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Thermodynamic Properties and Interaction Abilities of Ternary Liquid Mixtures at 308.15K and 318.15K

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ABSTRACT

Experimental densities, viscosities and ultrasonic velocities were measured for ternary liquid mixtures of diethylmalonate+ 1, 4-dioxane with cyclohexane and n-hexane at 308.15K and 318.15K and atmospheric pressure over the entire range of mole fractions. The calculated thermodynamic properties and some excess parameters such as V^E, ΔK_S, $\Delta\eta$, ΔV_F, ΔL_F, $\Delta\beta_T$, were calculated and applied to Redlich-Kister polynomial equation to determine the appropriate coefficients. The deviations of the ternary mixtures from their ideal behavior were determined, and the interaction ability of the liquids in the ternary liquid mixtures was studied.

Keywords: Diethylmalonate; Molecular interactions; Redlich-Kister equation; Ternary mixtures; Thermodynamic parameters.

1. INTRODUCTION

Many engineering fields requires the data about thermodynamic properties of the liquid mixtures. The study of fluid transport phenomena entails the information regarding the density and viscosity of the system (Aswathi *et al.* 1999). Other than density and viscosity, the ultrasonic study provides enormous information regarding the molecular interactions (Ali *et al.* 2002) and the structural behaviour of the Nano molecules in the mixture. The variation in thermodynamic and transport properties of liquid mixtures from their pure constituents is a dynamic tool to study the nature of molecular interactions between mixing liquids. The study of physical properties like density, viscosity, excess molar volume, volume fraction and adiabatic compressibility aid in understanding the nature and strength of intra and intermolecular interactions occurring in multi-component liquid systems. Also, the thermodynamic and transport properties of liquid systems are vital for engineering process design and operation. There are several predictive equations for estimating thermodynamic properties. The thermodynamic properties of organic liquids help in the separation of organic liquid mixtures through fractional distillation, which can be helpful to reduce pollution of the environment. Diethyl malonate is used in the synthesis of vitamin B1 and B6, pharmaceuticals, agrochemicals and industry of flavours and fragrances compounds (Shipra baluja *et al.* 2005). P-dioxane, the other compound, is a diether and excellent aprotic solvent with an electron-donating ability toward the aromatic ring (Giner *et al.* 2006). It has a zero dipole moment, is commonly used in polymerization (Acree, 1948) and other chemical reactions in the cleaning of polymer surfaces and electronic materials (Nain *et al.* 2008). Typical laboratory use of hexane is to extract oil and grease contaminants from water and soil for analysis. Since it cannot be deprotonated easily, so it is used in reactions in the laboratory that involves very strong bases (Price, 1995). Cyclohexane is colourless, flammable liquid with distinctive detergent, reminiscent of cleaning products (Gad Shayne, 2005). In the present work, a binary mixture of diethyl malonate (DEM) + 1,4-dioxane has been used to prepare ternary solutions by adding cyclohexane and n-hexane separately. The thermodynamic and transport properties of prepared ternary solutions have been studied at 308.15 K and 318.15K over a wide range of compositions. The investigated properties such as excess volume, viscosity, adiabatic compressibility, free length, free volume and isentropic compressibility can be used to parameterize the energy transfer process and interactions between the ternary mixtures. Therefore the detailed study of the thermodynamic and transport properties of the ternary mixtures of diethyl malonate (1) + 1,4-dioxane (2) with cyclohexane (3) and n-hexane (3) at 308.15 and 318.15K hence form the main scope of the present work.

2. EXPERIMENTAL METHODS

Diethyl malonate and 1,4 dioxane (Merck, Mumbai, India), cyclohexane and n-hexane (Loba, Mumbai, India), all Analar grades with 99% pure. All of the chemicals were obtained directly from the manufacturers and distilled using the double distillation

process. As a result, no methods for determining purity were used, but the observed densities, viscosities, and ultrasonic velocities were verified by comparing them to previous literature studies. Using an analytical balance with a precision of ± 0.0001g, ternary liquid mixtures is prepared by weight by volume in airtight stoppered bottles. The relative density method was used to determine the densities of pure liquids and their mixtures. Density relative to other objects chromic acid, purified water, and acetone were used to disinfect a 10ml container, which was then dry and used for density measurements (Csikos *et al*. 1976). An electronic balance was used to measure the density (Gokavi *et al.* 1986). In the relative density system, the precision of density measurement is dependent on the accuracy of mass measurement. Density values are accurate to ±0.0002 gcm^{-3}. An Ostwald viscometer was used to calculate viscosities. With chromic acid, the viscometer was carefully washed. An electronic digital stopwatch with the readability of ±0.01 s was used to measure the flow time of liquid between the marks. The ultrasonic velocity values were calculated using a 2MHz ultrasonic interferometer calibrated with water and nitrobenzene (Pico, Chennai, India). The measurement's average precision is ±0.2 percent. All of the measurements were taken with a wireless thermostat with a ±0.01 K precision. The methods and procedures for the measurements have already been defined in detail.

3. RESULTS & DISCUSSION

The excess volume values for the ternary mixtures were calculated using the relation.

$$V^E = \left(\frac{X_1M_1 + X_2M_2 + X_3M_3}{\rho_{mix}}\right) - \left(\frac{X_1M_1}{\rho_1}\right) - \left(\frac{X_2M_2}{\rho_2}\right) - \left(\frac{X_3M_3}{\rho_3}\right) \quad (1)$$

Where X_1, X_2 &X_3, M_1, M_2&M_3 and ρ_1, ρ_2&ρ_3 are the mole fractions, molar mass, densities of pure components 1, 2, 3, respectively.

