

Excess Dielectric and Thermodynamical Studies on Hydrogen Bonded Binary Mixtures of Propan-1-ol with Methyl and Ethyl Benzoates

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Abstract: The molecular interactions between the polar systems propan-1-ol with alkyl benzoates (methyl benzoate and ethyl benzoate) for various mole fractions at different temperatures were studied by determining the dielectric permittivity using - LF impedance analyzer, microwave bench and Abbe's refractometer in radio, microwave and optic frequency regions respectively. Dipole moment, excess dipole moment, excess Helmholtz free energy, excess permittivity, relaxation time, excess inverse relaxation time and excess thermodynamical values are calculated using experimental data. Hamiltonian quantum mechanical calculations are performed on both pure and equimolar binary systems of propan-1-ol with alkyl benzoates for the measurement of dipole moment using PC Spartan and Argus lab Modeling softwares and these theoretical values are in good agreement with the experimental values. These studies can give information on its structure and interaction.

Keywords: Dipole moment, Excess Helmholtz free energy, Relaxation time, Hamiltonian calculations

Introduction

Dielectric studies on mixtures of polar liquids either in pure state or in inert solvents have been a subject of interest because they provide useful information regarding the molecular complex formation in solution¹. Molecular mixtures bring about changes in thermodynamic properties like entropy, free energy and also in physical properties like density, molar volume, refractive index, dielectric permittivity *etc.*². Many studies on the fluid structures of polar and non-polar mixtures have been reported^{3,4}. There is an increased interest in the study of liquid mixtures leading to formation of hydrogen bonding in the system due to solute-solvent interactions during the recent times⁵. Hydrogen bonding is complex in liquid state because of the uncertainty in identifying the particular bonds and the number of molecules involved. The presence of hydrogen bond brings a considerable change in the dielectric properties of liquid mixtures⁶.

Alcohols are industrially and scientifically important organic compounds and their physical and chemical properties are largely determined by the –OH group. Alcohols are strongly associated in solution because of dipole-dipole interaction and hydrogen bonding. Aromatic ester solvents are a remarkable family of fluids with technological applications in very different fields⁷. The detailed knowledge of the molecular level structure of these fluids is required not only to improve the processes in which they are involved but also because of the theoretical importance of these compounds. Aromatic ester packings are disrupted upon mixing although very different effects arise depending on the nature of the second compounds of the mixture⁸⁻¹⁰. In order to get a deeper insight into the liquid structure of this mixture of fluids, we report here the values of dielectric data at different frequency regions; according to these experimental results, a better knowledge on their structure and dynamics can be gained. The nature of interaction between –CH and –OH groups plays an important role in biological systems and drug synthesis^{9,11}.

The present work aims at studying the dielectric behavior of pure and binary mixtures of propan-1-ol with methyl benzoate (System 1) and propan-1-ol with ethyl benzoate (System 2) in different frequency ranges for various mole fractions at different temperatures. From the experimental data, the dielectric parameters dipole moment, excess dipole moment, excess helmholtz free energy, excess permittivity, relaxation time, excess inverse relaxation time and excess thermodynamical values are calculated for the pure and binary mixtures¹²⁻¹⁶. Hamiltonian quantum mechanical calculations⁸ such as semi-empirical and *ab-initio* calculations are performed by optimized converged geometry operation using PC Spartan and Argus lab modeling softwares^{17,18}. The obtained theoretical values are further compared with the experimental values.

Experimental

The compounds propan-1-ol (1PN), methyl benzoate (MB), ethyl benzoate (EB) and benzene of AR grade are procured from E. Merck, Germany and were purified by standard methods. The binary mixtures were prepared for different mole fractions *i.e.*, mole fraction (x_2) of benzoates is varied from 0 to 1 in propan-1-ol (with a step increment of 0.1). The temperature, T= (303 to 323) K, controller system with a water bath, supplied by M/s Sakti Scientific Instruments Company-India, were used to maintain the constant temperature with an uncertainty ± 1 K. The mass measurements were performed on a digital electronic balance (Mettler Toledo AB 135, Switzerland) with an uncertainty of ± 0.00001 g. The Densities of the pure liquids were measured at corresponding temperatures by using a 10 mL specific gravity bottle.

The permittivity values at the spot frequencies 1 kHz (ϵ_{static}), 10 kHz, 100 kHz, 1 MHz and 10 MHz for the above systems were measured using a HP-LF impedance analyzer (Model No: 4192 A) at different temperatures. The real (ϵ') and imaginary (ϵ'') parts of the complex dielectric permittivity ($\epsilon^* = \epsilon' - j\epsilon''$) were determined with Microwave bench (X-Band, 8.60 GHz) using the Plunger technique¹⁹ at different temperatures. The high frequency dielectric permittivity ($\epsilon_\infty = n^2$) is obtained from the refractometer measurements using M/s ASCO make Abbe's refractometer with sodium D light as source at different temperatures. The average uncertainty in the measurement of ϵ_{static} , ϵ' , ϵ_∞ and density is 0.0002 and the average uncertainty in the measurement of ϵ'' , τ is 0.002. Dipole moments of the liquids in gaseous state are taken from literature²⁰.

