Correlation Studies of Alkyl Benzoates with Alkanols at Different Temperatures

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Abstract

Correlation studies have been carried out for the liquid mixtures of Methyl/Ethyl benzoate + 1-Propanol, or +1-Butanol, or +1-Pentanol over the entire range of composition at different temperatures (303, 308, 313, 318 and 323) K. Thermo-acoustic parameters such as relaxation time (τ), excess Gibb's free energy (ΔG^{*E}) and excess Enthalpy (H^E) have been calculated from the experimentally determined data. These parameters are used to interpret the intermolecular interactions present in these binary mixtures.

Key words: Speed of sound, density, relaxation time, Gibbs free energy, Enthalpy, viscosity.

INTRODUCTION

Though spectroscopic methods play a major role in the molecular interaction studies, the non-spectral studies such as calorimetric, magnetic, ultrasonic velocity and viscosity measurements have also been widely used, in the elucidation of the formation of complexes. The aim of this study is to understand intermolecular and intramolecular interactions in a molecular system. Extensive studies have been done to understand these interactions on different types of binary polar mixtures. In recent years several researchers[1-4] have shown interest in measuring density, viscosity and speed of sound for a wide range of binary mixtures containing alcohols as one of the components, and these properties were interpreted in terms of specific or nonspecific interactions. Among the associating liquids, alcohols are undoubtedly the centre of interest. The molecules with –OH groups form associative liquid due to hydrogen bonding, the effect of the presence of molecules with other functional groups on these molecules is very important to understand the behavior of hydrogen bonding. Alkyl benzoates are nonassociated in solution, good hydrogen bonding acceptors and important industrial chemicals that are widely used in perfumery and pesticides. The associative liquids selected for the present study are 1-propanol/1-butanol/1-pentanol and methyl benzoate or ethyl benzoate is selected as a non associative liquid.

As a part of continuing study [5-8] on alkanols and alkyl benzoates, the authors aim at studying the correlations among thermodynamic behavior of pure and binary mixtures of (Methyl/Ethyl benzoate + 1-Propanol), (Methyl/Ethyl benzoate + 1-Butanol), (Methyl/Ethyl benzoate + 1-Pentanol) over the entire composition range at temperatures of (303, 308, 313, 318 and 323) K. Excess properties like excess Gibb's free energy (ΔG^{*E}), and excess enthalpy (H^E) give us better understanding about the nature and extent of intermolecular interactions in a molecular system.

EXPERIMENTAL

Materials

The chemicals used in the present study are, Ethyl benzoate, 1-Propanol, 1-Butanol and 1-Pentanol which are of AR grade obtained from Merck Co. Inc., Germany, with purities of greater than 99%.

Methods

All binary mixtures were prepared gravimetrically in air-tight bottles. The mass measurements were performed on a digital electronic balance (Mettler Toledo AB 135, Switzerland) with an uncertainty of ±0.00001g. The experimental procedure has been performed as described elsewhere[6].

RESULTS AND DISCUSSION

The non-linear variation of relaxation time (τ), excess Gibb's free energy (ΔG^{*E}) and excess enthalpy (H^E) in the solution with concentration of the solute has been qualitatively described to hydrogen bonding and their result confirms that the sign and magnitude of such deviation depends on the strength of interaction between unlike molecules.

Relaxation time is the time taken for the excitation energy to appear as translational energy and it depends on temperature and on impurities. The dispersion of the speed of sound in the system should contain information about the characteristic time τ of the relaxation process that causes dispersion. The relaxation time which is in the order of 10^{-12} sec is due to structural relaxation process [9] and in such a situation it is suggested that the molecules get rearranged due to co-operative process [10]. The relaxation time (τ) of pure 1-alkanols are high 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. Increase in the number of self associated group causes to absorb more electromagnetic energy. Due to this molecules relax very slowly leading to higher relaxation times [11]. But the relaxation times of pure methyl benzoate and ethyl benzoate are very low compared to pure 1-alkanols, which are reported in Table 1. The relaxation times are found to decrease as the concentration of methyl benzoate and ethyl benzoate increases in 1-alkanols at all temperatures. The relaxation times of pure ethyl benzoate are greater than that of pure methyl benzoate due to increase in molecular size