Adiabatic compressibility (K_s) has been calculated from Laplace's equation (J. S. Rowlinson, 2013).

$$K_s = \frac{1}{\rho U^2} \quad (2)$$

where ρ and U are the density and ultrasonic velocity of liquid mixtures. From the above equation, excess adiabatic compressibility (ΔK_S) has been calculated by

$$K_S = K_S - \Phi_1 K_{S1} - \Phi_2 K_{S2} - \Phi_3 K_{S3} \quad (3)$$

K_{S1}, K_{S2}, K_{S3} are adiabatic compressibility of pure liquids and $\Phi_1\Phi_2\Phi_3$ are the volume fractions of pure liquids calculated by the relation

$$\Phi_1 = \frac{\left(\frac{X_1M_1}{\rho_1}\right)}{\left(\frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2} + \frac{X_3M_3}{\rho_3}\right)} \quad (4)$$

Viscosity has been calculated using the relation.

$$\eta = \left(At - \frac{B}{t}\right)\rho \quad (5)$$

A and B are the constant characteristics of viscometer calculated using the standard liquids water and nitrobenzene, t is the flow time, ρ is the density.

Excess viscosity values are calculated using the following relation.

$$\Delta\eta = \eta - \left(X_1\eta_1 + X_2\eta_2 + X_3\eta_3\right) \quad (6)$$

Where $\eta_1$and $\eta_2$are the viscosity values of pure components1 and 2 respectively.

Free length is calculated using the relation,

$$L_F = \frac{K}{u\rho^{\frac{1}{2}}} \quad (7)$$

K is Jacobsons constant (Jacobson, 1952) which is temperature-dependent constant but independent of the nature of the liquid.

Isothermal compressibility is calculated using the relation,

$$\beta_T = \frac{1.71X10^{-3}}{\left(\frac{T^4}{9u^2\rho^{\frac{4}{3}}}\right)} \quad (8)$$

Suryanarayana (Suryanarayana, *et al.* 1976) proposed a relation to calculate free volume

$$V_f = \left(\frac{M_{eff}u}{K\eta}\right)^{\frac{3}{2}} \quad (9)$$

K is a temperature-independent constant which is equal to $4.28x10^9$ for all the liquids; M_{eff} is effective molecular weight of the mixture calculated using the relation

$$M_{eff} = X_1M_1 + X_2M_2 + X_3M_3 \quad (10)$$

Where X_1, X_2, $X_3$and M_1,M_2, M_3 are the mole fractions and molar mass of pure components 1, 2, 3, respectively.

Excess values of other parameters are calculated using the relation

$$A^E = A\exp^{-A_{id}}; A_{id} = \sum X_i A_i \qquad (11)$$

Where X_i and A_i are mole fraction and parameters of the i[th] component.

All the calculated excess parameters were fitted to Redlich-Kister (Redlich, 1948) type polynomial equation by the method of least squares to derive the adjustable parameters a, b, c.

For binary

$$A^E = \left[X_1 X_2 \left(a + b(X_1 - X_2) + c(X_1 - X_2) \right) \right] \qquad (12)$$

For ternary

$$A^E = \left[X_1 X_2 X_3 \left(a + bX_1 (X_2 - X_3) + cX_1^2 (X_2 - X_3)^2 \right) \right] \qquad (13)$$

Using the theoretical values for all excess parameters were calculated, and the standard deviation values were calculated using the relation.

$$\sigma = \left[\frac{(A\exp^{-A_{cal}})^2}{(n-m)} \right]^{\frac{1}{2}} \qquad (14)$$

n is the number of measurements, and m is the number of adjustable parameters.

Calculated thermodynamic parameters and excess acoustical parameters for the ternary liquid mixtures of diethyl malonate, 1, 4-dioxane with cyclohexane, as well as n-hexane are represented in the following tables.

Table 1a. Thermodynamic and Physical Properties V^E, ΔK_s values of Ternary Liquid Mixtures of Diethylmalonate +1,4-Dioxane+Cyclohexane at 308.15K