Theory

The dipole moments for the pure and equi molar systems (System 1 and 2) were measured experimentally, by diluting them in non-polar solvent benzene, using Higasi's method¹².

$$\mu^2 = \frac{27kTM_2(a_0 - a_\infty)}{4\pi Nd_1(\epsilon_1 + 2)^2} \quad (1)$$

Where M_2 is molecular weight of solute, d_1 is density of solvent, ϵ_1 is the static dielectric permittivity of solvent (Benzene), a_0 and a_∞ are the slopes of ϵ_{static} and ϵ_∞ with respect to the weight fraction of the solute respectively. The excess dipole moments ($\Delta\mu$) of the systems are determined by the following equation¹³.

$$\Delta\mu = \mu_{12} - \mu_1 - \mu_2 \quad (2)$$

Where the dipole moment of 1PN is μ_1 , μ_2 is the dipole moment of either MB or EB and μ_{12} is the dipole moment of the equi molar solute mixtures 1PN + MB or 1PN+EB. The dipole moment increment is considered as a quantitative indication of the polarity of the hydrogen bond.

The excess Helmholtz free energy (ΔF^E) is a good dielectric parameter to evaluate the interaction between the components in the mixture through breaking mechanism of hydrogen bond and is expressed²¹ as

$$\Delta F^E = \Delta F_{or}^E + \Delta F_{rr}^E + \Delta F_{12}^E \quad (3)$$

Where ΔF_{or}^E represents the excess dipolar energy due to long range electrostatic interaction, ΔF_{rr}^E represents the excess dipolar energy due to the short range interaction between identical molecules and ΔF_{12}^E represents the excess free energy due to short-range interaction between dissimilar molecules. The above terms are given in detail in equation (4)

$$\Delta F^E = \frac{-N_A}{2} \left\{ \sum_{r=1,2} x_r^2 \mu_r^2 [R_{fr}^0 - R_{fr}^E] + \sum_{r=1,2} x_r^2 \mu_r^2 [g_{rr} - 1] [R_{fr}^0 - R_{fr}^E] \right. \\ \left. + x_1 x_2 \mu_1 \mu_2 [R_{f1}^0 + R_{f2}^0 - R_{f1}^E - R_{f2}^E] \right\} \quad (4)$$

$$\text{Where, } R_{fr}^0 = \left(\frac{8\pi N_A}{9V_r} \right) \frac{(\epsilon_r - 1)(\epsilon_{\infty r} + 2)}{(2\epsilon_r + \epsilon_{\infty r})}, \quad R_{fr}^E = \left(\frac{8\pi N_A}{9V_r} \right) \frac{(\epsilon_m - 1)(\epsilon_{\infty r} + 2)}{(2\epsilon_m + \epsilon_{\infty r})}, \quad g_{12} = g_f,$$

V_r is the molar volume of the components and ϵ_r , $\epsilon_{\infty r}$, $\epsilon_{\infty or}$ are the dielectric permittivity values at static and optic frequencies of the pure liquids respectively. The contribution of hydrogen bonds to the dielectric properties of the mixtures can be studied in terms of excess permittivity (ϵ^E). The excess permittivity, ϵ^E , which provides qualitative information about formation of multimers in the mixture, can be computed^{22,23} as,

$$\epsilon^E = (\epsilon_m - \epsilon_{\infty m}) - \left[(\epsilon_1 - \epsilon_{\infty m}) x_1 + (\epsilon_2 - \epsilon_{\infty m}) x_2 \right] \quad (5)$$

Where x mole fraction and suffix 1, 2 and m is represents liquid 1, liquid 2 and mixture respectively. The qualitative information provided by excess permittivity about the mixtures is as follows. $\epsilon^E = 0$ indicates that there is no interaction between the components in the mixture.

$\epsilon^E < 0$ indicates that the components in the mixture interact in such a way that the effective dipolar polarization gets reduced and the components may form multimers leading to less effective dipoles. $\epsilon^E > 0$ indicates that the components in the mixture interact in such a way that the effective dipolar polarization gets increased and the components may form multimers leading to more effective dipoles.

The dielectric data obtained *i.e.*, ϵ_{static} , ϵ^* , $\epsilon' - j\epsilon''$, ϵ_∞ and the data from LF-impedance analyzer is used to fit in an Argand diagram to calculate the relaxation time (τ). The distribution of relaxation time is witnessed from Cole-Cole arc plot¹⁵. Although Cole-Cole equations which signify the distribution of relaxation time, eventually a macroscopic relaxation time (predominant relaxation time) is measured using the equation.

$$\omega\tau = \left(\frac{v}{u}\right)^{\frac{1}{1-\alpha}} \quad (6)$$

Where α (distribution parameter), μ and v values are determined from their respective Cole plots.

The excess inverse relaxation time $\left(\frac{1}{\tau}\right)^E$ which gives information regarding the dynamics of solute- solvent interaction and represents the average broadening of dielectric spectra, can be defined²⁴ as

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left[\left(\frac{1}{\tau}\right)_1 x_1 + \left(\frac{1}{\tau}\right)_2 x_2 \right] \quad (7)$$

The thermodynamic parameters excess Gibb's energy of activation $(\Delta G^*)^E$, excess molar enthalpy of activation $(\Delta H^*)^E$ and excess molar entropy of activation $(\Delta S^*)^E$ at different mole fractions can be determined by fitting the Eyring rate equation^{25,26} as,

$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta G^*}{RT}\right) = \frac{h}{kT} \exp\left(\frac{\Delta H^* - T\Delta S^*}{RT}\right) \quad (8)$$

Where h is the Planck's constant, k is the Boltzmann constant, T is the temperature in Kelvin and R is the gas constant.

