid mixtures. The excess/deviation properties have been fitted to Redlich–Kister type polynomial and the corresponding standard deviations have been evaluated. The computed partial and excess partial molar volumes data also support the V_m^E results. The experimental viscosity data of the liquid mixtures investigated have been correlated with viscosity models such as Grunberg and Nissan; Hind, McLaughlin and Ubbelohde; Katti and Chaudhari.

INTRODUCTION: Studies on the viscosity and density of drugs of binary mixtures along with other thermodynamic properties are being increasingly used as tools for the investigation of the properties of pure components and the nature of intermolecular interactions between liquid mixture constituents [1].

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Thermodynamic properties of aqueous solutions play a very important role in the fields of chemistry and chemical engineering, in the synthesis of pharmaceuticals, waste water treatment, pollution control, design calculation, simulation processes, lacquers, resins, polymers, oxygenated fuels, paint, heat transfer, mass transfer, fluid flow [2, 3, 4]. The practical studies of binary mixtures reveal the importance of molecular interactions (hydrogen bonding, charge-transfer complexes, dipole-dipole, dipole-induced dipole, interstitial accommodate chain alignment) on the physical properties of these mixtures [5]. Aqueous solutions of glycol and alkanol have attracted a good deal of attention of the scientific community for decades for their unusual

non-ideal behaviour, especially in the low concentration range. Besides, their study gives important information about the nature of interactions between non-polar and polar groups with water and how these interactions affect the balance between hydrophobic and hydrophilic effects [6-9]. Water, glycol molecules and alcohols have strong hydrogen bonds [10].

Propylene glycol used as medical lubricant, moisturizer in medicines, tobacco products and cosmetics. Alkanol are interesting simple examples of biological and industrial important amphiphilic materials. 2-propanol is used a solvent for coatings for pharmaceutical applications and *tert*-butanol is primarily used as a solvent in pharmaceutical, as an intermediate in chemical synthesis and as a fuel.

Keeping in view of the importance of aqueous solutions, measurements of density and viscosity of drugs of aqueous propylene glycol liquid solutions (3m and 7m) with *tert*-butanol /2-propanol have been reported over the entire composition range of alkanols at 308.15 K. In the present study the data have been analysed and discussed in detail to know the nature of molecular interactions between the molecules of the components of the liquid solutions.

Experimental Details:

High purity and AR grade components of propylene glycol (PG), *tert*-butanol /2-propanol obtained from SD fine chemicals. All of the chemicals are further purified by standard methods [11, 12]. Molalities of 3m and 7m are prepared with propylene glycol using triply distilled water. These solutions in turn are used to prepare liquid mixtures with 2-propanol and *tert*-butanol so that entire composition range is covered (i.e. 0 to 100% alkanol). All the mixtures are prepared by weight and kept in airtight bottles. The weighing samples are measured using Metler Toledo (Swiss make) AB135 – S/FACT Digital balance with an accuracy ±0.01mg.

Densities of pure liquids and their mixtures have been determined by using a 5 cm^3 two stem double-walled Parker & Parker type pyknometer [13]. In this method the mass of a given volume of liquid sample is determined accurately. The volume of the pyknometer cell is calibrated using triply distilled water as it is not practically possible to determine this volume exactly from the geometry of the pyknometer cell. The estimated accuracy in this method is 3 in 10^5 parts. In the present investigation an Ostwald viscometer is used to measure the viscosity of the liquid mixtures through calibration of the same by the method described by Subramanyam Naidu and Ravindra Prasad [14]. In this method water is taken into the viscometer without air bubbles and is immersed into the constant temperature bath for a period of 30 min so that the water inside the viscometer attains the temperature of the bath.

The time of flow of given volume of water is measured using an electronic digital stopwatch with an accuracy of ±0.01 s. This procedure is repeated thrice and an average flow of time (t_o) for water is noted. The same procedure is also adopted for experimental mixtures under investigation and their average time of flow (t) is recorded.

The coefficient of viscosity of experimental mixture has been calculated using

$$\eta/\eta_o = (\rho t)/(\rho_o t_o) \qquad (1)$$

where ρ, ρ_o, t, t_o and η, η_o refer to density, flow of time and viscosity of liquid mixture and water respectively. The accuracy in the viscosity measurement is ± 0.2%.

In the present study, the constant temperature water bath (digital electronic) supplied by Concord Instruments Co. Ltd., Chennai (RAAGA type) has been used. This instrument can maintain an accuracy of temperature to ±0.01 K. The experimentally determined values of ρ and η at 308.15 K of all the pure liquids have been compared with the literature data [15-19] in **Table 1**.

Theory and Calculation:

The experimental values of density have been used to calculate the molar volume with the following equation

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho} \qquad (2)$$

Where M_1, M_2 are the molar masses of the pure components 1 (2-propanol/*tert*-butanol), 2 (aqueous PG) respectively and ρ is the density of the mixture.

In order to understand the nature of the molecular interactions between the component molecules of the liquid mixtures, it is of interest to discuss the same in terms of excess parameters rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their concentrations and it has been interpreted to arise from the presence of strong or weak interactions. The deviation/excess parameters are computed with the following equations.

Excess molar volume

$$V_m^E = V_m - (x_1 V_1^* + x_2 V_2^*) \qquad (3)$$

Deviation in viscosity

$$\Delta\eta = \eta - (x_1\eta_1^* + x_2\eta_2^*) \qquad (4)$$

Excess Gibbs free energy of activation for viscous flow

$$\Delta G^{*E} = RT\left[\ln(\eta V) - x_1 \ln(\eta_1^* V_1^*) - x_2 \ln(\eta_2^* V_2^*)\right] (5)$$

where η_1^*, V_1^* are the viscosities, molar volumes of pure component 1 (*tert*-butanol/2-propanol) and η_2^*, V_2^* are the viscosities, molar volumes of component 2 (aqueous PG) respectively and x_1 represents the mole fraction of the component '1' in the mixture. The experimentally measured values of ρ, η and evaluated values of V_m, V_m^E, $\Delta\eta$ and ΔG^{*E} for all the systems under study have been presented along with mole fraction x_1 in **Table 2.**

TABLE 1: COMPARISON OF EXPERIMENTAL VALUES OF DENSITY ρ, AND VISCOSITY η, OF PURE LIQUIDS WITH THE LITERATURE VALUES CONCERNED AT 308.15 K

Liquid	ρ /kg.m^{-3}		η / 10^{-3} N.s .m^{-2}	
	Present work	Literature	Present work	Literature
Water	994.06	994.10[15]	0.719	0.721[15]
2-propanol	773.58	772.417[16]	1.546	1.542 [17]
***tert*-butanol**	768.37	771.1[18]	2.697	2.6959[18]
Propylene Glycol	1026.15	1026.17 [19]	25.334	25.336 [19]