X_1	X_2	$\rho x10^{-3}$ (kgm^{-3})	$V^E x 10^6$ (m^3mol^{-1})	U (ms^{-1})	ϕ_1	ϕ_2	ΔK_s (TPa^{-1})
0.0300	0.4465	0.8664	0.4095	1252	0.0459	0.3816	-38.9938
0.0486	0.4719	0.8794	0.4170	1260	0.0742	0.4025	-42.9610
0.0678	0.4219	0.8742	0.4072	1230	0.1015	0.3527	-11.2278
0.0657	0.3132	0.8496	0.1911	1224	0.0960	0.2556	-16.2517
0.0547	0.3998	0.8659	0.2017	1250	0.0819	0.3344	-40.6416
0.0346	0.2572	0.8257	0.1580	1220	0.0506	0.2099	-18.1839
0.0325	0.1947	0.8116	0.0816	1210	0.0468	0.1568	-9.4562
0.0355	0.1093	0.7947	0.0316	1200	0.0501	0.0862	0.0234
0.3637	0.0747	0.8962	-0.0843	1232	0.4507	0.0517	-22.1531
0.4248	0.0630	0.9112	-0.0828	1242	0.5142	0.0426	-28.6187
0.4302	0.0713	0.9144	-0.0831	1246	0.5206	0.0482	-31.7042
0.5170	0.1252	0.9487	-0.0713	1250	0.6135	0.0830	-20.0236
0.5834	0.0167	0.9438	-0.0659	1252	0.6640	0.0106	-26.9814
0.6019	0.0438	0.9537	-0.0539	1256	0.6843	0.0278	-25.9482
0.7180	0.0187	0.9765	-0.0411	1262	0.7833	0.0114	-21.4633
0.7583	0.0202	0.9859	-0.0373	1264	0.8172	0.0122	-18.5277
0.2668	0.5553	0.9711	0.5679	1290	0.3789	0.4405	-30.0494
0.2523	0.5797	0.9731	0.5417	1292	0.3624	0.4652	-30.1896
0.2460	0.6448	0.9882	0.5140	1292	0.3595	0.5265	-19.8041
0.1815	0.7645	0.9031	0.2660	1294	0.2804	0.6600	-10.8391
0.1484	0.7192	0.9802	0.2372	1290	0.2302	0.6231	-21.6778
0.1099	0.7721	0.9825	0.2205	1284	0.1757	0.6895	-12.3812
0.0893	0.8114	0.9872	0.1914	1294	0.1455	0.7388	-17.7734
0.0598	0.8556	0.9902	0.1894	1280	0.0999	0.7990	-0.6366

0.0300	0.4465	0.8726	-0.1604	1.7549	0.3608	-2.4623	0.0300
0.0486	0.4719	0.8861	-0.1513	1.4693	-0.9122	-2.6185	0.0486
0.0678	0.4219	0.8800	-0.1643	1.9445	3.5625	-2.6810	0.0678
0.0657	0.3132	0.8549	-0.1924	2.3863	3.3457	-2.3664	0.0657
0.0547	0.3998	0.8721	-0.1693	1.7943	-0.3806	-2.4775	0.0547
0.0346	0.2572	0.8305	-0.2099	2.7989	4.2659	-2.0280	0.0346
0.0325	0.1947	0.8159	-0.2259	3.1653	5.8721	-1.8624	0.0325
0.0355	0.1093	0.7985	-0.2469	3.587	7.4461	-1.6527	0.0355
0.3637	0.0747	0.9208	-0.2181	1.5870	-3.6378	-3.4679	0.3637
0.4248	0.0630	0.9487	-0.2077	1.2290	-5.2603	-3.8433	0.4248
0.4302	0.0713	0.9604	-0.1972	1.1302	-5.7092	-3.9539	0.4302
0.5170	0.1252	1.0181	-0.1621	5.8755	-4.1730	-4.7585	0.5170
0.5834	0.0167	1.0558	-0.1467	6.0725	-6.1069	-5.1484	0.5834
0.6019	0.0438	1.0884	-0.1183	4.1595	-5.7497	-5.4688	0.6019
0.7180	0.0187	1.1364	-0.1038	-0.4394	-5.1201	-6.1888	0.7180
0.7583	0.0202	1.1696	-0.0819	-1.6972	-4.5010	-6.5618	0.7583
0.2668	0.5553	0.9753	-0.1207	-1.2861	-3.1515	-3.9314	0.2668
0.2523	0.5797	1.0221	-0.0691	-1.6989	-3.1277	-4.2494	0.2523
0.2460	0.6448	1.0379	-0.0493	-3.4298	-1.8742	-4.4099	0.2460
0.1815	0.7645	1.0765	0.0113	-4.9817	-0.8706	-4.5559	0.1815
0.1484	0.7192	1.0475	-0.0100	-1.7761	-0.1673	-4.2290	0.1484
0.1099	0.7721	1.0454	0.0006	-1.1601	-0.3173	-4.1641	0.1099
0.0893	0.8114	1.0594	0.0216	-2.7838	-1.2155	-4.1870	0.0893
0.0598	0.8556	1.0536	0.0255	-1.3244	1.1303	-4.1449	0.0598

Table 1b. Values of a, b, c and Corresponding Standard Deviation for the Ternary Liquid Mixtures of Diethyl Malonate (1) +1,4-Dioxane (2) + Cyclohexane (3) at 308.15K

Properties	a	b	c	σ
V^E x10^6(m^3mol^{-1})	20.6458	80.976	-424.499	0.0053
ΔK_s (TPa^{-1})	-1521.3	4802.8	-2687.361	0.6691
$\Delta\eta$ (cP)	-11.2272	50.2628	226.557	0.0047
ΔL_F x 10^{-10} (m)	127.07	-647.08	-5653.2	0.0564
$\Delta\beta_T$ x 10^{-12} ($kg^{-1}K^{-1}m^2s$)	139.9	-338.4	-1891.6	0.0266
ΔV_F x 10^{-10} (m^3mol^{-1})	139.07	-338.41	-1819.6	0.0828

Table 2a. Thermodynamic and Physical Properties V^E, ΔK_s values of Ternary Liquid Mixtures of Diethyl Malonate + 1,4-Dioxane+Cyclohexane at 318.15K

