

Excess Thermodynamic Properties of Binary Mixtures of Dimethyl Malonate with some Branched Alkanols

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Abstract

The intermolecular hydrogen bond interactions in the dimethyl malonate with some branched alkanols (2-methyl-1-propanol, 2-propanol, and 2-butanol) binary mixture have been studied experimentally and theoretically. The ultrasonic velocities U , densities ρ of binary mixtures of dimethyl malonate with 2-methyl-1-propanol, 2-propanol, 2-butanol from 303.15 K to 318.15 K were measured. Excess molar volume (V^E), deviation in adiabatic compressibility ($\Delta\beta_{ad}$) and excess intermolecular free length (L_f^E) have been calculated from the measured experimental data. It is observed that the order of interactions in dimethyl malonate – branched alkanols mixtures is 2-methyl-1-propanol > 2-propanol > 2-butanol.

Keywords: Dimethyl malonate; Branched alcohols; Deviation in adiabatic compressibility; Excess molar volumes; Excess intermolecular free lengths.

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1. Introduction

Optical and ultrasonic techniques have been used to investigate complex formations in liquid mixtures. The formation of hydrogen bonds in solutions and their impact on mixture physical characteristics have gotten much attention. Even though many experimental and theoretical investigations have been conducted to understand hydrogen bonding better, it is still a topic of current research. Theoretical and process design considerations necessitate knowledge of the physicochemical properties of liquid mixtures generated by two or more components linked by hydrogen bonds. Volumetric features of

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these mixes are key sources of information for characterization of the interactions between the components and for comprehending the liquid state theory from a theoretical standpoint. Furthermore, alcohols and amines are frequently employed in various industrial and consumer applications; thus, understanding their physical properties is crucial from a practical standpoint. The liquids used in this study were chosen because of their industrial significance. Dimethyl malonate is employed as a reagent in the manufacturing of barbiturates, artificial flavorings, vitamin B1, and vitamin B6. Alcohols are employed as hydraulic fluids in pharmaceuticals and cosmetics, as well as in animal remedies, perfumes, paint removers, flavors, and dyestuffs, as well as for defrosting and antibacterial purposes.

We report here the excess molar volume V^E , Deviation in adiabatic compressibility $\Delta\beta_{ad}$ and excess intermolecular free length L_f^E of the binary systems: dimethyl malonate with (2-propanol, 2-butanol, and 2-methyl-1-propanol). These findings have been used to analyze the branching effect in the alkanol and hydroxyl group's position in the interaction with the dimethyl malonate in terms of hydrogen bonding and dipole-dipole interaction. According to a literature review, these parameters are not provided for the selected systems.

The goal of this study was to see how the position of an alcohol molecule's -OH group affects the sign and amplitude of numerous thermodynamic functions when mixed with dimethyl malonate. Recently, substantial research work has been reported on the excess properties of 2-butanol + Monoethanol amine [1], Formamide + 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol [2], 2-propanol + *n*-alkanes (C6-C10) systems [3], nitro methane with 2-propanol, 2-butanol and 2-pentanol [4], benzyl alcohol with 1-butanol, 2-butanol, 2-methyl-1-butanol and 30-butanol [5] butyl acetate with 2-propanol, 2-butanol and 2-pentanol [6], N-propylamine + 2-alkanols (2-propanol, 2-butanol, 2-pentanol) [7], aniline and nitro benzene with 2-methyl-1-propanol [8] and N,N-dimethylformamide with 2-butanol and 2-pentanol [9]. In terms of hydrogen bonding, dipole-dipole interaction, proton-acceptor interaction, and dispersive forces, the findings have been utilized to explain the nature of the interaction between dissimilar molecules.