TABLE 2: EXPERIMENTAL VALUES OF DENSITIES, ρ, VISCOSITIES, η, MOLAR VOLUMES, V_m, DEVIATION IN VISCOSITIES, $\Delta\eta$, EXCESS MOLAR VOLUMES, V_m^E AND EXCESS GIBB'S FREE ENERGY OF ACTIVATION OF VISCOUS FLOW, ΔG^{*E}, AS A FUNCTION OF THE MOLE FRACTION OF *TERT*-BUTANOL OR 2-PROPANOL (x_1), FOR ALL THE SYSTEMS AT T = 308.15K

x_1	ρ /	η/10^{-3}	V_m/10^{-5}	$\Delta\eta$ / 10^{-3}	V_m^E /10^{-5}	ΔG^{*E} /
kJ	kg.m^{-3}	N.s.m^{-2}	m^3.mol^{-1}	N.s.m^{-2}	m^3.mol^{-1}	.mol^{-1}
aqueous PG (3 m)+*tert*-butanol						
0.0000	1019.80	1.548	3.0241	0.000	0.0000	0.0000
0.1399	968.29	2.775	3.8103	1.067	-0.1403	1.4733
0.2958	918.92	3.449	4.7493	1.562	-0.2337	1.9123
0.3128	913.99	3.486	4.8554	1.579	-0.2402	1.9195
0.4231	884.05	3.584	5.5598	1.550	-0.2662	1.8521
0.5911	844.31	3.387	6.6827	1.160	-0.2558	1.4421
0.6232	837.41	3.320	6.9037	1.056	-0.2474	1.3323
0.7887	804.76	2.940	8.0739	0.486	-0.1732	0.6941
0.8523	793.29	2.816	8.5376	0.289	-0.1307	0.4470
0.9254	780.69	2.720	9.0806	0.109	-0.0718	0.1951
1.0000	768.37	2.697	9.6464	0.000	0.0000	0.0000
aqueous PG (7 m)+*tert*-butanol						
0.0000	1029.70	3.829	4.6586	0.000	0.0000	0.0000
0.1360	972.07	4.421	5.3007	0.746	-0.0362	0.5677
0.2012	947.02	4.552	5.6209	0.951	-0.0412	0.7301
0.3223	906.51	4.583	6.2215	1.119	-0.0447	0.8902
0.4343	875.58	4.414	6.7757	1.077	-0.0491	0.9046

0.5838	840.60	3.993	7.5228	0.826	-0.0477	0.7712
0.6128	834.34	3.896	7.6701	0.761	-0.0450	0.7293
0.7941	800.70	3.255	8.5844	0.326	-0.0350	0.3826
0.8613	789.25	3.036	8.9316	0.182	-0.0230	0.2403
0.9012	783.07	2.918	9.1353	0.110	-0.0183	0.1582
1.0000	768.37	2.697	9.6464	0.000	0.0000	0.0000
aqueous PG (3 m) + 2-propanol						
0.0000	1019.80	1.548	3.0241	0.000	0.0000	0.0000
0.1669	960.63	2.074	3.7188	0.735	-0.0972	1.5810
0.2561	931.98	2.224	4.1131	1.069	-0.1262	2.2616
0.3691	898.65	2.304	4.6336	1.371	-0.1419	2.9440
0.4212	884.40	2.305	4.8806	1.455	-0.1421	3.1900
0.5911	842.84	2.185	5.7111	1.451	-0.1178	3.6653
0.6383	832.63	2.124	5.9471	1.374	-0.1058	3.6950
0.7519	810.42	1.948	6.5202	1.069	-0.0717	3.5292
0.8434	794.97	1.784	6.9837	0.718	-0.0423	3.0390
0.9124	784.76	1.657	7.3318	0.412	-0.0216	2.2851
1.0000	773.58	1.546	7.7691	0.000	0.0000	0.0000
aqueous PG (7 m) + 2-propanol						
0.0000	1029.70	3.829	4.6586	0.000	0.0000	0.0000
0.1616	973.40	4.000	5.1295	0.592	-0.0318	1.1060
0.2561	943.14	4.038	5.4156	0.726	-0.0396	1.6040
0.3688	909.62	4.006	5.7654	0.787	-0.0404	2.1050
0.4157	896.49	3.964	5.9133	0.811	-0.0383	2.3030
0.5838	853.43	3.654	6.4506	0.738	-0.0239	2.8010
0.6322	842.18	3.512	6.6065	0.718	-0.0186	2.9130
0.7519	816.59	3.049	6.9913	0.661	-0.0061	3.0890
0.8212	803.21	2.701	7.2124	0.598	-0.0005	3.0610
0.9021	789.28	2.213	7.4641	0.343	-0.0005	2.4540
1.0000	773.58	1.546	7.7691	0.000	0.0000	0.0000

The excess/deviation properties have been fitted to a Redlich-Kister type polynomial equation [20].

$$Y^E = x_1 x_2 \sum_{i=o}^{j} A_i (x_2 - x_1)^i \qquad (6)$$

where Y^E = V_m^E, Δη , ΔG^{*E} and x_1 is the mole fraction of the solute (2-propanol/*tert*-butanol) and A_i are the adjustable parameters of the function; and are determined using the least square method. In the present investigation '*i*' values taken from 0 to 4. The corresponding standard deviations $\sigma(Y^E)$ were calculated using the expression.

$$\sigma(Y^E) = \left[\frac{\Sigma \left(Y^E_{exp} - Y^E_{cal} \right)^2}{(m-n)} \right]^{1/2} \qquad (7)$$

Where 'm' is the total number of experimental points and 'n' is the number of coefficients in equation (6). The calculated values of the coefficients A_i along with the standard deviations (σ) are given in **Table 3**.

TABLE 3: COEFFICIENTS A_i OF REDLICH-KISTER TYPE POLYNOMIAL Eq. (6) AND THE CORRESPONDING STANDARD DEVIATION *σ*, OF ALL THE SYSTEMS AT 308.15 K

	A_0	A_1	A_2	A_3	A_4	σ
aqueous PG (3 m)+*tert*-butanol						
V_m^E **/10^{-5}m^3.mol^{-1}**	-1.0422	-0.0972	-0.0543	0.0169	0.0022	0.0019
Δη/10^{-3} N.s.m^{-2}	5.646	4.614	-0.195	0.002	-0.002	0.013
ΔG^{*E} / kJ.mol^{-1}	6.8008	4.7580	1.3353	2.5570	1.3387	14.9155
aqueous PG (7 m)+*tert*-butanol						
V_m^E **/10^{-5} m^3.mol^{-1}**	-0.1926	0.0048	-0.0824	-0.1406	-0.0649	0.0013
Δη/10^{-3} N.s.m^{-2}	3.951	3.289	0.008	0.068	-0.106	0.001