and effective radius of the rotating unit [12]. Further, the relaxation time increases with increasing alkyl chain length of ester, indicating that the degree of cooperativity for reorientation of the molecules increases with increasing length and the bulk of cluster increases. This is due to two effects: (i) the increase of viscosity as chain length increases and (ii) the increase of molecular size as the chain length increases. In all the systems, as the concentration of alcohols increases in the mixture, the relaxation time increases indicating the formation of multimers through linking of chain like structures of alcohols. Also, the systematic increase in the relaxation time indicates that the formation of multimers is concentration dependent. At low concentration of alkanols 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. Similar trend has been observed by earlier workers [13]. Figures 1(a) to 1(c) represent the excess Gibb's free energy of activation (ΔG^{*E}) with respect to mole fraction x_1, over the entire composition range and at T = (303, 308, 313, 318, and 323) K. It can be observed from figures 1(a) to 1(c) that the ΔG^{*E} values are positive at all temperatures and over the entire range of mole fraction.

Table.1 Relaxation time (τ x10^{-12} sec) for liquid mixtures of methyl/ethyl benzoates with 1-alkanols at various temperatures.

X₁	1-propanol					1-butanol					1-pentanol				
	303K	308K	313K	318K	323K	303K	308K	313K	318K	323K	303K	308K	313K	318K	323K
Methyl Benzoate															
0.0000	1.8834	1.7539	1.6676	1.5980	1.5642	2.2810	2.0825	1.8978	1.7701	1.6777	3.1716	2.8810	2.5164	2.3293	2.1990
0.0604	1.7534	1.6090	1.5519	1.4944	1.4725	2.0792	1.9174	1.7643	1.6452	1.5677	2.8375	2.5860	2.2543	2.1153	2.0232
0.1263	1.6401	1.5155	1.4553	1.4016	1.3909	1.9157	1.7748	1.6396	1.5355	1.4717	2.5355	2.3322	2.0485	1.9268	1.8538
0.1986	1.5509	1.4313	1.3696	1.3206	1.3049	1.7796	1.6536	1.5279	1.4361	1.3814	2.2724	2.0836	1.8628	1.7621	1.7055
0.2782	1.4573	1.3548	1.2871	1.2447	1.2294	1.6427	1.5354	1.4247	1.3425	1.2980	2.0067	1.8769	1.6861	1.6041	1.5646
0.3664	1.3720	1.2843	1.2225	1.1768	1.1634	1.5281	1.4294	1.3322	1.2589	1.2200	1.7852	1.6748	1.5206	1.4600	1.4302
0.4645	1.3009	1.2134	1.1600	1.1176	1.1072	1.4148	1.3264	1.2408	1.1791	1.1467	1.5889	1.5108	1.3803	1.3324	1.3134
0.5743	1.2321	1.1517	1.0994	1.0586	1.0460	1.3127	1.2303	1.1633	1.1065	1.0785	1.4301	1.3586	1.2554	1.2128	1.1958
0.6982	1.1647	1.0972	1.0421	1.0076	0.9917	1.2197	1.1431	1.0822	1.0406	1.0139	1.2880	1.2281	1.1420	1.1062	1.0922
0.8388	1.1100	1.0436	0.9888	0.9566	0.9467	1.1305	1.0666	1.0121	0.9741	0.9553	1.1671	1.1006	1.0371	1.0074	0.9906
1.0000	1.0552	0.9939	0.9436	0.9151	0.8998	1.0552	0.9939	0.9436	0.9151	0.8998	1.0552	0.9939	0.9436	0.9151	0.8998
Ethyl Benzoate															
0.0000	1.8834	1.7539	1.6676	1.5980	1.5642	2.2810	2.0825	1.8978	1.7701	1.6777	3.1716	2.8810	2.5164	2.3293	2.1990
0.0738	1.8297	1.7092	1.6140	1.5404	1.5179	2.1145	2.0351	1.7970	1.6530	1.5952	2.8789	2.6240	2.3885	2.2172	2.0368
0.1519	1.7474	1.6330	1.5389	1.4785	1.4546	2.0038	1.9154	1.7023	1.5770	1.5069	2.6591	2.4336	2.1950	2.0486	1.8996
0.2350	1.6635	1.5529	1.4678	1.4063	1.3865	1.8857	1.7952	1.6073	1.4965	1.4191	2.4482	2.2353	2.0236	1.9004	1.7679
0.3233	1.5878	1.4768	1.4027	1.3466	1.3205	1.7726	1.6892	1.5304	1.4212	1.3426	2.2457	2.0573	1.8658	1.7575	1.6449
0.4175	1.5317	1.4118	1.3376	1.2860	1.2565	1.6713	1.5877	1.4467	1.3460	1.2751	2.0435	1.8920	1.7134	1.6309	1.5346
0.5181	1.4587	1.3556	1.2687	1.2269	1.1963	1.5800	1.4810	1.3702	1.2888	1.2100	1.8574	1.7185	1.5703	1.4946	1.4083
0.6258	1.4029	1.3011	1.2204	1.1723	1.1425	1.4897	1.3896	1.2960	1.2293	1.1538	1.6832	1.5639	1.4403	1.3629	1.2987
0.7414	1.3463	1.2516	1.1677	1.1289	1.0946	1.4034	1.3060	1.2308	1.1720	1.1025	1.5129	1.4149	1.3181	1.2545	1.1907
0.8658	1.2924	1.2069	1.1257	1.0850	1.0414	1.3336	1.2289	1.1701	1.1219	1.0503	1.3715	1.2798	1.1992	1.1438	1.0943
1.0000	1.2369	1.1534	1.0730	1.0296	0.9857	1.2369	1.1534	1.0730	1.0296	0.9857	1.2369	1.1534	1.0730	1.0296	0.985