2. Experimental Techniques

2.1. Material and methods

Using a single crystal variable-path multi-frequency ultrasonic interferometer operating at 3 MHz, the ultrasonic velocities in pure liquids and in their binary mixtures were measured. Using conductivity water, the double-arm pycnometer is optimized with as density of 995.61 kg m⁻³ at 303.15 K. To hold the temperature constant, a thermostat with an accuracy of ± 0.01 K is used. The weighings are carried out using the digital balance of Mettler Toledo (Switzerland make) ABB5-S /FACT with a precision of ± 0.01 mg. The liquid samples; (dimethyl malonate, 2-propanol, 2-methyl-1-propanol, 2-butanol) used for the present investigation are of analytical grade quality, obtained from Loba chemicals, with > 99 % purity.

2.2. General procedure

2.2.1. Ultrasonic velocity measurement

In the cell, which is mounted on the pedestal, the liquid mixture in which the ultrasonic speed must be overcome is taken. The micrometer head is gradually shifted so that the reflector is as far away from the crystal as possible. The reflector is now gently rotated towards the crystal by gently rotating the micrometer head. The current in the micrometer is highest at a particular location of the reflector. The 0th peak corresponds to this reading. Micrometer readings for the 1st, 2nd, 3rd, 4th, 5th, 6th, 7th, 8th, 9th, and 10th peaks are taken similarly by turning the head in the same direction, removing backlash error. The distance shifted by the reflector for five peaks is calculated by subtracting the micrometer readings corresponding to the 0th and 5th peaks. Similarly, the difference between the readings for the 1st and 6th, 2nd and 7th, and 3rd and 8th peaks are noted, followed by the average value of the distance moved by the reflector for 5 peaks.

2.2.2. Density measurements

The density of the liquids was used as one of the purity requirements. The density (ρ) of pure liquids and all liquid mixtures is determined in this study using a 10^5 m^3 double-arm pycnometer at 303.15, 308.15, 313.15, and 318.15 K. At 303.15 K, as described by Nikkam *et al.* [10,11]. The pycnometer is calibrated using conductivity water with a density of 995.61 kg m^3 . A moving microscope with a resolution of 0.01 mm records the location of the liquid levels in the two arms of the air bubble-free pycnometer. The density values obtained from triplicate replication at each temperature are repeatable within $2 \times 10^{-1} \text{ kg/m}^3$, with a measurement uncertainty of 2 parts in 10^4 parts. To achieve thermal equilibrium, the pycnometer was placed in the thermostat for 20 min.

3. Result and Discussion

The investigational values of speed of sound and densities, deviation in adiabatic compressibility, excess molar volume, the excess intermolecular free length of liquid mixtures of DMM with 2-methyl-1-propanol, 2-propanol, 2-butanol over the entire composition range expressed in mole fraction X_1 of DMM ($0 \leq X_1 \leq 1$), at different temperatures, are listed in Table 2. From Table 1, it is clear that experimental values are in strong agreement with the literature values.

Table 1. Comparison of experimental values with literature data at 303.15 K.

Liquid	Ultrasonic velocity (U)m/s		Density (ρ) Kg/m ³	
	Experimental	Literature	Experimental	Literature
Dimethyl malonate	1365.2	1365.2 [12]	1.1423	1.1423[12]
2-Methyl-1-propanol	1104.7	1105.6 [15]	0.7895	0.7902[14]
2- Propanol	1105.0	1115.1 [15]	0.7715	0.7724[16]
2-Butanol	1141.0	1140.5 [13]	0.7936	0.7941[16]

Studying the excess parameters is necessary to substantiate the existence of interaction among the molecules. Excess liquid mixture parameters are used to calculate the deviation from ideality in liquid mixture behavior. The molecular interactions are explained by considering both a positive and a negative contribution of the excess parameters.