Minimum energy structures of the pure monomers of IPN, MB, EB and their equi molar hydrogen bonded complexes are obtained from Semi-empirical Hamiltonian quantum mechanical calculations such as Austin Model 1 (AM1), Parameterized Model number 3 (PM3) and Modified Neglect of Differential Overlap (MNDO) by converged geometry optimization procedure using PC Spartan and Argus lab Modeling softwares. *ab-initio* calculations have been carried out using PC Spartan modeling software and the geometry optimizations are done at the Hartree-Fock (HF) level using 6-31G* basis set.

Results and Discussion

We studied²⁷ the temperature dependence on dielectric relaxation in pure and binary mixtures of propan-1-ol with methyl benzoate and ethyl benzoate at different frequencies to understand the nature of molecular orientation processes. The dielectric data is used to calculate Kirkwood effective correlation factor, corrective Kirkwood correlation factor, Bruggeman parameter, relaxation time and the thermodynamic parameters- Gibb's energy of activation, molar enthalpy and molar entropy of activation. Conformational analysis of the formation of hydrogen bond between equimolar mixtures of propan-1-ol with benzoates is studied from FT-IR spectra. The theoretical vibrational frequencies of the pure and equi-molar hydrogen bonded systems are obtained from Hamiltonian quantum mechanical calculations using Spartan modeling software. The same data is used to study excess dielectric parameters and reporting in this communication.

The dipole moment (μ) values for pure and equi molar systems (1 and 2) at room temperature are determined experimentally with Higasi's method and theoretically with Hamiltonian quantum mechanical calculations (*ab-initio* and Semi-empirical) and the corresponding values are given in Table 1. The dipole moments for these systems are measured experimentally by diluting them in non-polar solvent benzene. It is very clear from the experimental and theoretical dipole moment values, that there is an increase in the dipole moment of equi molar binary mixture when compared to the individual systems. This may be due to the formation of hydrogen bonding between the mixture systems¹³. The theoretical dipole moment values are in good agreement with the experimental values. The small deviation between the theoretical and experimental values may be due to the model dependency in theoretical case and in experimental case, the π electron cloud of non-polar solvent benzene affecting the dipole moment value of the solute systems²⁸.

Table 1. Experimental, Theoretical dipole moment (μ) and excess dipole moment ($\Delta\mu$) values in Debye for pure 1PN, MB, EB and equi molar systems (1PN+MB and 1PN+EB) at room temperature (PCS- PC Spartan, AGS- Argus Lab)

Com-pound	Experi- mental		Theoretical													
			HF 6-31G*		AM1				PM3				MNDO			
	PCS				PCS		AGS		PCS		AGS		PCS		AGS	
	μ	$\Delta\mu$	μ	$\Delta\mu$	μ	$\Delta\mu$	μ	$\Delta\mu$	μ	$\Delta\mu$	μ	$\Delta\mu$	μ	$\Delta\mu$	μ	$\Delta\mu$
1PN	1.57	---	1.67	---	1.53	---	1.54	---	1.42	---	1.40	---	1.38	---	1.36	---
MB	1.81	---	2.08	---	2.10	---	2.11	---	2.07	---	2.05	---	2.22	---	2.23	---
EB	2.05	---	2.18	---	2.12	---	2.12	---	2.09	---	2.07	---	2.25	---	2.10	---
1PN+ MB	2.96	-0.42	3.51	-0.24	3.19	-0.44	3.37	-0.28	3.08	-0.41	3.04	-0.41	3.01	-0.59	2.96	-0.63
1PN+ EB	3.21	-0.41	3.12	-0.73	3.44	-0.21	3.48	-0.18	3.45	-0.06	3.21	-0.26	3.19	-0.44	3.36	-0.10

The dipole moment values, measured for the pure and equi molar systems, are significantly affected by the variation in temperature and are given in Table 2.

Table 2. Experimental dipole moment (μ) and excess dipole moment ($\Delta\mu$) values in Debye for pure 1PN, MB, EB and equi molar systems (1PN+MB and 1PN+EB) at temperatures (303 to 323) K

T / K	1PN μ	MB μ	EB μ	1PN+ MB μ	1PN+ MB ($\Delta\mu$)	1PN+ EB μ	1PN+ EB ($\Delta\mu$)
303	1.57	1.81	2.05	2.96	-0.42	3.21	-0.41
308	1.59	1.83	2.08	2.98	-0.44	3.24	-0.43
313	1.60	1.84	2.10	3.09	-0.35	3.27	-0.43
318	1.58	1.86	2.12	3.19	-0.25	3.31	-0.39
323	1.62	1.88	2.14	3.30	-0.20	3.32	-0.44

The excess dipole moment ($\Delta\mu$) values obtained theoretically and experimentally at different temperatures are given in Tables 1 and 2. It is observed that in all cases the values of $\Delta\mu$ are negative, which indicates the absence of any contribution from ionic structure of

the binary system to the total dipole moment since the formation of an ionic structure involves a very high positive value for $\Delta\mu^{29}$. The excess dipole moment value is a qualitative index for the presence of hydrogen bonding in both the systems (1 and 2).