These positive values indicate the existence of strong intermolecular interaction through hydrogen bonding between the component molecules of the liquid mixtures under study. But as the ester chain increases the methylene (-CH$_2$) groups increase which produce greater steric hindrance to the formation of hydrogen bonds between the ethyl benzoate and alkanol molecule. So relatively weaker hydrogen bonding is expected in ethyl benzoate + 1-alkanol systems which are reflected from the values of ΔG^{*E} in these mixtures. The positive values of ΔG^{*E} are due to the formation of β-clusters and these β-clusters are characterized by reduced internal energy, making ΔG^{*E} positive. The higher positive values of ΔG^{*E}, in the case of methyl benzoate + 1-alkanols system compared to that of ethyl benzoate + 1-alkanols, indicate that the formation of β-clusters is high in methyl benzoate system. 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 energy. The negative values of ΔG^{*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. In the present work, in both the systems, it is observed that the orientation of dipoles has been changed from parallel to anti parallel which should form β-clusters with positive values of ΔG^{*E}. This effect is witnessed for all temperatures. Similar trend for ΔG^{*E} has been observed by earlier workers [14].

From figures 2(a) to 2(c) it is evident that the excess values of Enthalpy (H^E) are negative with respect to the mole fraction, x_1, over the entire composition range and at T = (303, 308, 313, 318, and 323) K. The negative H^E values suggest the existence of inter molecular hydrogen bond and the breaking of associated structures in case of these benzoates with 1-propanol or 1-butanol or 1-pentanol. As the length of the 1-alkanols increases the H^E values also decrease. The negative values of H^E insist the fact that there are strong specific interactions between unlike molecules in these liquid mixtures [15]. This may be due to the intermediate compound formation between binary liquids. This observation confirms the formation of hydrogen bonding in binary mixtures. With increase in the temperature the thermal agitation increases and the dipole requires more energy in order to attain the equilibrium with the applied field and results in negative H^E values. This indicates that the activated state is more ordered than the normal state, which is true because in the activated state the dipoles try to align with the applied field. In the present systems the H^E values in case of ethyl benzoate system are less than in the methyl benzoate system, which indicates that the strength of bond formation in ethyl benzoate system is greater than in methyl benzoate system. This also leads to the conclusion that the heterogeneous interaction between the compounds in the binary liquid systems, possibly between the –OH group of alcohol and –CH group of benzoates, is in such a way to form multimers with decreasing parallel orientation of electric dipoles. The strength of the heterogeneous interaction is found to depend

on the temperature and concentration of the mixture, which shows that temperature and concentration variations impact the structural properties.