The excess values of molar volume (V^E) and intermolecular free length (L_f^E), and deviation in adiabatic compressibility ($\Delta\beta_{ad}$) are shown in Table 2. They are calculated by using the following standard relations:

$$\text{Excess volume} \quad (V^E) : V^E = (V - (V_1X_1 + V_2X_2)) \quad (1)$$

$$\text{Deviation in adiabatic compressibility} \quad (\Delta\beta_{ad}) : \Delta\beta_{ad} = \beta_{ad1}X_1 + \beta_{ad2}X_2 \quad (2)$$

$$\text{Excess intermolecular free length} \quad (L_f^E) : L_f^E = L_f - (L_{f1}X_1 + L_{f2}X_2) \quad (3)$$

Table 2. Ultrasonic velocity (U), density (ρ), deviation in adiabatic compressibility ($\Delta\beta_{ad}$), excess molar volume (V^E) and excess intermolecular free length L_f^E of DMM + 2-M1-P, +2-propanol, +2-butanol systems at 303.15, 308.15, 313.15, and 318.15 K.

Mole fraction X_1	Velocity U m/s	Density ρ gm/cm ³	$\Delta\beta_{ad}X10^{-12}$ m ² N ⁻¹	V^E cm ³ mol ⁻¹	L_f^E Å
2-Methyl-1-propanol					
303.15 K					
0.0000	1111.0	0.7933	0.0000	0.0000	0.0000
0.0824	1125.2	0.8298	-3.6532	-0.1837	-0.0291
0.1680	1140.8	0.8657	-6.5399	-0.2929	-0.0523
0.2572	1158.1	0.9013	-8.7284	-0.3630	-0.0699
0.3500	1177.5	0.9367	-10.2282	-0.4084	-0.0819
0.4469	1199.2	0.9720	-11.0281	-0.4466	-0.0882
0.5479	1223.7	1.0070	-11.0255	-0.4510	-0.0879
0.6534	1251.7	1.0415	-10.0938	-0.4011	-0.0802
0.7637	1283.9	1.0756	-8.1166	-0.3182	-0.0641
0.8791	1321.3	1.1091	-4.8401	-0.1732	-0.0379
1.0000	1365.20	1.1423	0.0000	0.0000	0.0000
308.15 K					
0.0000	1104.7	0.7895	0.0000	0.0000	0.0000
0.0824	1118.9	0.8268	-3.6909	-0.2711	-0.0295
0.1680	1134.3	0.8630	-6.5423	-0.3936	-0.0525
0.2572	1151.3	0.8989	-8.7351	-0.4804	-0.0703
0.3500	1170.1	0.9345	-10.2624	-0.5295	-0.0826
0.4469	1191.4	0.9701	-11.0633	-0.5754	-0.0890
0.5479	1215.5	1.0052	-11.0394	-0.5660	-0.0886
0.6534	1243.0	1.0399	-10.1188	-0.5175	-0.0809
0.7637	1274.1	1.0740	-8.2241	-0.3952	-0.0654
0.8791	1311.2	1.1075	-4.8638	-0.2219	-0.0384
1.0000	1354.50	1.1405	0.0000	0.0000	0.0000
313.15 K					
0.0000	1096.0	0.7853	0.0000	0.0000	0.0000
0.0824	1108.9	0.8230	-3.7020	-0.2923	-0.0299
0.1680	1123.2	0.8598	-6.5497	-0.4686	-0.0531
0.2572	1138.6	0.8960	-8.7419	-0.5542	-0.0710
0.3500	1155.8	0.9321	-10.2901	-0.6266	-0.0838