The long range and short-range interactions between dipoles can be studied from the thermo dynamical parameter excess Helmholtz free energy (ΔF^E) and its constituent parameters ΔF_{or}^E , ΔF_{rr}^E , ΔF_{12}^E ³⁰. The value of ΔF_{or}^E represents the long range interaction between the dipoles in the mixture. In both systems (1 and 2), the positive values of ΔF_{or}^E indicate the existence of attractive forces between the dipoles and the larger separation between the interacting molecules, which are given in Table 3. Negative values of ΔF_{or}^E indicate the repulsive force between dipoles and interacting molecules are at closer distance. In system 1, the values of ΔF_{or}^E are positive for low concentration of methyl benzoate in 1PN and negative for remaining concentrations but in system 2, the values of ΔF_{or}^E are positive up to equimolar concentration and negative for remaining concentrations. For both the systems, as the temperature increases the values of ΔF_{or}^E are also increases for all the mole fractions. This shows that the strength of dipole-dipole interaction depends on the concentration and temperature of the mixture. The values of ΔF_{or}^E for system 2 are greater than system 1. This may be due to the interaction of the compounds in the mixture which produces structural changes.

Table 3. Values of ΔF_{or}^E in Joule/ mole with mole fraction (x_2) of System 1 and System 2 at temperatures (303 to 323) K

x_2	T=303 K		T=308 K		T=313 K		T=318 K		T=323 K	
	System 1	System 2	System 1	System 2	System 1	System 2	System 1	System 2	System 1	System 2
0	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000
0.1	13.1903	13.5517	14.6358	19.5747	14.6057	22.8874	14.6358	24.6943	15.0575	25.2966
0.2	12.7386	13.2506	14.3949	18.6713	15.4791	24.6943	16.0512	27.7058	16.2621	28.9104
0.3	-00.2108	15.0575	01.8671	16.5632	02.3790	15.6598	04.2763	12.9494	05.4207	11.4437
0.4	-22.4959	14.1540	-20.8998	15.9609	-15.8103	17.7678	-12.4374	17.1655	-08.4322	18.6713
0.5	-26.6517	02.1080	-25.5375	00.9034	-24.8749	01.2046	-26.0193	01.2046	-30.4161	02.1080
0.6	-46.1060	-06.0230	-43.2451	-03.3126	-42.7633	-00.6023	-40.0529	02.1080	-40.3541	03.0115
0.7	-66.3734	-36.7403	-61.3743	-32.2230	-53.9058	-27.4046	-45.9253	-26.2000	-43.9679	-24.092
0.8	-63.5125	-47.2805	-54.5984	-44.5702	-53.1529	-40.6552	-48.1538	-38.2460	-47.2805	-34.3311
0.9	-45.8049	-29.2115	-42.1007	-24.3931	-38.6676	-21.6828	-34.4214	-22.5862	-36.1380	-19.2736
1	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000

The values of ΔF_{rr}^E predict the information on the short range interaction between similar molecules. In both the systems, the values of ΔF_{rr}^E are highly positive at all mole fractions and are given in Table 4, indicating the existence of short range interaction through hydrogen bonding. The values of ΔF_{rr}^E for system 2 are greater than system 1 indicating the strong short range interaction between the components of similar molecules of the system 2.

Table 4. Values of ΔF_{rr}^E in Joule/ mole with mole fraction (x_2) of System 1 and System 2 at temperatures (303 to 323) K

x^2	T=303 K		T=308 K		T=313 K		T=318 K		T=323 K	
	System 1	System 2	System 1	System 2	System 1	System 2	System 1	System 2	System 1	System 2
0	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000
0.1	43.1547	44.8412	45.8350	58.3628	44.7508	64.6569	43.8474	66.4035	43.4438	65.7711
0.2	74.5045	80.9491	77.1847	91.6098	77.7870	101.9995	77.5160	105.7638	76.4017	104.4087
0.3	92.6939	136.3306	95.8560	136.9329	94.5912	130.5786	96.5788	120.6406	97.5424	112.8409
0.4	99.1988	182.3162	101.2466	181.2320	107.2696	177.7086	110.8232	170.9628	116.0632	166.0239
0.5	125.4590	187.3153	125.7301	181.0513	123.8027	174.7272	120.3997	168.7644	114.8586	161.9283
0.6	107.0889	164.9699	108.9259	162.5005	106.8179	158.5554	106.3997	155.5740	106.9684	148.4669
0.7	72.9987	105.3422	74.4442	104.5893	76.0704	102.0296	78.1785	98.7772	79.2626	94.6213
0.8	38.8483	55.0803	40.7757	53.5444	40.3239	51.6773	40.7154	49.3584	41.0467	47.3407
0.9	10.1186	16.1416	10.9618	15.6598	11.0522	14.9972	11.2027	14.5455	11.3232	13.0397
0.1	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000

The values of ΔF_{12}^E predict the information on the strength of interaction between unlike molecules. In both the systems, the values of ΔF_{12}^E have appreciable change with respect to concentration and temperature, are given in Table 5. This reveals that hetero association is involving between the compounds which are varying with concentration and temperatures.