ΔG^{*E} / kJ.mol^{-1}	3.4604	1.6829	-0.0427	0.5045	-0.0983	0.5091
aqueous PG (3 m)+2-propanol						
V_m^E /10^{-5}m^3.mol^{-1}	-0.5402	-0.2799	0.0609	0.0025	-0.0023	0.0004
Δη /10^{-3} N.s.m^{-2}	6.025	-0.133	-1.431	-0.057	-0.091	0.001
ΔG^{*E}/ kJ.mol^{-1}	13.9898	-5.5734	2.8795	-6.3129	9.0351	0.0222
aqueous PG (7 m)+2-propanol						
V_m^E /10^{-5} m^3.mol^{-1}	-0.1309	0.1821	0.0766	0.0262	-0.1209	0.0006
Δη/10^{-3} N.s.m^{-2}	3.048	0.534	3.444	-0.596	-2.467	0.022
ΔG^{*E} /kJ.mol^{-1}	1.0309	-5.8120	6.3190	-9.6046	9.0374 1	1.7622

RESULTS AND DISCUSSION: Water and alcohol mixtures show unique maxima and minima in their thermodynamic and viscometric properties at low alcohol concentrations [21, 22]. The variation of viscosity in the mixtures of aqueous PG (3m, 7m) with *tert*-butanol/2-propanol is represented in **Fig. 1** and **2** respectively. The viscosity of the systems increases with concentration of alcohols and attain a maximum value. Further increase in alkanol concentration resulted in decrease of viscosity of the systems.

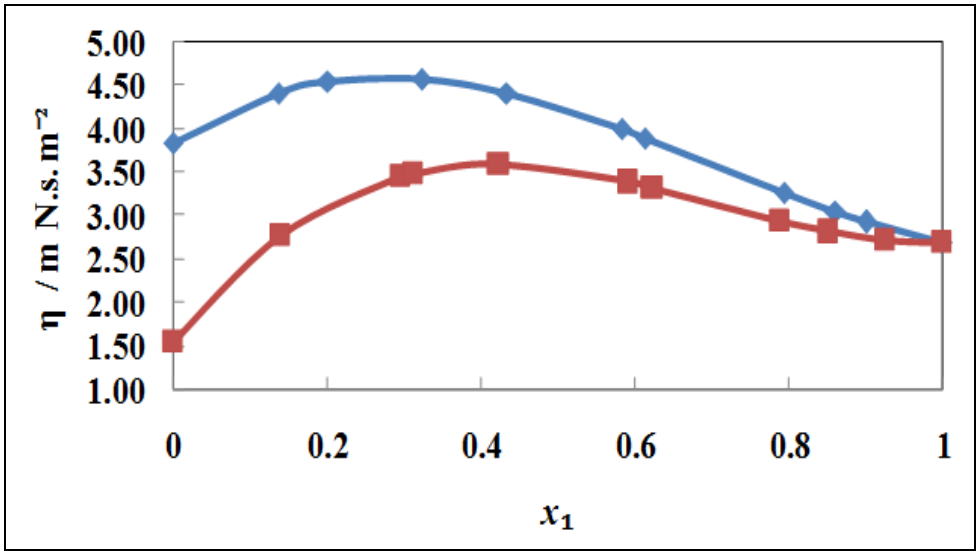


FIG.1: PLOTS OF VISCOSITY (*η*) AGAINST MOLE FRACTION OF *TERT*-BUTANOL (x_1) FOR BINARY SYSTEM OF TERT-BUTANOL WITH AQUEOUS PG OF 3m (■) AND 7m (♦).

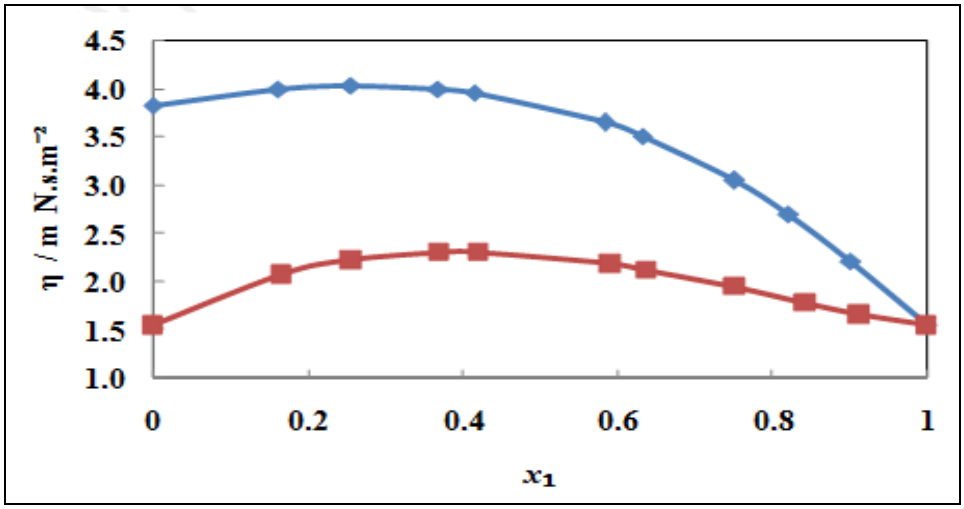
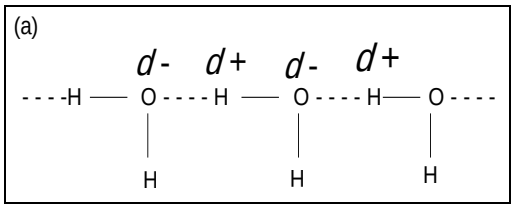


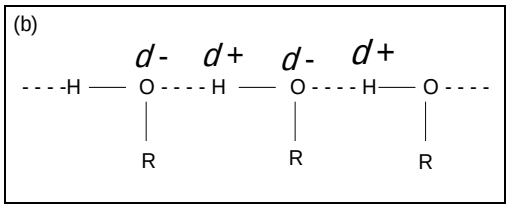
FIG. 2: PLOTS OF VISCOSITY (*η*) AGAINST MOLE FRACTION OF 2-PROPANOL (x_1) FOR BINARY SYSTEM OF 2-PROPANOL WITH AQUEOUS PG OF 3m (■) AND 7m (♦).

In order to explain the observed peculiar behaviour of η in the aqueous PG + alkanol (*tert*-butanol/2-propanol), we should consider the chemical and physical interaction between water and PG (i.e., aqueous PG) and then between aqueous PG and alkanol. Water, unlike many other liquids, exhibits anomalies in its physical properties as a function of temperature. This peculiarity has been attributed to its hydrogen bonded structure. When a solute either electrolyte or non-electrolyte or both is added to water. It affects the structural equilibrium existing between hydrogen bonded clusters and monomers. The possible structural changes are (a) stabilization of hydrogen bonded clusters against thermal collapse, (b) promotions of long range order, (c) formation of clathrate hydrate like structures and (d) collapse of the hydrogen bonded clusters.