X_1	X_2	ρx10^{-3} (kgm^{-3})	V^E x 10^6 (m^3mol^{-1})	U (ms^{-1})	ϕ_1	ϕ_2	ΔK_s (TPa^{-1})
0.0300	0.4465	0.8667	0.3743	1244	0.0455	0.3801	-67.3234
0.0486	0.4719	0.8796	0.3938	1248	0.0734	0.4011	-66.2330
0.0678	0.4219	0.8743	0.3953	1220	0.1005	0.3515	-36.1993
0.0657	0.3132	0.8499	0.1536	1216	0.0950	0.2546	-46.3319

0.0547	0.3998	0.8659	0.2017	1240	0.0811	0.3332	-66.4030
0.0346	0.2572	0.8259	0.1322	1210	0.0500	0.2088	-47.1323
0.0325	0.1947	0.8117	0.0683	1200	0.0463	0.1559	-38.6483
0.0355	0.1093	0.7948	0.0178	1116	0.0495	0.0857	91.8781
0.3637	0.0747	0.8961	-0.0634	1220	0.4474	0.0517	-47.4035
0.4248	0.0630	0.9111	-0.0688	1234	0.5109	0.0426	-58.3270
0.4302	0.0713	0.9143	-0.0691	1240	0.5173	0.0482	-63.1164
0.5170	0.1252	0.9486	-0.0575	1238	0.6106	0.0832	-42.9703
0.5834	0.0167	0.9437	-0.0514	1242	0.6609	0.0107	-53.3865
0.6019	0.0438	0.9536	-0.0396	1246	0.6814	0.0279	-51.2111
0.7180	0.0187	0.9764	-0.0338	1250	0.7810	0.0115	-43.6434
0.7583	0.0202	0.9858	-0.0198	1258	0.8152	0.0122	-45.8299
0.2668	0.5553	0.9713	0.5453	1280	0.3768	0.4411	-50.4685
0.2523	0.5797	0.9735	0.4971	1284	0.3604	0.4657	-52.0406
0.2460	0.6448	0.9889	0.4385	1286	0.3576	0.5273	-42.5449
0.1815	0.7645	1.0033	0.2459	1290	0.2789	0.6609	-33.4345
0.1484	0.7192	0.9809	0.1657	1280	0.2288	0.6234	-40.0021
0.1099	0.7721	0.9827	0.2007	1276	0.1746	0.6896	-32.1559
0.0893	0.8114	0.9876	0.1528	1282	0.1446	0.7389	-32.3295
0.0598	0.8556	0.9907	0.1424	1268	0.0992	0.7989	-14.7530

Table 2b. Physical Properties $\Delta\eta$, ΔV_F, ΔL_F, $\Delta\beta_T$ values of Ternary Liquid Mixtures of Diethyl Malonate + 1,4-Dioxane+Cyclohexane at 318.15K

X_1	X_2	η (cP)	$\Delta\eta$ (cP)	ΔL_F x10^{-10} (m)	$\Delta\beta_T$ x10^{-12} ($kg^{-1}K^{-1}m^2s$)	ΔV_F x10^{-07} (m^3mol^{-1})
0.0300	0.4465	0.6752	0.0138	1.6749	-8.7314	-2.3916
0.0486	0.4719	0.6856	0.0109	1.4404	-8.7597	-2.3860
0.0678	0.4219	0.6808	0.0062	1.8932	4.9293	-2.419
0.0657	0.3130	0.6613	0.0072	2.3046	-7.0286	-2.4734
0.0547	0.3998	0.6740	0.0094	1.7410	-9.3958	-2.4250
0.0346	0.2572	0.6423	0.0129	2.7520	-6.7895	-2.4896
0.0325	0.1947	0.6304	0.0133	3.1216	-5.9700	-2.5205
0.0355	0.1093	0.6181	0.0150	4.7721	13.127	-2.5650
0.3637	0.0747	0.6969	-0.0538	1.5216	-12.904	-2.7118
0.4248	0.0630	0.7179	-0.0593	1.0979	-14.702	-2.7418
0.4302	0.0713	0.7110	-0.0702	0.9710	-15.320	-2.7397
0.5170	0.1252	0.7701	-0.0616	0.4969	-11.027	-2.7465
0.5834	0.0167	0.7981	-0.0451	0.4799	-13.954	-2.8277
0.6019	0.0438	0.8129	-0.0438	0.2859	-13.017	-2.8212
0.7180	0.0187	0.8587	-0.0479	-0.1256	-11.039	-2.8797
0.7583	0.0202	0.8769	-0.0489	-0.3713	-10.782	-2.8940
0.2668	0.5553	0.7387	-0.0533	-0.2179	-7.6954	-2.4296
0.2523	0.5797	0.7804	-0.0093	-0.2832	-7.8253	-2.4115
0.2460	0.6448	0.7792	-0.0192	-0.4807	-6.0638	-2.3759

0.1815	0.7645	0.8145	0.0247	-0.6459	-4.4239	-2.2897
0.1484	0.7192	0.7896	0.0235	-0.2538	-5.4996	-2.2997
0.1099	0.7721	0.7844	0.0267	-0.2060	-4.0958	-2.2577
0.0893	0.8114	0.8017	0.0467	-0.3203	-4.2167	-2.2296
0.0598	0.8556	0.8009	0.0517	-0.1678	-1.5918	-2.1956

Table 2c. Values of a, b, c and corresponding standard deviation for the binary liquid mixtures of diethyl malonate (1) + 1,4-dioxane (2) and cyclohexane (3) at 318.15K