Table 5. Values of ΔF_{12}^E in Joule/ mole with mole fraction (x_2) of System 1 and System 2 at temperatures (303 to 323) K

x_2	T=303 K		T=308 K		T=313 K		T=318 K		T=323 K	
	System 1	System 2	System 1	System 2	System 1	System 2	System 1	System 2	System 1	System 2
0	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000
0.1	00.9173	01.1323	01.0249	01.7692	00.8395	01.9902	00.9000	02.0915	00.8360	02.0273
0.2	02.6945	02.9091	02.8205	03.8669	02.6288	04.5447	02.7218	04.8081	02.6039	04.6672
0.3	04.0743	07.1977	04.1967	07.0299	03.9549	06.4580	04.2339	05.8547	04.2399	05.1666
0.4	04.4631	04.6599	04.4423	04.1202	04.8211	03.5890	05.0108	03.5356	05.2529	03.0285
0.5	02.2165	-08.4738	02.3892	-07.7962	01.8530	-07.5579	01.9851	-07.2970	02.4356	-07.0941
0.6	-05.1186	-29.0299	-05.8334	-29.8438	-05.8063	-30.2912	-06.4419	-30.7884	-06.5477	-29.6860
0.7	-09.7080	-29.5104	-10.9730	-30.6160	-13.0503	-31.5484	-15.5178	-30.9474	-16.6009	-30.2181
0.8	-12.2071	-24.9527	-14.2054	-25.0304	-14.2371	-24.9118	-15.3242	-24.7805	-15.9133	-24.5865
0.9	-06.6343	-12.8349	-07.0053	-13.2430	-07.3298	-13.0686	-07.6779	-12.3885	-07.5748	-12.1759
1	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000

Finally the high positive values of ΔF^E , as reported in Table 6, for both the systems (1 and 2) indicate the formation of β - clusters with anti-parallel alignment. Due to the formation of β - clusters the effective dipole moment will be decreased when compared to the sum of individual systems and thereby it destructs the angular correlation between non ideal molecules which may decrease its internal energy³¹. The decrement in the internal energy of molecule leads to the increment in the excess free energy value. The negative values of ΔF^E indicate the formation of α - clusters. Due to the formation of these α - clusters the effective dipole moment will be increased which increases the internal energy.

The excess permittivity (ϵ^E) is another dielectric parameter, which gives information about the interaction between the components of the mixture. Mehrotra *et. al.*³² had pointed

out that the change in the value of ϵ^E with concentration is due to the interaction between dissimilar molecules which may produce structural changes. In system 1 and system 2, negative values of ϵ^E are obtained for all mole fractions at different temperatures³³ and are shown in Figures 1 and 2 respectively. These negative values indicate that the molecules in the mixture form multimers through Hydrogen bonding in such a way that the effective dipole moment gets reduced³⁴. The more negative deviations in ϵ^E values of system 2 compared to system 1 indicate that the strength of hydrogen bond formation is more in system 2 than in system 1.

Table 6. Values of ΔF^E in Joule/ mole with mole fraction (x_2) of System 1 and System 2 at temperatures (303 to 323) K

x_2	T=303 K		T=308 K		T=313 K		T=318 K		T=323 K	
	System 1	System 2	System 1	System 2	System 1	System 2	System 1	System 2	System 1	System 2
0	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000
0.1	57.2623	59.5252	61.4957	79.7067	60.196	89.5345	59.3832	93.1893	59.3373	93.095
0.2	89.9376	97.1091	94.4001	114.148	95.8949	131.2385	96.2890	138.2777	95.2677	137.9863
0.3	96.5574	158.5858	101.9198	160.526	100.9251	152.6964	105.0890	139.4447	107.2030	129.4512
0.4	81.1660	201.1301	83.7891	201.3131	96.2804	199.0654	103.3966	191.6639	112.8839	187.7237
0.5	101.0238	180.9495	102.5818	174.1585	100.7808	168.3739	96.3655	162.672	86.8781	156.9422
0.6	55.8643	129.917	59.8474	129.3441	58.2483	127.6619	60.5037	126.8936	60.0666	121.7924
0.7	-03.0827	39.0915	02.0969	41.7503	09.1143	43.0766	16.7354	41.6298	18.6938	40.3112
0.8	-36.8713	-17.1529	-28.0281	-16.0562	-27.0661	-13.8897	-22.7626	-13.6681	-22.1471	-11.5769
0.9	-42.3206	-25.9048	-38.1442	-21.9763	-34.9452	-19.7542	-30.8966	-20.4292	-32.3896	-18.4098
1	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000

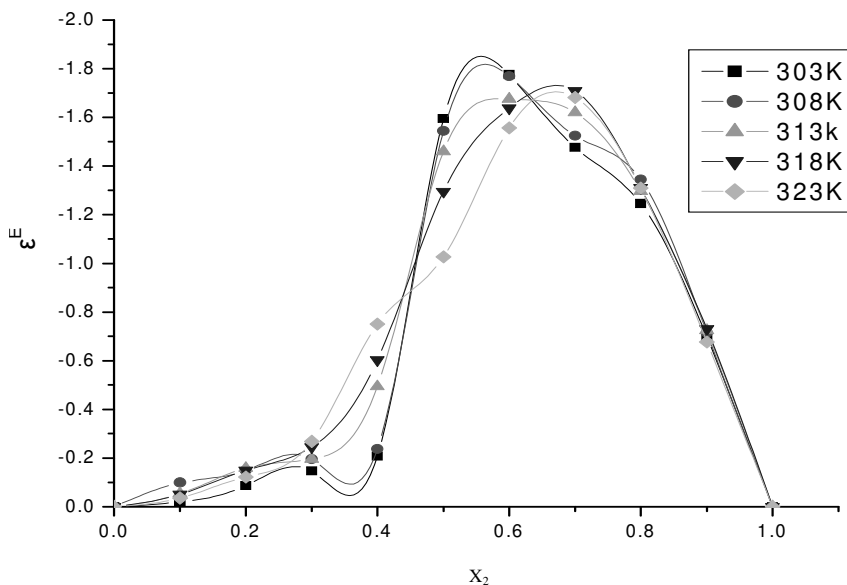


Figure 1. Plot of excess permittivity (ϵ^E) with mole fraction (x_2) of methyl benzoate in propan-1-ol for different temperatures