0.4469	1175.2	0.9680	-11.1208	-0.6750	-0.0906
0.5479	1197.6	1.0035	-11.0520	-0.6647	-0.0900
0.6534	1222.8	1.0383	-10.1618	-0.5808	-0.0826
0.7637	1252.0	1.0728	-8.2623	-0.4651	-0.0669
0.8791	1287.3	1.1069	-4.8894	-0.3039	-0.0393
1.0000	1328.25	1.1396	0.0000	0.0000	0.0000
318.15 K					
0.0000	1089.5	0.7800	0.0000	0.0000	0.0000
0.0824	1101.7	0.8181	-3.7092	-0.3302	-0.0300
0.1680	1115.2	0.8553	-6.5563	-0.5254	-0.0534
0.2572	1129.4	0.8919	-8.8279	-0.6462	-0.0722
0.3500	1145.6	0.9282	-10.3228	-0.7111	-0.0846
0.4469	1163.8	0.9645	-11.1586	-0.7685	-0.0916
0.5479	1185.0	1.0006	-11.1087	-0.7898	-0.0913
0.6534	1209.0	1.0359	-10.2105	-0.7278	-0.0838
0.7637	1236.8	1.0707	-8.2927	-0.5977	-0.0679
0.8791	1270.4	1.1045	-4.9020	-0.3699	-0.0399
1.0000	1309.65	1.1370	0.0000	0.0000	0.0000
2-Propanol					
303.15 K					
0.0000	1110.0	0.7763	0.0000	0.0000	0.0000
0.0692	1127.7	0.8145	-2.9030	-0.1599	-0.0229
0.1434	1146.6	0.8524	-5.1290	-0.2859	-0.0406
0.2229	1166.9	0.8898	-6.6784	-0.3574	-0.0530
0.3086	1188.7	0.9268	-7.6121	-0.3937	-0.0604
0.4010	1212.3	0.9638	-8.0024	-0.4331	-0.0634
0.5010	1237.9	1.0003	-7.7564	-0.4238	-0.0614
0.6097	1265.6	1.0364	-6.8791	-0.3791	-0.0543
0.7281	1295.8	1.0719	-5.3026	-0.2750	-0.0416
0.8576	1328.9	1.1070	-3.0060	-0.1294	-0.0235
1.0000	1365.2	1.1423	0.0000	0.0000	0.0000
308.15 K					
0.0000	1105.0	0.7715	0.0000	0.0000	0.0000
0.0692	1122.3	0.8105	-3.0475	-0.2231	-0.0241
0.1434	1140.8	0.8489	-5.3316	-0.3753	-0.0424
0.2229	1160.6	0.8865	-6.8956	-0.4538	-0.0549
0.3086	1182.0	0.9239	-7.8518	-0.5052	-0.0625
0.4010	1205.0	0.9615	-8.2795	-0.5730	-0.0659
0.5010	1230.0	0.9982	-8.0110	-0.5582	-0.0637
0.6097	1257.1	1.0342	-7.0441	-0.4649	-0.0559
0.7281	1286.7	1.0700	-5.4407	-0.3524	-0.0430
0.8576	1319.0	1.1052	-3.0911	-0.1802	-0.0243
1.0000	1354.5	1.1405	0.0000	0.0000	0.0000
313.15 K					
0.0000	1097.0	0.7676	0.0000	0.0000	0.0000
0.0692	1113.0	0.8073	-3.1973	-0.2838	-0.0255
0.1434	1130.2	0.8462	-5.5461	-0.4630	-0.0444
0.2229	1148.6	0.8840	-7.1091	-0.5388	-0.0571
0.3086	1168.4	0.9219	-8.0990	-0.6138	-0.0652
0.4010	1189.8	0.9597	-8.4917	-0.6698	-0.0684
0.5010	1213.0	0.9963	-8.1460	-0.6167	-0.0656
0.6097	1238.1	1.0329	-7.1991	-0.5486	-0.0579
0.7281	1265.5	1.0689	-5.5510	-0.4183	-0.0446