The glycol is a dihydric alcohol having two hydroxyl groups. PG and water, both are associated liquids. They may be associated through H-bonding.

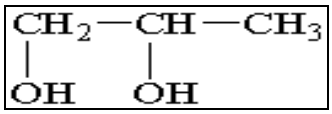


Water molecule



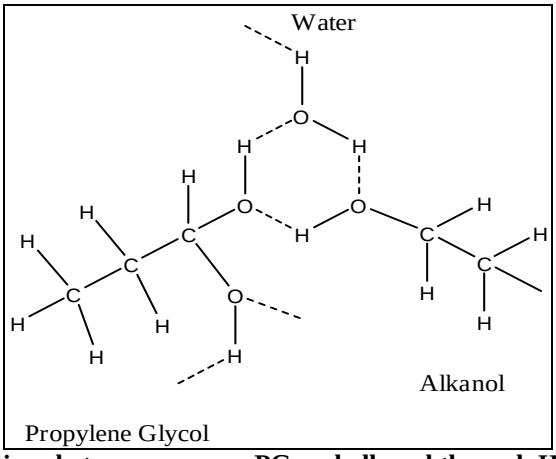
Alkanol molecule

(c)



Propylene Glycol

When PG is added to water, association between these molecules takes place through Hydrogen bonding (O-H…O) forming aqueous PG. This leads to the increase of open structures in the solution since it acts as a structure maker. Whenever alkanol (*tert*-butanol/2-propanol) is added to aqueous PG former gets completely soluble because of the oxygen atom of the hydroxyl group in it by forming hydrogen bonds with aqueous PG molecules.



Probable interactions between aqueous PG and alkanol through H-bonding

The observed peak in the variation of viscosity vs mole fraction (x_1) of alkanol (*tert*-butanol/2-propanol) (**Fig.1** and **2**) is an indication of strong interactions involving dipole-dipole associations, acceptor-donor type interactions and other complex formation favouring interactions between component molecules. It is evident that alkanol's are polar and they can donate and accept protons[23]. Hence, dipole-dipole interactions and acceptor-donor type interactions are possible in addition to

the hydrogen bonding interactions in the present systems.

Viscosity of a system increases generally when number of bulk/larger entities increase or number of smaller entities in the liquid system decrease. Viscosity of a liquid system decreases when number of bulk/larger entities decrease or number of smaller entities increase [24]. In the low concentration region of alkanol, rise in the viscosity of the systems is due to long-range order in water giving rise to hydrogen bonded structure [25, 26].

This structure has many cavities and these, cavities can accommodate solute molecules (alkanol molecules). These alkanol molecules fill up cavities in the hydrogen bonded structures and setting up of long range order through dipole-dipole, donor-acceptor, hydrogen bonding interactions and other complex formation favouring interactions between component molecules. This process continues till all the cavities are filled and then viscosity attains a maximum. In the alkanol rich region of the mixtures the viscosity decreased with increase in concentration of alkanol. This decrease in the viscosity indicates increase of smaller entities in the alkanol rich region of the mixtures. This is due to disruption of long range order in aqueous PG and medium range order in hydrogen bonded water. This effect is possible due to domination of dissociation of hydrogen bonded open structures and water-PG aggregates over associative interaction between component molecules, because all cavities in the hydrogen bonded aggregates are already occupied by alkanol molecules and addition of alkanol resulting in large number of monomer alkanol molecules.

The variation of Δη gives a qualitative estimation of strength of molecular interaction. The variation of deviation in viscosity Δη with mole fraction of *tert*-butanol/2-propanol is presented in **Fig.3** and **4** respectively. The Δη is positive over the entire composition range. The negative values of Δη indicate the dispersive forces arising from weak molecular interaction and the positive values suggest the presence of strong interactions between the molecules[27]. The variation Δη in the present study suggest specific interactions such as formation of new hydrogen bonds between unlike molecules, formation of charge transfer complexes, dipole-dipole interactions and other complex formation favouring interactions are dominant in the systems studied.

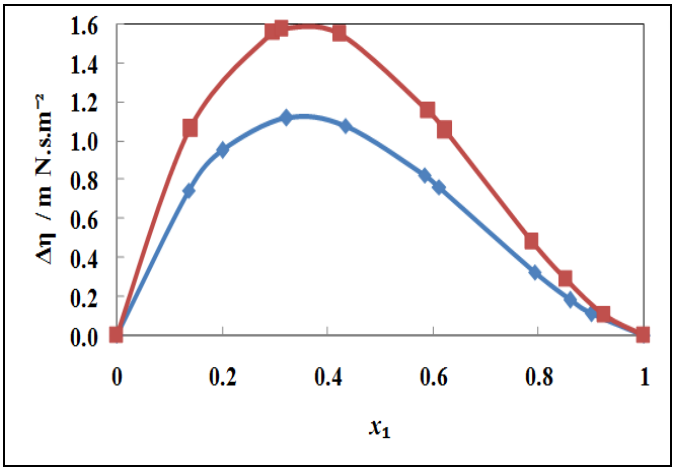


FIG.3: PLOTS OF DEVIATION IN VISCOSITY (Δ*η*) AGAINST MOLE FRACTION OF *TERT*-BUTANOL (x_1) FOR BINARY SYSTEM OF *TERT*-BUTANOL WITH AQUEOUS PG OF 3m (■) AND 7m (♦).

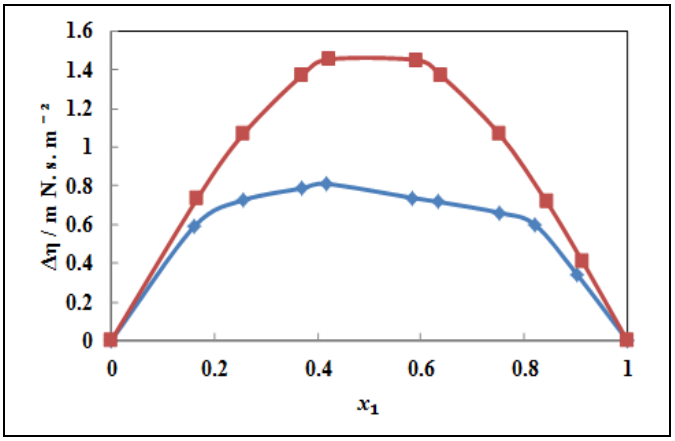


FIG.4: PLOTS OF DEVIATION IN VISCOSITY (Δ*η*) AGAINST MOLE FRACTION OF 2-PROPANOL (x_1) FOR BINARY SYSTEM OF 2-PROPANOL WITH AQUEOUS PG OF 3m (■) AND 7m (♦).