Observing the FT-IR spectra given in Fig.3, 4 for the equi molar binary mixture of methyl benzoate + 1-propanol, there is a hypsochromic shift of 163 cm^{-1} wave number in the position of –OH and a hypsochromic shift of 11 cm^{-1} wave number in the position of –CH for the mixture compared with the pure spectrums of propan-1-ol and methyl benzoate respectively. Similarly the FT-IR spectra for the equi molar mixture ethyl benzoate + 1-propanol, there is a hypsochromic shift of 199 cm^{-1} wave number in the position of –OH and a bathochromic shift of 12 cm^{-1} wave number in the position of –CH for the mixture compared with the pure spectrums of 1-propanol and ethyl benzoate respectively. These shifts are caused by the strong interaction between the high electro-negative charge of oxygen in 1-propanol and hydrogen of the benzoates.
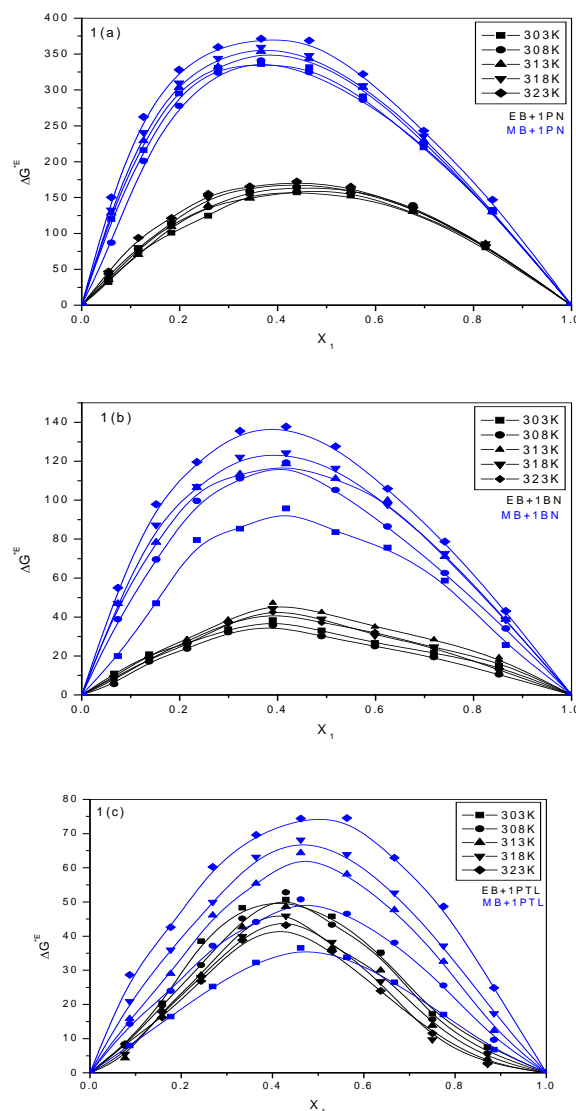