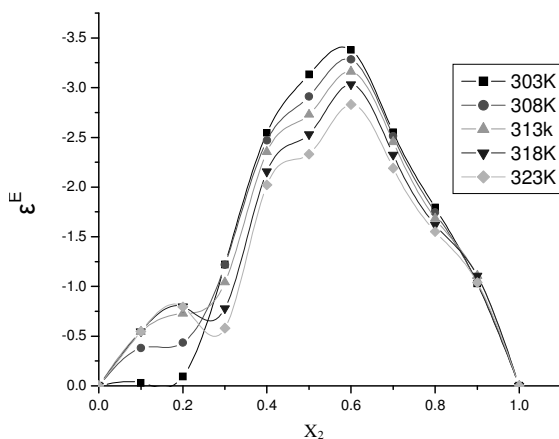


Figure 2. Plot of excess permittivity (ϵ^E) with mole fraction (x_2) of ethyl benzoate in propan-1-ol for different temperatures

The relaxation times (τ) of pure 1PN are higher and is due to the formation of intra molecular hydrogen bonding between one alcohol molecule and another (R—O—H...OH—R), which leads to the formation of self associated groups. The increase in the number of self associated groups causes to absorb more electromagnetic energy. Due to this molecules relax very slowly leading to higher relaxation times³⁵. But the relaxation times of pure MB and EB are very low²⁹ compared to pure 1PN. The relaxation times of pure EB are greater than that of pure MB due to the increase in molecular size and effective radius of the rotating unit³⁶. The relaxation times are found to decrease as the concentration of MB and EB increases in 1PN at all temperatures are given in Table 7.

Table 7. Values of relaxation time (τ in pico second) with mole fraction (x_2) of System 1 and System 2 at temperatures (303 to 323) K

x_2	T=303 K		T=308 K		T=313 K		T=318 K		T=323 K	
	System 1	System 2	System 1	System 2	System 1	System 2	System 1	System 2	System 1	System 2
0	246.23	246.23	216.72	216.72	186.71	186.71	169.25	169.25	157.68	157.68
0.1	216.16	217.21	200.51	201.22	177.52	179.51	162.26	163.44	150.12	153.55
0.2	191.94	197.27	184.56	189.45	171.58	173.21	158.48	159.33	144.52	147.42
0.3	168.41	173.42	162.78	167.54	155.26	160.96	147.27	151.55	139.82	140.44
0.4	142.25	145.42	135.38	137.23	129.63	130.15	122.83	126.24	117.61	120.15
0.5	117.13	121.24	110.88	114.67	104.23	108.25	97.66	101.45	91.25	96.76
0.6	94.57	98.59	87.64	92.73	81.37	86.94	75.94	81.24	68.66	76.34
0.7	66.12	86.23	59.15	79.45	51.53	75.21	44.54	69.49	39.21	66.21
0.8	46.73	61.25	39.96	54.21	32.52	48.24	26.84	42.15	21.52	39.27
0.9	25.15	36.21	19.54	29.28	15.15	24.13	11.54	19.49	9.62	13.76
1	12.82	13.42	11.49	11.81	8.25	10.24	7.28	07.94	5.71	07.13

At high concentrations of alcohol in the mixture, there are a large number of 1PN molecules surrounding the benzoate molecules and these associative alcohol molecules are forming hydrogen bond with the benzoate molecules. Thus dipole-dipole interaction occurs in such ways that the effective dipole moment gets increased and linear α -multimers are

formed³⁷. At low concentration of 1PN in the mixtures, there are only a small number of alcohol molecules to enable dipole-dipole interaction through hydrogen bonding with the non-associative benzoate molecules. As a result, weak intermolecular interaction occurs. The relaxation time increases with increasing alkyl chain length of benzoate indicating that the degree of cooperation for reorientation of the molecules increases with increasing length and the bulk of cluster increases. So the formation of hydrogen bonding between hydroxyl group (-OH) of 1PN and -CH group of benzoates restricts the free internal rotation of the molecules.

The excess inverse relaxation times are determined from the data of relaxation times obtained from the Cole-Cole plots. The calculated values of excess inverse relaxation time $\left(\frac{1}{\tau}\right)^E$, for both the systems, are negative and are presented in Figures 3 and 4 for the systems 1 and 2 respectively. These negative values indicate the slower rotation of dipoles due to the formation of hydrogen-bonded structures producing a field, which hinders the effective dipole rotation^{16,24}.