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0.8576	1295.5	1.1049	-3.2358	-0.2813	-0.0259
1.0000	1328.5	1.1396	0.0000	0.0000	0.0000
318.15 K					
0.0000	1090.0	0.7625	0.0000	0.0000	0.0000
0.0692	1105.2	0.8027	-3.3071	-0.3271	-0.0264
0.1434	1121.5	0.8418	-5.6934	-0.5187	-0.0457
0.2229	1139.0	0.8803	-7.3458	-0.6426	-0.0593
0.3086	1157.8	0.9183	-8.3145	-0.7077	-0.0673
0.4010	1178.1	0.9562	-8.6779	-0.7519	-0.0704
0.5010	1200.0	0.9934	-8.3606	-0.7262	-0.0679
0.6097	1223.9	1.0300	-7.3547	-0.6299	-0.0597
0.7281	1249.9	1.0667	-5.7428	-0.5387	-0.0466
0.8576	1278.4	1.1025	-3.3265	-0.3419	-0.0269
1.0000	1309.7	1.1370	0.0000	0.0000	0.0000
2-Butanol					
303.15 K					
0.0000	1150.0	0.7984	0.0000	0.0000	0.0000
0.0819	1167.6	0.8342	-2.0037	-0.1567	-0.0155
0.1671	1186.0	0.8695	-3.4670	-0.2579	-0.0269
0.2560	1205.1	0.9045	-4.4598	-0.3240	-0.0347
0.3486	1225.0	0.9396	-5.0648	-0.3905	-0.0394
0.4453	1245.8	0.9744	-5.2526	-0.4281	-0.0409
0.5463	1267.6	1.0087	-5.0015	-0.4134	-0.0390
0.6519	1290.3	1.0427	-4.3570	-0.3693	-0.0340
0.7625	1314.1	1.0762	-3.2926	-0.2746	-0.0256
0.8784	1339.0	1.1091	-1.7981	-0.1211	-0.0140
1.0000	1365.2	1.1423	0.0000	0.0000	0.0000
308.15 K					
0.0000	1141.0	0.7936	0.0000	0.0000	0.0000
0.0819	1158.5	0.8300	-2.0887	-0.2111	-0.0162
0.1671	1176.7	0.8659	-3.6148	-0.3553	-0.0282
0.2560	1195.6	0.9014	-4.6386	-0.4459	-0.0363
0.3486	1215.4	0.9367	-5.2217	-0.5037	-0.0409
0.4453	1236.1	0.9720	-5.4356	-0.5623	-0.0426
0.5463	1257.6	1.0066	-5.1747	-0.5438	-0.0406
0.6519	1280.2	1.0406	-4.4722	-0.4614	-0.0351
0.7625	1303.8	1.0743	-3.3820	-0.3474	-0.0265
0.8784	1328.5	1.1074	-1.8685	-0.1767	-0.0146
1.0000	1354.5	1.1405	0.0000	0.0000	0.0000
313.15 K					
0.0000	1137.5	0.7896	0.0000	0.0000	0.0000
0.0819	1153.1	0.8266	-2.2617	-0.2612	-0.0176
0.1671	1169.4	0.8630	-3.9071	-0.4428	-0.0305
0.2560	1186.3	0.8987	-4.9504	-0.5248	-0.0388
0.3486	1204.0	0.9345	-5.5880	-0.6099	-0.0439
0.4453	1222.5	0.9700	-5.7794	-0.6588	-0.0455
0.5463	1241.7	1.0046	-5.4444	-0.6045	-0.0430
0.6519	1261.9	1.0391	-4.7212	-0.5305	-0.0373
0.7625	1283.0	1.0730	-3.5654	-0.4011	-0.0282
0.8784	1305.1	1.1070	-2.0592	-0.2737	-0.0163
1.0000	1328.3	1.1396	0.0000	0.0000	0.0000
318.15 K					
0.0000	1132.4	0.7845	0.0000	0.0000	0.0000

0.0819	1146.9	0.8221	-2.4187	-0.3224	-0.0188
0.1671	1162.0	0.8587	-4.1089	-0.5102	-0.0320
0.2560	1177.8	0.8950	-5.2471	-0.6397	-0.0411
0.3486	1194.2	0.9308	-5.8531	-0.7008	-0.0460
0.4453	1211.3	0.9665	-6.0279	-0.7422	-0.0476
0.5463	1229.3	1.0017	-5.7271	-0.7213	-0.0453
0.6519	1248.0	1.0363	-4.9588	-0.6319	-0.0394
0.7625	1267.6	1.0709	-3.8130	-0.5320	-0.0303
0.8784	1288.1	1.1047	-2.1848	-0.3415	-0.0174
1.0000	1309.7	1.1370	0.0000	0.0000	0.0000

4. Discussion

There is interdependence between the intermolecular free length and ultrasonic velocity. As a consequence of combining materials, the ultrasonic velocity decreases if the intermolecular free length increases or vice versa. This is found for DMM + 2-methyl-1-propanol, DMM + 2-propanol, and DMM + 2-butanol systems in the present investigation. With an increase in temperature, we also see a drop in velocity due to splitting hetero and homo molecular clusters.