Properties	a	b	C	σ
$V^E x10^6 (m^3mol^{-1})$	18.8243	69.724	-384.156	0.0316
$\Delta Ks\ (TPa^{-1})$	-2813.09	9513.36	-17740.6	0.4300
$\Delta\eta$ (cP)	0.7471	3.886	-145.884	0.00087
$\Delta L_F \times 10^{-10}$ (m)	128.44	-662.72	-6088.2	1.1597
$\Delta\beta_T \times 10^{-12}\ (kg^{-1}K^{-1}m^2s)$	-427.85	1635.6	-9273.9	0.0229
$\Delta V_F \times 10^{-07}\ (m^3mol^{-1})$	-180.18	345.1	0.00012	0.0514

The calculated thermodynamic parameters of diethyl malonate +-dioxane+cyclohexane were represented in the Tables 1a and 2a for 308.15K and 318.15K, respectively. Negative V^E values at a higher mole fraction of DEM indicates that there is a volume contraction on mixing, which may be due to the ability of diethyl malonate to pull the molecules closer. The positive values lower the mole fraction of DEM results due to lesser probability for interaction. The deviations incompressibility are directly proportional to the different size and shape of the components and inversely proportional to velocity. The negative ΔK_s values may occur due to a change in the free volume of the components in the mixtures (Uma sivakami *et al.* 2018). The ΔK_s values are negative for the entire considered mole fractions at both 308.15K and 318.15K. The negative values of ΔK_s clearly indicate the presence of Nano molecular interactions and which make the system flexible and compressible (Nayak *et al.* 2003). The deviation in viscosity is low negative for maximum mole fractions of the ternary mixtures at 308.15K and 318.15K, but the value decreases with an increase in temperature suggest the presence of specific interactions. The deviation in isothermal compressibility, $\Delta\beta_T$ are negative at both the temperatures may be due to interstitial accommodation of the component molecules to each other, but the values get decreased at 318.15 than at 308.15K. The presence of specific interactions is suggested by the negative values of ΔV_F. The low positive and low negative values of ΔL_F values at both the temperature supports the above facts i.e., the interactions between the DEM and cyclohexane make the system well compact may due to the low negative values and vice versa due to the higher concentration of dioxane which disturbs the compactness of the system (Canosa, 1999). The deviation in isothermal compressibility, $\Delta\beta_T$ is low positive values at 308.15K and shows low negative values at 318.15K. The low positive value may be due to the weak dipole-dipole type of interaction. The low negative values of $\Delta\beta_T$ at 318.15K may be due to the better interstitial accommodation of the molecules than at 308.15K.

The ΔV_F value is negative at 308.15K and 318.15K. The value may be due to the presence of weak interactions between the molecules of the system. The calculated excess thermodynamic parameters were fitted to Redlich – Kister polynomial equation to determine the adjustable coefficients and tabulated in Table 1b for 308.15K and tabulated in Table 2b for 318.15K. Figure1 and 1a represent 3D schematic diagrams of excess volume (V^E) of cyclohexane versus mole fractions plots for DEM (X_1) + p-dioxane (X_2) at 308.15K and 318.15K, respectively. Figure2 and 2a represent 3D schematic diagrams of adiabatic compressibility (ΔK_s) of cyclohexane versus volume fractions plots for DEM (ϕ_1) + p-dioxane (ϕ_2) at 308.15K and 318.15K, respectively.