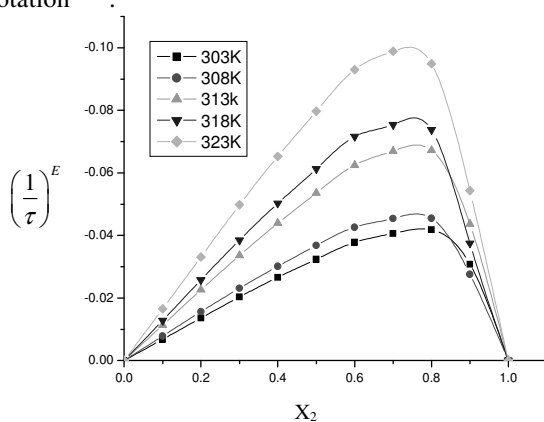


Figure 3. Plot of excess inverse relaxation time $\left(\frac{1}{\tau}\right)^E$ with mole fraction (x_2) of methyl benzoate in propan-1-ol for different temperatures

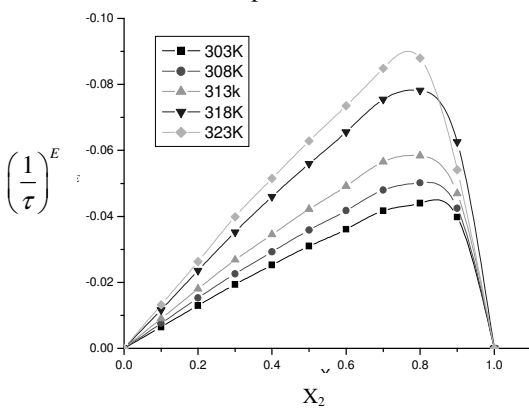


Figure 4. Plot of excess inverse relaxation time $\left(\frac{1}{\tau}\right)^E$ with mole fraction (x_2) of ethyl benzoate in propan-1-ol for different temperatures

The variation of excess Gibb's energy of activation ($\Delta G^*{}^E$) values, with mole fraction and temperature, for system 1 and system 2 are shown in Figures 5 and 6 respectively. The values of $\Delta G^*{}^E$ are positive, in both the systems, which indicates the presence of interaction between the molecules of the mixtures. The magnitude of $\Delta G^*{}^E$ is an excellent indicator of the strength of interaction between unlike molecules in liquid mixtures³⁸. It was reported by some researchers³⁹ attributed the increasing positive values of $\Delta G^*{}^E$ in few binary liquid mixtures, to hydrogen bond formation between unlike molecules, which supports the present investigation. Further, it is observed that $\Delta G^*{}^E$ values of system 2 are greater than that of system 1 indicating a stronger bond formation in system 2. The excess molar enthalpy ($\Delta H^*{}^E$) and excess molar entropy ($\Delta S^*{}^E$) values are shown in Figures 7 and 8 respectively. The negative values of ($\Delta H^*{}^E$), for both the systems, show that strong attractive interactions are present between unlike molecules of the mixtures⁴⁰. The formation of hydrogen bonding between the components in system 1 and system 2 is also justified by the negative values of excess molar entropy¹⁶.

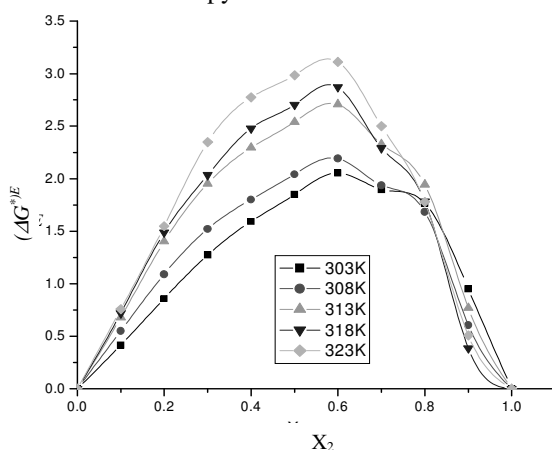


Figure 5. Plot of excess Gibb's energy of activation ($\Delta G^*{}^E$) with mole fraction (x_2) of methyl benzoate in propan-1-ol for different temperatures

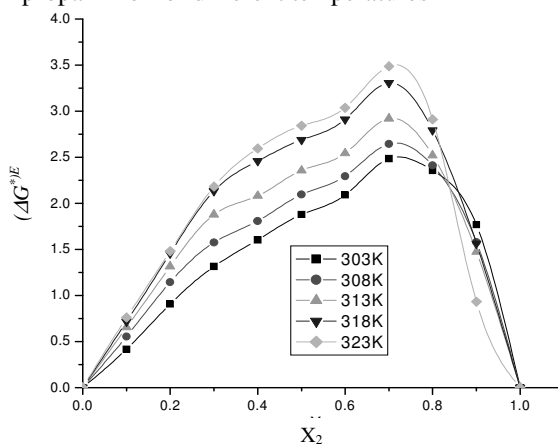


Figure 6. Plot of excess Gibb's energy of activation ($\Delta G^*{}^E$) with mole fraction (x_2) of ethyl benzoate in propan-1-ol for different temperatures