Fig.5 and **6** represent the variation of excess molar volume, V_m^E for aqueous propylene glycol (3m, 7m) with mole fraction of *tert*-butanol/2-propanol respectively. The sign of V_m^E depends upon the contraction and expansion of volume of the liquids due to mixing. The factors that are mainly responsible for the expansion of molar volume, i.e. positive values of V_m^E are the following (i) breaking of the structure of one or both of the components in a solution, i.e. the loss of dipolar association between the molecules (dispersion forces). (ii) H-bond rupture and stretching of self-associated

molecules (like alcohols). (iii) The geometry of molecular structures which does not favour the fitting of molecules of one component into other molecules of second component. (iv) steric hindrance of the molecules. The negative values of V_m^E are due to the (i) association of molecules through the formation of hydrogen bond, i.e. strong specific interactions and (ii) accommodation of molecules because of large differences in their molar volumes. In the present case the sign of V_m^E is found to be negative over the entire composition range.

This implies that molecules in the liquid mixture might be more compactly arranged than in the component liquids. This is probably due to fitting of component molecules into each other's structures because of the observed considerable difference in their molar volumes. The volume of mixtures is thereby decreased resulting in negative V_m^E values in the mixtures investigated. This fact is clearly evident from the values of molar volume for the molecules in study. The molar volumes of *tert*-butanol, 2-popanol, aqueous PG of 3m and 7m are 9.6474, 7.7691, 3.0241 and 4.6586 (x 10^{-5}) $m^3.mol^{-1}$ respectively. The strength of interactions in the present investigated systems follow the order i.e., aqueous PG (3m) + *tert*-butanol/2-propanol > aqueous PG (7m) + *tert*-butanol/2-propanol. Therefore, the interaction is more in *tert*-butanol rather than 2-propanol when compared among the present alkanols.

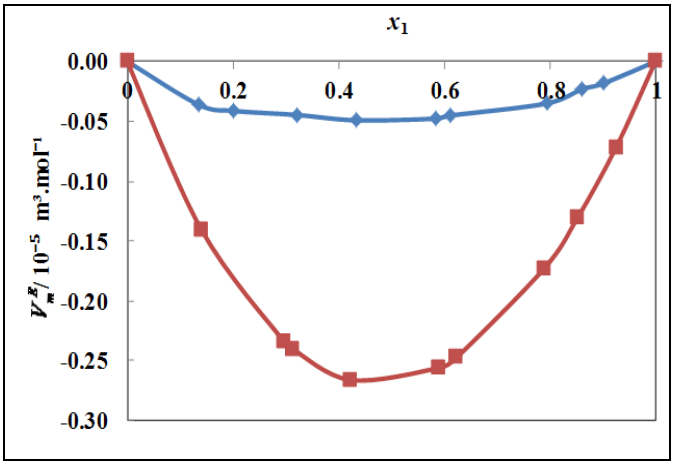


FIG. 5: PLOTS OF EXCESS MOLAR VOLUME (V_m^E) AGAINST MOLE FRACTION OF *TERT*-BUTANOL (x_1) FOR BINARY SYSTEM OF *TERT*-BUTANOL WITH AQUEOUS PG OF 3m(■) AND 7m (♦).

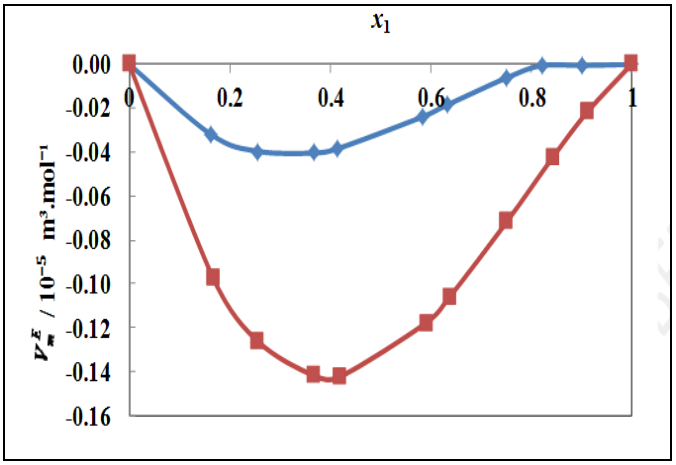


FIG.6: PLOTS OF EXCESS MOLAR VOLUME (V_m^E) AGAINST MOLE FRACTION OF 2-PROPANOL (x_1) FOR BINARY SYSTEM OF 2-PROPANOL WITH AQUEOUS PG OF 3m (■) AND 7m (♦).

The strong molecular interactions in the systems are well reflected in the properties of partial molar volumes. The partial molar volumes $\overline{V}_{m,1}$ of component 1(2-propanol/*tert*-butanol) and $\overline{V}_{m,2}$ of component 2 (aqueous PG of 7m or 3m) in the mixtures over the entire composition range have been calculated by using the following relations.

$$\overline{V}_{m,1} = V_m^E + V_1^* + x_2\left(\frac{\partial V_m^E}{\partial x_1}\right)_{T,P} \qquad (8)$$

$$\overline{V}_{m,2} = V_m^E + V_2^* - x_1\left(\frac{\partial V_m^E}{\partial x_1}\right)_{T,P} \qquad (9)$$

where V_1^* and V_2^* are the molar volumes of components of 2-propanol/*t*-butanol and aqueous PG of 7m or 3m respectively. The derivative in Eqs (8) and (9) are obtained by differentiating Eq. (6) which lead to the following equations for $\overline{V}_{m,1}$ and $\overline{V}_{m,2}$.

$$\overline{V}_{m,1} = V_1^* + x_2^2\sum_{i=0}^{j} A_i(x_2 - x_1)^i - 2x_1x_2^2\sum_{i=1}^{j} A_i(i)(x_2 - x_1)^{i-1} \quad (10)$$

$$\overline{V}_{m,2} = V_2^* + x_1^2\sum_{i=0}^{j} A_i(x_2 - x_1)^i + 2x_2x_1^2\sum_{i=1}^{j} A_i(i)(x_2 - x_1)^{i-1} \quad (11)$$

using the above equations $\overline{V}_{m,1}^E, \overline{V}_{m,2}^E$ have been calculated and are shown below,

$$\overline{V}_{m,1}^E = \overline{V}_{m,1} - V_1^* \qquad 12)$$

$$\overline{V}_{m,2}^E = \overline{V}_{m,2} - V_2^* \qquad (13)$$

The values of $\overline{V}_{m,1}$ and $\overline{V}_{m,2}$ are furnished in **Table 4**. From this table, the values of $\overline{V}_{m,1}$ and $\overline{V}_{m,2}$ for both the components in the mixtures are less than their respective molar volumes in the pure state i.e., contraction of volume takes place on alkanol with aqueous PG. This data is also supporting the observed negative values of V_m^E in all the binary systems. **Fig.7, 8, 9** and **10** represent the variation of excess partial molar volumes of $\overline{V}_{m,1}^E$ and $\overline{V}_{m,2}^E$. Examination of these figures not only reveals the existence of strong forces between the unlike molecules in the liquid mixtures but also supports the conclusion drawn from V_m^E. This support the conclusions drawn from $\Delta\eta$ and V_m^E.