In a binary liquid mixture, the relative degree of expansion or contraction is responsible for the sign of (V^E). In this investigation, the V^E values for all binary mixtures of DMM with sub-alkanols are negative over the entire composition spectrum and are shown in Figs. 1A, 1B, and 1C. The negative V^E values suggest that volume contraction occurs when dimethyl malonate is combined with sub-alkanols due to the formation of hydrogen bonds between different molecules.

The negative algebraic V^E values of dimethyl malonate with alkanols fell in the order of: 2-methyl-1-propanol > 2-propanol > 2-butanol. 2-methyl-1-propanol has two $-CH_3$ groups on its α -carbon atom; hence its negative V^E value grows as the number of $-CH_3$ groups increases [17]. V^E plots against mole fractions are of parabolic shape characterized by well-defined minima occurring at around 0.5 mole fractions suggesting the existence of complex formation.

Deviation in adiabatic compressibility is observed to be negative over the mole fraction of DMM from Figs. 2A, 2B, and 2C, indicating the existence of strong interactions among the molecules. As a consequence of molecular interaction between the component molecules in the liquid mixtures, the sign, and magnitude of $\Delta\beta_{ad}$ play a vital role in determining molecular structure. The negative $\Delta\beta_{ad}$ in the studied mixtures can be explained by hydrogen bonding between the oxygen atom of dimethyl malonate and the hydrogen atom of the hydroxyl group of 2-alkanol molecules based on the complex formation between dimethyl malonate and 2-alkanol molecules. This is in line with the view put forward by Fort and Moore [18] that liquids of different molecular sizes typically combine with volume decreases that yield negative values in intermolecular free length, adiabatic compressibility.

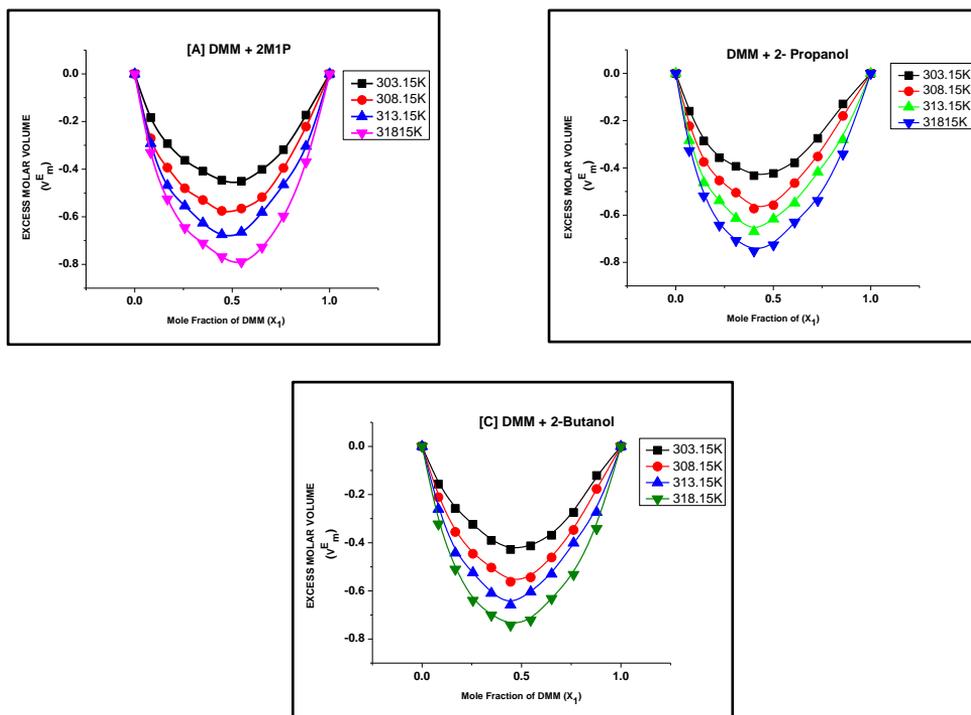


Fig. 1. Variation of excess molar volume with the mole fraction of DMM for the systems [A] DMM + 2-M1-P, [B] DMM + 2-propanol and [C] DMM + 2-butanol.