Fig. 1(a), 1(b), 1(c) represents the variation of excess Gibb's free energy with respect to mole fraction at various temperatures.
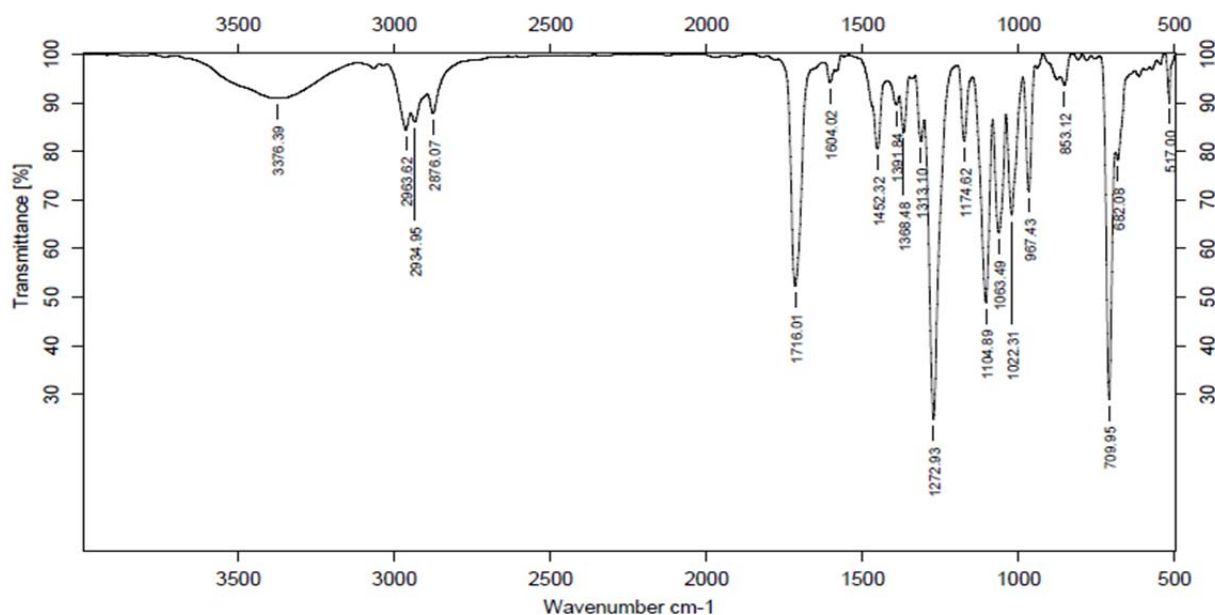
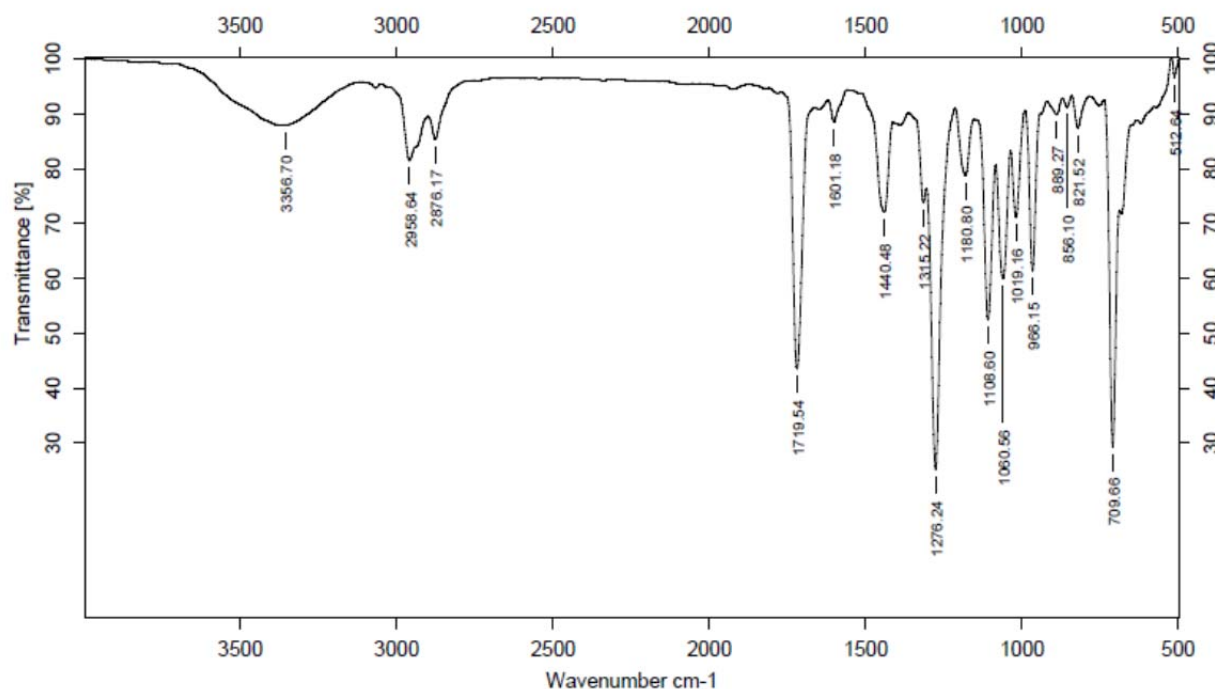Fig.3 FT-IR of Ethylbenzoate + propanol mixture.

Fig.4 FT-IR of Methylbenzoate + propanol mixture.