TABLE 4: PARTIAL MOLAR VOLUMES $\overline{V}_{m,2}$ OF AQUEOUS PG OF 3M OR 7M AND $\overline{V}_{m,1}$, OF 2-PROPANOL/*TERT*-BUTANOL WITH MOLE FRACTION (x_1) OF 2-PROPANOL/*TERT*-BUTANOL FOR ALL THE SYSTEMS AT 308.1

aqueous PG(3 m)+2-propanol			aqueous PG(7 m)+2-propanol			aqueous PG(3 m)+tert-butanol			aqueous PG(7 m)+tert-butanol		
x_1	$\overline{V}_{m,2}$	$\overline{V}_{m,1}$	x_1	$\overline{V}_{m,2}$	$\overline{V}_{m,1}$	x_1	$\overline{V}_{m,2}$	$\overline{V}_{m,1}$	x_1	$\overline{V}_{m,2}$	$\overline{V}_{m,1}$
	/10^{-5} $m^3.mol^{-1}$			/10^{-5} $m^3.mol^{-1}$			/10^{-5} $m^3.mol^{-1}$			/10^{-5} $m^3.mol^{-1}$	
0.0000	3.0241	7.0100	0.0000	4.6586	7.8022	0.0000	3.0241	8.4717	0.0000	4.6586	9.1705
0.1669	2.9958	7.3280	0.1616	4.6668	7.7212	0.1399	2.9967	8.8283	0.1360	4.6385	9.5869
0.2561	2.9604	7.4633	0.2561	4.6797	7.6751	0.2958	2.9108	9.1351	0.2012	4.6278	9.6498
0.3691	2.9012	7.5983	0.3688	4.6890	7.6631	0.3128	2.8986	9.1632	0.3223	4.6173	9.6586
0.4212	2.8705	7.6467	0.4157	4.6877	7.6697	0.4231	2.8083	9.3218	0.4343	4.6120	9.6200
0.5911	2.7704	7.7478	0.5838	4.6536	7.7147	0.5911	2.6412	9.4937	0.5838	4.5941	9.5771
0.6383	2.7465	7.7621	0.6322	4.6366	7.7268	0.6232	2.6057	9.5182	0.6128	4.5885	9.5736
0.7519	2.7053	7.7776	0.7519	4.5814	7.7478	0.7887	2.4022	9.6080	0.7941	4.5484	9.5939
0.8434	2.6971	7.7765	0.8212	4.5334	7.7554	0.8523	2.3122	9.6279	0.8613	4.5384	9.6149
0.9124	2.7108	7.7724	0.9021	4.4388	7.7631	0.9254	2.1975	9.6417	0.9012	4.5354	9.6277
1.0000	2.7589	7.7691	1.0000	4.1985	7.7691	1.0000	2.0644	9.6464	1.0000	4.5368	9.6464

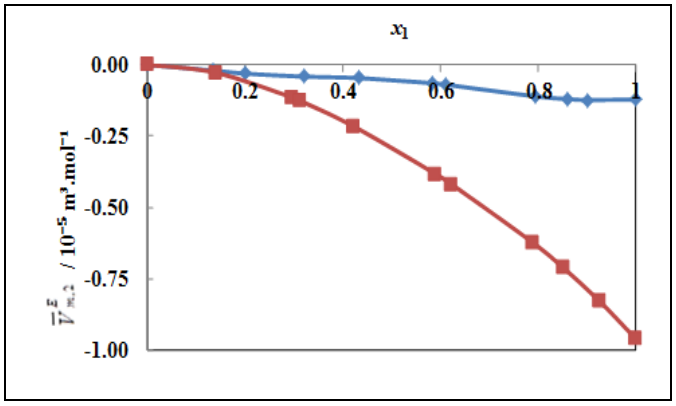


FIG.7: PLOTS OF EXCESS PARTIAL MOLAR VOLUME OF AQU PG ($\overline{V}_{m,2}$) AGAINST MOLE FRACTION OF *TERT-BUTANOL* (x_1) FOR BINARY SYSTEM OF *TERT*-BUTANOL WITH AQUEOUS PG OF 3m (■) and 7m (♦).

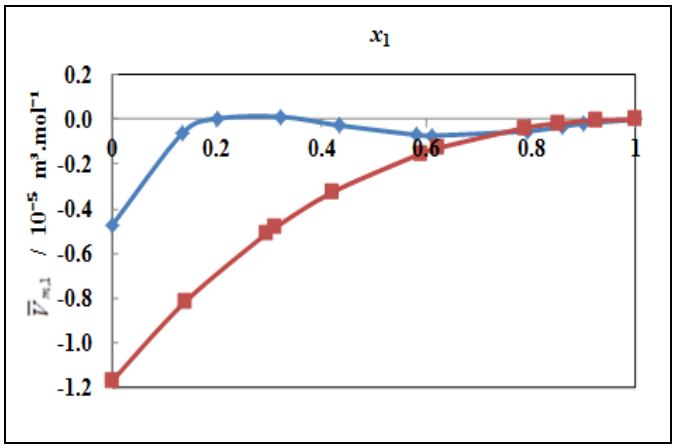


FIG. 8: PLOTS OF EXCESS PARTIAL MOLAR VOLUME OF *TERT*-BUTANOL ($\overline{V}_{m,1}$) AGAINST MOLE FRACTION OF *TERT*-BUTANOL (x_1) FOR BINARY SYSTEM OF *TERT*-BUTANOL WITH AQUEOUS PG OF 3m (■) AND 7m (♦).

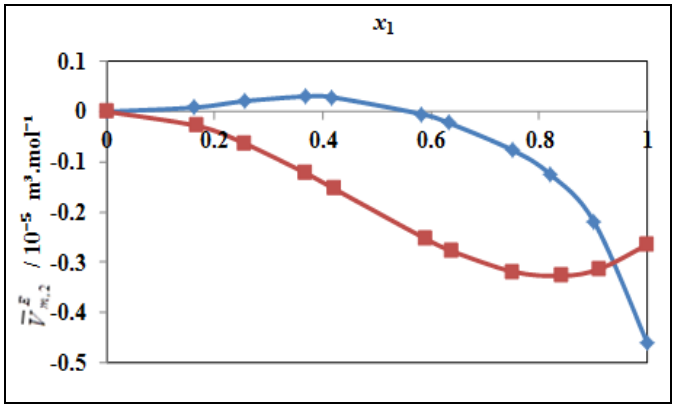


FIG. 9: PLOTS OF EXCESS PARTIAL MOLAR VOLUME OF AQU PG ($\overline{V}_{m,2}$) AGAINST MOLE FRACTION OF 2-PROPANOL (x_1) FOR BINARY SYSTEM OF 2-PROPANOL WITH AQUEOUS PG OF 3m (■) AND 7m (♦).