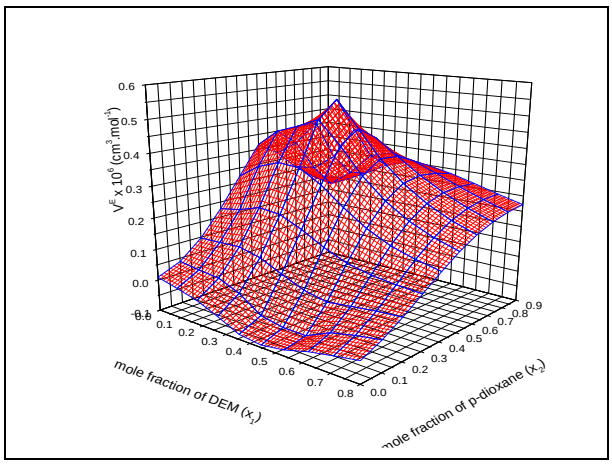

Fig. 1: Mole Fraction Vs. VE for Cyclohexane Ternary Mixture 308.15K

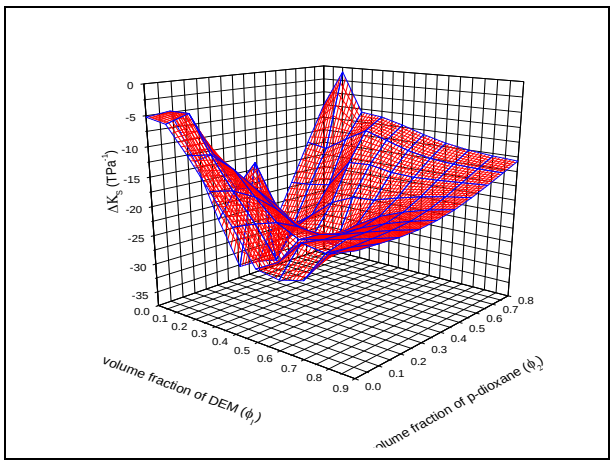

Fig. 2: Volume Fraction Vs. ΔKs for Cyclohexane Ternary Mixture at 308.15K

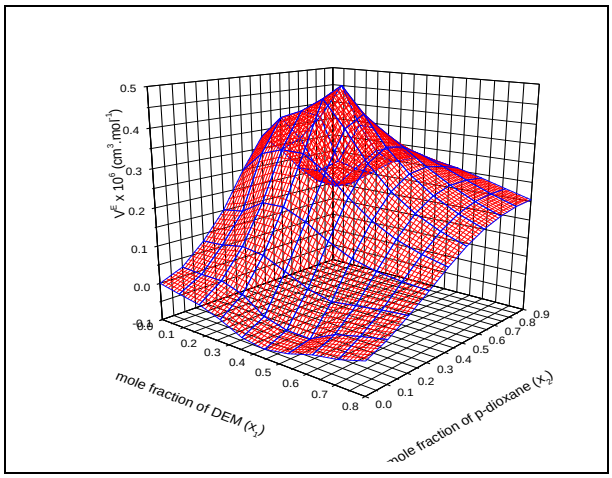

Fig. 1a: Mole Fraction Vs. VE for Cyclohexane Ternary Mixture at 318.15K

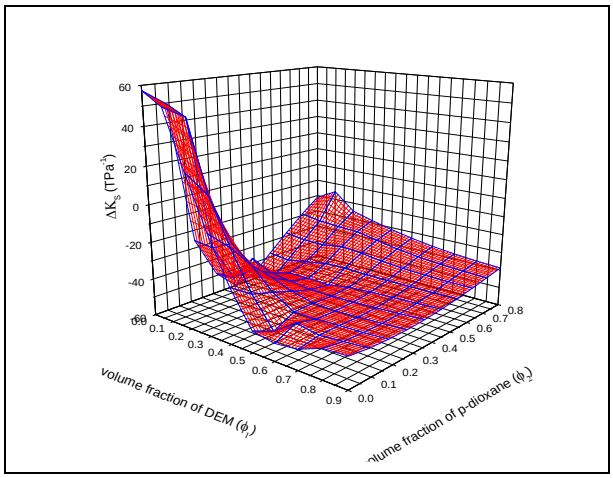

Fig 2a: Volume Fraction Vs ΔKs for Cyclohexane Ternary Mixture at 318.15K

Table 3a. Thermodynamic and Physical Properties VE, ΔKs values of Ternary Liquid Mixtures of Diethyl Malonate + 1,4-dioxane+ n-hexane at 308.15K

X_1	X_2	$\rho x10^{-3}$ (kgm^{-3})	$V^E \times 10^6$ (m^{3}mol^{-1})	U (ms^{-1})	ϕ_1	ϕ_2	ΔK_s (TPa^{-1})
0.0338	0.4879	0.6710	-0.0971	1139	0.0471	0.3814	60.9745
0.0355	0.4622	0.6816	-0.1080	1100	0.0488	0.3574	104.8512
0.0291	0.4499	0.6897	-0.1248	1150	0.0399	0.3466	-26.8476
0.0329	0.4485	0.6894	-0.1309	1120	0.0451	0.3451	36.3856
0.0325	0.3977	0.7116	-0.0963	1090	0.0436	0.2999	19.8296
0.0327	0.3922	0.7141	-0.0782	1140	0.0438	0.2950	-89.6492
0.0254	0.3771	0.7236	-0.0655	1100	0.0338	0.2823	-44.7222
0.0325	0.3288	0.7458	-0.0467	1060	0.0424	0.2413	-22.5193
0.3144	0.0665	0.7761	0.7590	1200	0.3559	0.0423	-226.6078
0.4068	0.0398	0.7594	0.8550	1240	0.4498	0.0247	-199.5702
0.2751	0.0794	0.7839	0.6118	1218	0.3148	0.0510	-289.3346
0.2265	0.0794	0.8018	0.5846	1218	0.2611	0.0514	-354.4229

0.1934	0.0691	0.8220	0.4181	1212	0.2234	0.0449	-405.3521
0.1483	0.0969	0.8271	0.2435	1202	0.1742	0.0640	-422.2235
0.1196	0.0673	0.8598	0.2219	1206	0.1397	0.0442	-506.6735
0.0849	0.0609	0.8839	0.1924	1204	0.0996	0.0401	-564.0600
0.2959	0.6344	0.5829	0.7159	1298	0.4155	0.5005	353.7302
0.3642	0.5843	0.5896	0.8081	1284	0.4943	0.4456	383.6207
0.3858	0.5535	0.5954	0.8427	1280	0.5152	0.4153	371.2181
0.4647	0.4819	0.6061	0.8656	1276	0.5947	0.3465	367.3005
0.4548	0.4720	0.6096	0.8478	1274	0.5810	0.3387	345.7510
0.5678	0.3736	0.6232	0.7346	1270	0.6857	0.2535	344.9099
0.6575	0.3209	0.6272	0.5587	1266	0.7678	0.2106	377.7213
0.7265	0.2591	0.6353	0.3760	1264	0.8214	0.1646	373.7681

Table 3b. Thermodynamic and Physical Properties $\Delta\eta$, ΔVF, ΔLF, $\Delta\beta T$ values of Ternary Liquid Mixtures of Diethyl Malonate + 1,4-Dioxane+Cyclohexane at 318.15K