According to Jacobson, the intermolecular free length refers to the distance among the surfaces of neighboring molecules [19]. Due to the mixing phase, an increase in free length contributes to a decrease in sound velocity. This implies that free duration is the primary factor in evaluating the essence of the variance of ultrasonic velocity in the liquid mixture. Even the structural changes are observed to affect the intermolecular free length variation. Figs. 3A, 3B, and 3C show the variance of excess intermolecular free length for the whole dimethyl malonate composition spectrum for the three systems under analysis. The negative L_f^E values suggest that the sound wave has a longer distance to travel [20]. It is due to the prevailing existence of interactions among molecules that are not identical. The occurrence of β_{ad} and L_f^E minima at the same concentrations confirms the occurrence of molecular interactions [21].

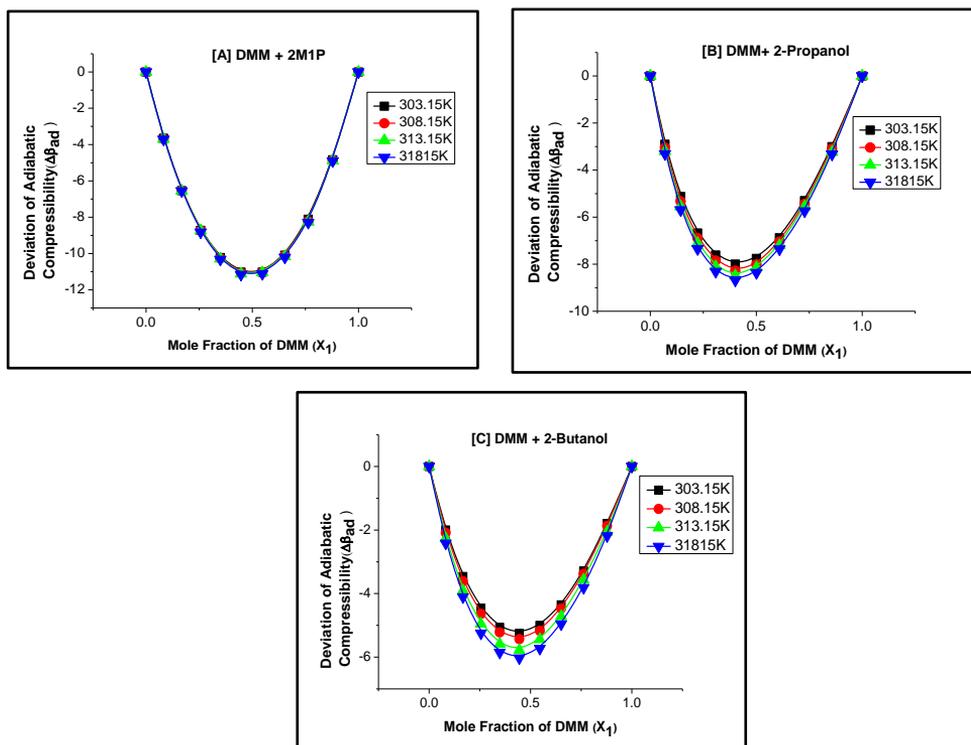


Fig. 2. Variation of Adiabatic Compressibility with the mole fraction of DMM for the systems [A] DMM + 2-M1-P, [B] DMM + 2-propanol and [C] DMM + 2-butanol.