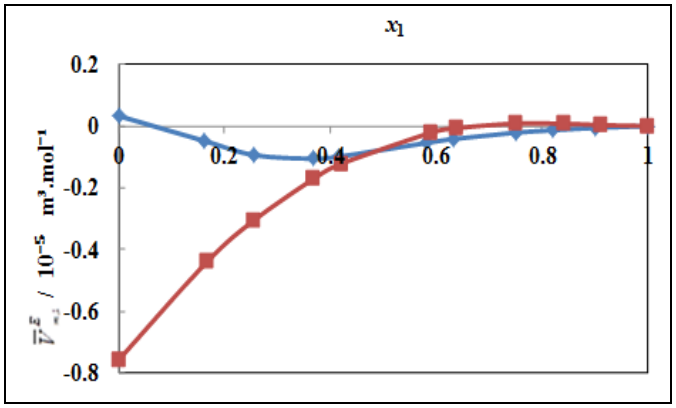


FIG. 10: PLOTS OF EXCESS PARTIAL MOLAR VOLUME OF *2*-PROPANOL ($\overline{V}_{m,1}$) AGAINST MOLE FRACTION OF *TERT*-BUTANOL (x_1) FOR BINARY SYSTEM OF 2-PROPANOL WITH AQUEOUS PG OF 3m (■) AND 7m (♦).

The variation of excess Gibbs free energy of activation of viscous flow ΔG^{*E} with mole fraction of *tert*-butanol/2-propanol for two different molalities of aqueous PG are presented in **Fig. 11** and **12** respectively. These values are positive over the entire range of composition of alkanol. According to Kondaiah *et al*.[28], negative values of ΔG^{*E} indicate the presence of weak physical forces such as dispersive forces in the system. On the other hand positive values of it suggest strong specific interactions. This further supports the conclusion drawn from $\Delta\eta$, V_m^E and partial molar volumes ($\overline{V}_{m,1}$,$\overline{V}_{m,2}$,).

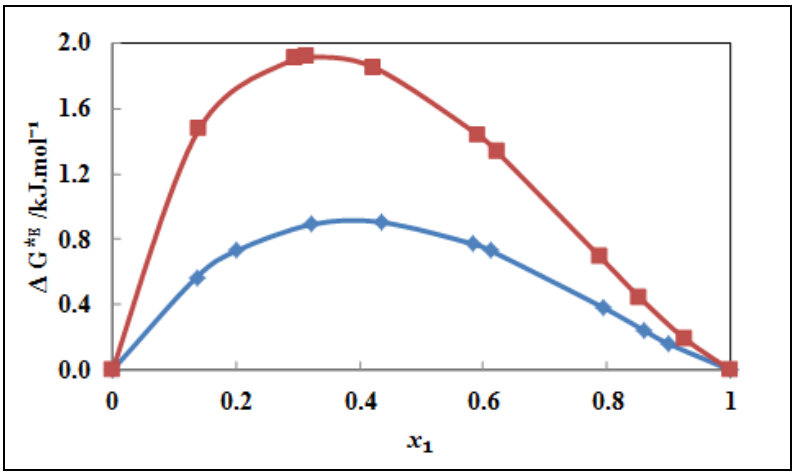


FIG.11: PLOTS OF EXCESS GIBB'S FREE ENERGY OF ACTIVATION OF VISCOUS FLOW (ΔG^{*E}) AGAINST MOLE FRACTION OF *TERT*-BUTANOL (x_1) FOR BINARY SYSTEM OF *TERT*-BUTANOL WITH AQUEOUS PG OF 3m (■) AND 7m(♦).

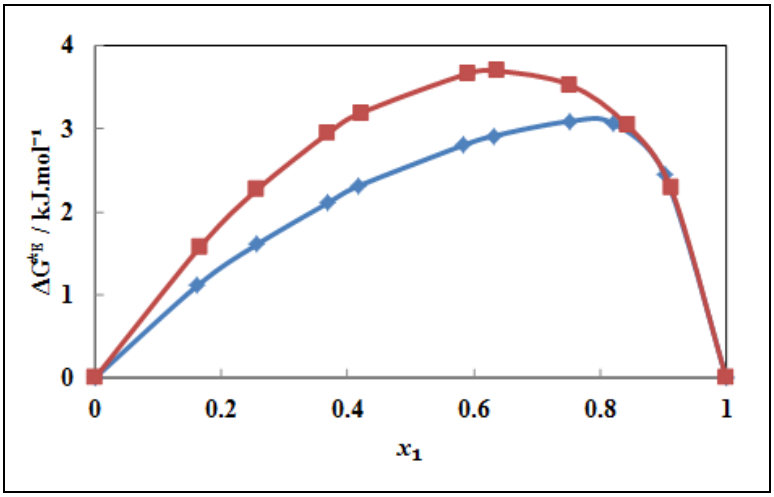


FIG.12: PLOTS OF EXCESS GIBB'S FREE ENERGY OF ACTIVATION OF VISCOUS FLOW (ΔG^{*E}) AGAINST MOLE FRACTION OF 2-PROPANOL (x_1) FOR BINARY SYSTEM OF 2-PROPANOL WITH AQUEOUS PG OF 3m (■) AND 7m (♦).

The dynamic viscosities of the liquid mixtures have been calculated using the several empirical relations.

Gruenberg and Nissan [29] proposed the following equation for the measurement of viscosity of liquid mixtures

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \qquad (14)$$

here G_{12} is an interaction parameter, which is the function of components 1 and 2 as well as temperature.

Hind, McLaughlin and Ubbelohde [30] suggested an equation for the viscosity of binary liquid mixtures as

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2 x_1 x_2 H_{12} \qquad (15)$$

here H_{12} is an interaction parameter and is attributed to unlike pair interaction.