Thus the IR analysis convinces intermolecular hydrogen bonding of the equi molar binary mixtures effectively with proportionate variations in stretching frequencies of –OH and –CH compared to their respective pure systems [16]. Similarly the results also support the hydrogen bond formation in the mixtures of methyl/ethyl benzoate with 1-butanol/1-pentanol. Also the existence of hydrogen bond is confirmed by earlier workers [13] both theoretically and experimentally, and hence the results obtained here support the same.

Apart from these studies the hydrogen bond formation was confirmed from the evaluation of other excess parameters like excess isentropic compressibility, excess molar volume and excess free length [6,7]. The variations in the above parameters with mole fraction and temperature predict the presence of hydrogen bonding between the compounds in these systems. The strength of bond formation between the compounds in ethyl benzoate system is more than that of methyl benzoate, because of the increased chain length and larger effective radius of the rotating unit of pure ethyl benzoate when compared to that of pure methyl benzoate. Further, the parameters determined, in this paper, correlate with one another and at the same time each parameter supports the formation of hydrogen bonding in the mixture systems.
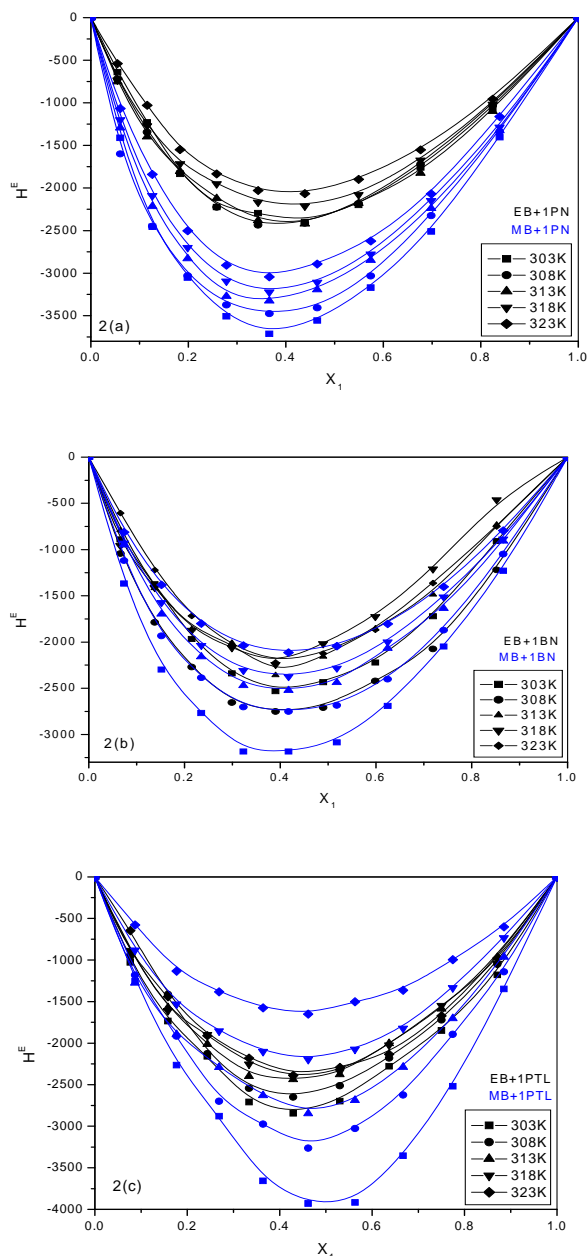
Fig. 2(a), 2(b), 2(c) represents the variation of excess enthalpy with respect to mole fraction at various temperatures.

CONCLUSION

Relaxation time, excess Gibb's free energy and excess enthalpy have been calculated and compared for binary mixtures of 1-alkanols and alkyl benzoates. Further, the information about the molecular association has been analyzed from relaxation time studies. The formation of hydrogen bonding in the equimolar binary mixture systems is confirmed from the FT-IR spectra. The kind of changes that take place in these systems when the alkanol and alkyl chain length increases has been explained in terms of the interactions present in these systems and found that the strength of interactions is more in ethyl benzoate system. Correlations studied in the present study among the parameters provide valuable information to understand the underlying physics.

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