X_1	X_2	η (cP)	$\Delta\eta$ (cP)	$\Delta L_F \times 10^{-10}$ (m)	$\Delta\beta_T \times 10^{-12}$ ($kg^{-1}K^{-1}m^2s$)	$\Delta V_F \times 10^{-10}$ (m^3mol^{-1})
0.0338	0.4879	0.8807	0.0536	5.3099	2.8348	-7.5215
0.0355	0.4622	0.8766	0.0668	5.8779	3.3809	-7.7717
0.0291	0.4499	0.9233	0.1293	4.8316	1.1898	-7.989
0.0329	0.4485	0.8824	0.853	5.3853	2.1915	-7.8125
0.0325	0.3977	0.8648	0.1057	5.5971	1.5739	-8.0616
0.0327	0.3922	0.8873	0.1321	4.623	-0.1968	-8.0626
0.0254	0.3771	0.8766	0.1403	5.2251	0.3957	-8.2318
0.0325	0.3288	0.8126	0.1046	5.6762	0.3635	-8.1254
0.3144	0.0665	0.9460	0.1322	3.6208	-2.7311	-9.5941
0.4068	0.0398	1.0389	0.1467	2.8715	-2.7037	-1.0009
0.2751	0.0794	0.8526	0.0711	2.2938	-5.2073	-8.4303
0.2265	0.0794	0.8263	0.0964	2.1059	-6.3536	-8.2890
0.1934	0.0691	0.7517	0.0647	1.9800	-7.3244	-7.5848
0.1483	0.0969	0.6289	-0.0307	2.0948	-7.4841	-5.6884
0.1196	0.0673	0.6471	0.0399	1.6942	-9.1094	-6.3041
0.0849	0.0609	0.6671	0.1014	1.8452	-9.6670	-7.0026
0.2959	0.6344	1.1082	-0.1059	4.0258	7.8937	-7.1994
0.3642	0.5843	1.1728	-0.0767	4.0926	8.2764	-7.7631
0.3858	0.5535	1.1938	-0.0560	4.0430	8.0126	-8.0141
0.4647	0.4819	1.2011	-0.0795	3.8853	7.8129	-8.3358
0.4548	0.4720	1.2137	-0.0492	3.8595	7.4260	-8.4699
0.5678	0.3736	1.2206	-0.0895	3.6429	7.2487	-8.8928
0.6575	0.3209	1.2332	-0.1334	3.5989	7.7773	-9.1436
0.7265	0.2591	1.2539	-0.1403	3.4668	7.6501	-9.5062

Table 3c. Values of a, b, c and Corresponding Standard Deviation for the Binary Liquid Mixtures of Diethyl Malonate (1) + 1,4-dioxane (2) and n-hexane (3) at 308.15K

Properties	a	b	C	σ
$V^E x10^6 (m^3mol^{-1})$	-7.5975	-28.1217	2228.03	0.0039
$\Delta Ks\ (TPa^{-1})$	-2032.2	186975	-102263	0.6933
$\Delta\eta$ (cP)	9.1758	-35.9602	-255.585	0.00006
$\Delta L_F \times 10^{-10}$ (m)	591.49	673.81	-11437	0.0072
$\Delta\beta_T \times 10^{-12}$ $(kg^{-1}K^{-1}m^2s)$	-473.27	3262.3	2886.3	1.7629
$\Delta V_F \times 10^{-07}$ (m^3mol^{-1})	-948.57	-257.33	7738.1	0.8168

Table 4a. Thermodynamic and Physical Properties VE, ΔKs values of Ternary Liquid Mixtures of Diethylmalonate + 1,4-dioxane+ n-hexane at 318.15K

X_1	X_2	$\rho x10^{-3}$ (kgm^{-3})	$V^E \times 10^6$ (m^3mol^{-1})	U (ms^{-1})	ϕ_1	ϕ_2	ΔK_s (TPa^{-1})
0.0338	0.4879	0.8002	-0.0926	1136	0.0468	0.3797	-203.5455
0.0355	0.4622	0.7921	-0.0938	1090	0.0486	0.3558	-131.6078
0.0291	0.4499	0.7847	-0.1108	1130	0.0396	0.3450	-214.9228
0.0329	0.4485	0.7862	-0.1155	1100	0.0448	0.3434	-158.4349
0.0325	0.3977	0.7687	-0.0756	1080	0.0434	0.2983	-140.5331
0.0327	0.3922	0.7669	-0.0658	1120	0.0435	0.2935	-221.2013
0.0254	0.3771	0.7583	-0.0559	1080	0.0336	0.2808	-152.2554
0.0325	0.3288	0.7464	-0.0323	1040	0.0421	0.2399	-76.6491
0.3144	0.0665	0.7910	0.7419	1180	0.3540	0.0421	-302.9923
0.4068	0.0398	0.8206	0.8374	1210	0.4477	0.0246	-304.9945
0.2751	0.0794	0.7791	0.5882	1210	0.3130	0.0508	-364.9307
0.2265	0.0794	0.7585	0.5620	1200	0.2596	0.0512	-377.0443
0.1934	0.0691	0.7423	0.4022	1204	0.2220	0.0446	-405.8116
0.1483	0.0969	0.7311	0.2318	1190	0.1731	0.0636	-398.1412
0.1196	0.0673	0.7106	0.2022	1200	0.1387	0.0439	-438.7608
0.0849	0.0609	0.6936	0.1879	1190	0.0988	0.0399	-440.2130
0.2959	0.6344	0.9819	0.7019	1290	0.4150	0.5004	-85.0613
0.3642	0.5843	0.9919	0.7920	1280	0.4938	0.4456	-60.3734
0.3858	0.5535	0.9887	0.8274	1270	0.5147	0.4152	-58.3468
0.4647	0.4819	0.9945	0.8567	1270	0.5942	0.3465	-53.7474
0.4548	0.4720	0.9863	0.8475	1260	0.5804	0.3387	-59.8606
0.5678	0.3736	0.9972	0.7241	1264	0.6852	0.2535	-54.2256
0.6575	0.3209	1.0151	0.5411	1250	0.7675	0.2107	-14.3186
0.7265	0.2591	1.0206	0.3608	1260	0.8212	0.1647	-21.1299