Katti and Chaudari [31] proposed the following equation

$$\ln (\eta\ V) = x_1 \ln (\eta_1 V_1) + x_2 \ln (\eta_2 V_2) + x_1 x_2\ W_{vis}/\ RT \qquad (16)$$

where W_{vis} / RT is an interaction term

The theoretical viscosity values using Eqs. (14) to (16) along with the percentage error are compiled in **Table 5**. The evaluated values of parameters G_{12}, H_{12}, and W_{vis} /RT and standard deviations (σ) are presented in **Table 6.** The estimated values of σ are smaller for aqueous PG + *tert*-butanol indicating that the viscosities are well correlated by all the three viscosity models than for aqueous PG +2-propanol. In the present systems, differences between experimental and theoretical viscosities are greater where the mole fraction of alkanol varies in the region 0.3 to 0.7. Hence it can be qualitatively inferred that the strength of interaction in the binary mixtures is more in this range of composition of binary mixtures. Kondaiah *et al.*[32] reported positive values of interaction parameters corresponding to systems with negative excess molar volumes. This is also consistent with our results.

TABLE 5: EXPERIMENTAL AND CALCULATED VALUES OF THE VISCOSITY, $\eta/10^{-3}$N.s.m^{-2}, OF ALL THE SYSTEMS FROM VARIOUS EQS [(14) - (16)] AND PERCENTAGE ERROR WITH MOLE FRACTION, x_1 OF 2-PROPANOL/*TERT*-BUTANOL AT T = 308.15K

x_1	Expt.	Grunberg	Hind	Katti	%Grunberg	% Hind	% Katti
aqueous PG (3 m)+2-propanol							
0.0000	1.548	1.548	1.548	1.548	0.000	0.000	0.000
0.1669	2.074	2.103	1.889	3.400	1.398	-8.920	63.934
0.2561	2.296	2.252	1.981	4.348	-1.916	-13.720	89.373
0.3691	2.458	2.231	2.007	4.988	-9.235	-18.348	102.929
0.4212	2.476	2.143	1.985	4.976	-13.449	-19.830	100.969
0.5911	2.260	1.606	1.765	3.701	-28.938	-21.903	63.761
0.6383	2.124	1.420	1.663	3.153	-33.145	-21.704	48.446

0.7519	1.677	0.978	1.346	1.864	-41.682	-19.738	11.151
0.8434	1.212	0.670	1.016	1.057	-44.720	-16.172	-12.789
0.9124	0.819	0.481	0.724	0.634	-41.270	-11.599	-22.588
1.0000	0.298	0.298	0.298	0.298	0.000	0.000	0.000
aqueous PG (7 m)+2-propanol							
0.0000	3.829	3.829	3.829	3.829	0.000	0.000	0.000
0.1616	3.850	3.721	3.214	6.746	-3.351	-16.519	75.221
0.2561	3.651	3.417	2.862	7.888	-6.409	-21.611	116.050
0.3688	3.313	2.889	2.451	8.029	-12.798	-26.019	142.348
0.4157	3.171	2.637	2.282	7.662	-16.840	-28.035	141.627
0.5838	2.506	1.717	1.688	4.991	-31.484	-32.642	99.162
0.6322	2.315	1.473	1.521	4.090	-36.371	-34.298	76.674
0.7519	1.835	0.953	1.113	2.161	-48.065	-39.346	17.766
0.8212	1.527	0.713	0.881	1.359	-53.307	-42.305	-11.002
0.9021	0.987	0.491	0.615	0.724	-50.253	-37.690	-26.646
1.0000	0.298	0.298	0.298	0.298	0.000	0.000	0.000
aqueous PG (3 m)+*tert*-butanol							
0.0000	1.548	1.548	1.548	1.548	0.000	0.000	0.000
0.1399	2.775	2.383	2.137	2.242	-14.126	-22.991	-19.207
0.2958	3.449	3.365	2.628	3.029	-2.435	-23.804	-12.177
0.3128	3.486	3.464	2.672	3.107	-0.631	-23.351	-10.872
0.4231	3.584	4.012	2.902	3.546	11.942	-19.029	-1.060
0.5911	3.387	4.373	3.086	3.871	29.111	-8.887	14.290
0.6232	3.320	4.363	3.099	3.875	31.416	-6.657	16.717
0.7887	2.940	3.914	3.047	3.598	33.129	3.639	22.381
0.8523	2.816	3.597	2.975	3.375	27.734	5.646	19.851
0.9254	2.720	3.170	2.857	3.061	16.544	5.037	12.537
1.0000	2.697	2.697	2.697	2.697	0.000	0.000	0.000
aqueous PG (7 m)+*tert*-butanol							
0.0000	3.829	3.829	3.829	3.829	0.000	0.000	0.000
0.1360	4.421	4.131	3.637	4.142	-6.560	-17.733	-6.311
0.2012	4.552	4.225	3.549	4.241	-7.184	-22.034	-6.832
0.3223	4.583	4.303	3.393	4.325	-6.109	-25.966	-5.629
0.4343	4.414	4.258	3.257	4.282	-3.534	-26.212	-2.990
0.5838	3.993	4.029	3.089	4.052	0.902	-22.640	1.477
0.6128	3.896	3.964	3.058	3.986	1.745	-21.509	2.310
0.7941	3.255	3.443	2.877	3.456	5.776	-11.613	6.175
0.8613	3.036	3.210	2.815	3.219	5.731	-7.279	6.027
0.9012	2.918	3.066	2.780	3.072	5.072	-4.729	5.277
1.0000	2.697	2.697	2.697	2.697	0.000	0.000	0.000

TABLE 6: VARIOUS PARAMETERS CALCULATED FROM EQS. [(14) - (16)] AND THE CORRESPONDING STANDARD DEVIATIONS σ /10^{-3} N.s.m^{-2}

G_{12}	σ	H_{12}	σ	W_{vis}/RT	σ
aqueous PG (3 m)+2-propanol					
4.181	0.575	0.003	0.446	0.031	1.908
aqueous PG (7 m)+2-propanol					
2.835	0.770	0.002	0.907	0.040	3.612
aqueous PG (3 m)+*tert*-butanol					
2.939	0.833	0.004	2.396	0.007	1.935
aqueous PG (7 m)+*tert*-butanol					
1.052	0.254	0.003	1.009	0.006	0.248

CONCLUSIONS:

- The mixtures of drugs of alkanol (2-propanol or *tert*-butanol) and 3m and 7m of aqueous propylene glycol (PG) drug solutions are prepared in which density, viscosity measurements have been performed at 308.15 K. From the experimental data of density and viscosity some of the deviation/excess properties have been evaluated.
- The positive and negative deviation/excess properties have been attributed to strong specific interactions such as formation of hydrogen bond, dipole-dipole interactions and geometrical fitting of smaller entities in to the larger entities.
- Strength of interaction follows the order (3 m aqueous PG + *tert*- butanol/2-propanol) > (7 m aqueous PG + *tert*- butanol/2-propanol).

Further (aqueous PG (3 m/7 m) + 2-propanol) <(aqueous PG (3 m/7 m) + *tert*- butanol).

- The measured values of viscosity for all the investigated drug solutions are compared with the theoretically estimated values using different empirical relations.

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