DMM is a substance that is polar and linked to it. Sub Alkanols are polar liquids, closely connected by hydrogen bonding to the degree of polymerization, which may vary depending on the OH group, temperature, chain length, and location. The probability of intramolecular hydrogen bonding within 2-alcohol molecules and their property to bind hydrogen bonds with other molecules generates fascinating solution behavior. When mixing certain highly-associated alcohols with extremely polar solvents, the H-bonds break, and complicated interactions ensue. When describing the interaction between DMM and alkanol mixtures, it is crucial to consider the length of the alkanol chain and the position of the alkanol hydroxyl group. The order of strong interaction in binary liquids between the component molecules is as follows: DMM + 2-methyl-1-propanol > DMM + 2-propanol > DMM + 2-butanol. The intensity increase of the temperature interaction is as follows: (303.15 < 308.15 < 313.15 < 318.15) K.

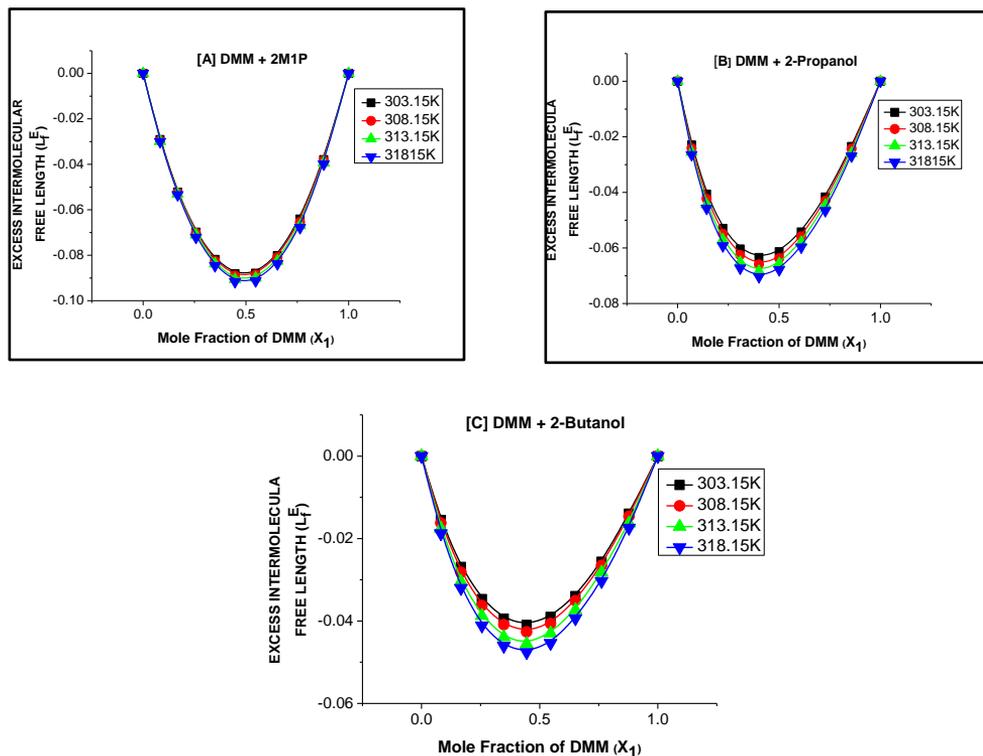


Fig. 3. Variation of Intermolecular Free length with the mole fraction of DMM for the systems [A] DMM + 2-M1-P, [B] DMM +2-propanol and [C] DMM + 2-butanol.

5. Conclusion

The ultrasonic velocities and densities (at 303.15, 308.15, 313.15, and 318.15 K) have been determined over the entire composition range for the binary mixtures of dimethyl malonate with 2-methyl-1-propanol, 2-propanol, and 2-butanol. From the experimental data, deviation in adiabatic compressibility, excess molar volume, and intermolecular free length has been calculated. The excess values and deviations are observed to be negative for all the mixtures at all the temperatures studied. This indicates there exists strong interactions among the binary mixtures.

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