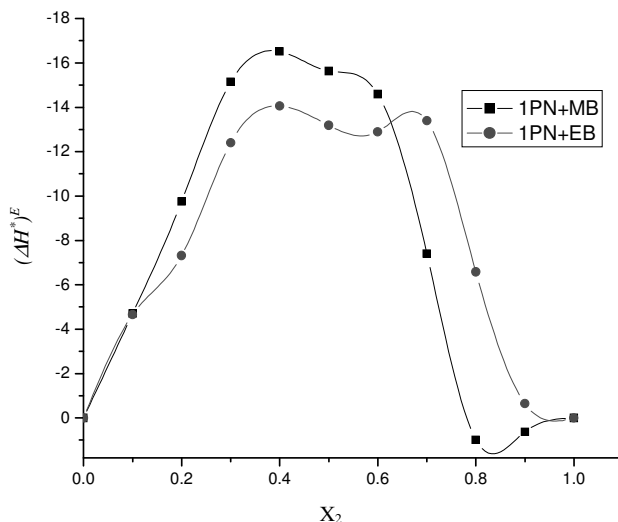


Figure 7. Plot of excess molar enthalpy $(\Delta H^*)^E$ with mole fraction (x_2) of methyl and ethyl benzoates in propan-1-ol for different temperatures

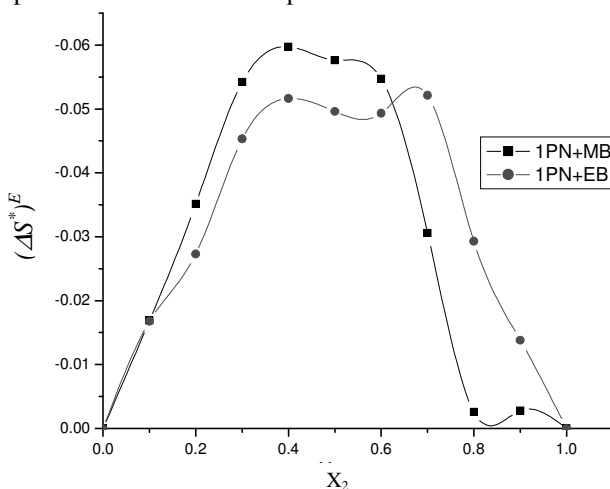
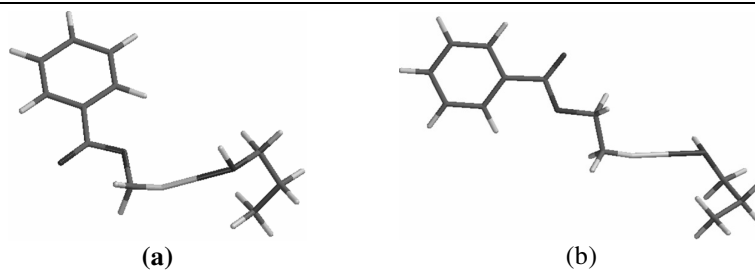


Figure 8. Plot of excess molar entropy $(\Delta S^*)^E$ with mole fraction (x_2) of methyl and ethyl benzoates in propan-1-ol for different temperatures

The hydrogen bonding energy or the interaction energy (ΔE) values are calculated, for both the systems, using Hamiltonian quantum mechanical calculations and are given in Table 8. The interaction energy between the components of a mixture should be negative if that mixture is stabilized by the presence of hydrogen bonds. Moreover the magnitude of the interaction energy would be a measure of the hydrogen-bonding stabilization. The hydrogen bonding energies in the present study are found to be negative in both the binary complexes, in all theoretical models, indicating the formation of hydrogen bonding²⁸. The optimized converged geometrical structures of hydrogen bonded systems 1 and 2, which are obtained from Hamiltonian quantum mechanical calculations, are shown in Figures 9(a), 9(b) respectively.

Table 8. Heat of formation (E, kcal mol⁻¹) and hydrogen bonding energy (ΔE , kcal mol⁻¹) (PCS- PC Spartan, AGS- Argus Lab)

Com- pound	AM1				PM3				MNDO			
	PCS		AGS		PCS		AGS		PCS		AGS	
	E	ΔE	E	ΔE	E	ΔE	E	ΔE	E	ΔE	E	ΔE
propan-1-ol	-69.53	---	-67.51	---	-66.35	---	-60.83	---	-67.72	---	-65.88	---
methyl benzoate	-61.18	---	-59.65	---	-57.90	---	-57.07	---	-57.99	---	-55.45	---
ethyl benzoate	-66.96	---	-65.07	---	-62.68	---	-57.07	---	-63.20	---	-55.45	---
propan-1-ol + methyl benzoate	-133.06	-2.34	-130.45	-3.28	-125.19	-0.94	-121.21	-3.30	-127.76	-2.05	-123.62	-2.28
propan-1-ol + ethyl benzoate	-139.57	-3.08	-135.50	-2.91	-129.71	-0.68	-125.55	-2.91	-132.74	-1.81	-128.51	-7.18

**Figure 9.** Optimized converged geometrical structure of hydrogen bonded methyl benzoate and propan-1-ol. methyl benzoate + 1PN, (b) ethyl benzoate + 1PN (Red: Oxygen, Black: Carbon, White: Hydrogen)

Conclusion

The excess dielectric and thermodynamical parameters - dipole moment, excess dipole moment, excess Helmholtz free energy, excess permittivity, relaxation time, excess inverse relaxation and excess thermodynamical values are computed for the pure and binary mixtures of system 1 (1PN + Methyl Benzoate) and system 2 (1PN + Ethyl Benzoate) for various mole fractions at different temperatures. The formation of Hydrogen bonding between the mixture systems is identified by studying the variations in the parameters determined. The values of dipole moment and excess dipole moment are determined theoretically using quantum mechanical calculations and are in good agreement with the experimental values.

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