Table 4b. Thermodynamic and Physical Properties Δη, ΔVF, ΔLF, ΔβT values of Ternary Liquid Mixtures of Diethylmalonate + 1,4-dioxane+ n-hexane at 318.15K

X_1	X_2	η (cP)	Δη (cP)	ΔL_F x10^{-08} (m)	$\Delta\beta_T$ x10^{-08} ($kg^{-1}K^{-1}m^2s$)	ΔV_F x10^{-10} (m^3mol^{-1})
0.0338	0.4879	0.6631	0.1530	-1.7509	-1.8008	-4.8740
0.0355	0.4622	0.6637	0.1663	-1.7893	-0.7153	-5.7934
0.0291	0.4499	0.6991	0.2137	-1.8323	-1.9666	-6.142
0.0329	0.4485	0.6681	0.1803	-1.8225	-1.1227	-5.8747
0.0325	0.3977	0.6458	0.1863	-1.9175	-0.8725	-5.9065
0.0327	0.3922	0.6632	0.2066	-1.9353	-2.1199	-5.9558
0.0254	0.3771	0.6641	0.2218	-1.9707	-1.0221	-6.3076
0.0325	0.3288	0.6136	0.1921	-2.0428	0.0597	-5.9735
0.3144	0.0665	0.7121	0.2032	-2.0460	-5.1250	-6.7116
0.4068	0.0398	0.7602	0.1901	-1.9277	-5.3603	-7.0360
0.2751	0.0794	0.6447	0.1610	-2.1000	-5.9655	-5.3863
0.2265	0.0794	0.6296	0.1859	-2.1903	-6.0455	-5.3958
0.1934	0.0691	0.5792	0.1683	-2.2734	-6.4472	-4.4350
0.1483	0.0969	0.4917	0.1026	-2.3023	-6.0771	-2.0739
0.1196	0.0673	0.5124	0.1631	-2.4153	-6.7238	-3.0575
0.0849	0.0609	0.5323	0.2150	-2.4911	-6.6251	-4.0373
0.2959	0.6344	0.7964	-0.0096	-0.9926	-1.0502	-4.6563
0.3642	0.5843	0.8464	0.0119	-0.9590	-0.7503	-5.3427
0.3858	0.5535	0.8635	0.0282	-0.9763	-0.7338	-5.6715
0.4647	0.4819	0.8799	0.0192	-0.9656	-0.7076	-5.9599
0.4548	0.4720	0.8738	0.0267	-1.0024	-0.7966	-6.0196
0.5678	0.3736	0.8797	-0.0062	-0.9791	-0.7755	-6.1994
0.6575	0.3209	0.8950	-0.0356	-0.9089	-0.1938	-6.4554
0.7265	0.2591	0.9114	-0.0419	-0.8990	-0.2983	-6.6963

Table 4c. Values of a, b, c and Corresponding Standard Deviation for the Binary Liquid Mixtures of Diethyl Malonate (1) + 1,4-dioxane (2) and n-hexane (3) at 318.15K

Properties	a	b	C	σ
$V^E x10^6 (m^3mol^{-1})$	-6.5616	-23.8511	2150.15	0.0038
ΔK_s (TPa^{-1})	-21077.5	113664	-75785.8	0.5969
Δη (cP)	4.8094	15.5294	847.152	0.0193
ΔL_F x 10^{-08} (m)	-253.08	212.98	3876.5	0.3341
$\Delta\beta_T$ x 10^{-11}($kg^{-1}K^{-1}m^2s$)	-283.76	1338.8	-530.33	0.5203
ΔV_F x 10^{-10} (m^3mol^{-1})	-0.0008	-0.0167	4.8870	3.1702

The calculated thermodynamic properties for the considered binary liquid mixtures of DEM +p-dioxane + n-hexane are tabulated in the Tables 3a and 4b for 308.15K and 318.15K. The V^E values for the ternary mixtures show negative values in initially considered mole fractions, Where the mole fractions of DEM are low. When the mole fraction of the DEM is gradual increases, the V^E results in positive values for both at 308.15K and 318.15K. On comparing the V^E values between the two temperatures, the value decreases with higher temperatures of 318.15K than at 308.15K. The survey of ΔKs values for the ternary mixture shows both positive and negative values at both 308.15K and 318.15K. The positive (Rathnam *et al.* 2009) values may

due to weak association of difference in molar volume, size and shape of the mixing components. The compressibility values decrease with an increase in temperature from 308.15K to 318.15K. The viscosity value of the liquid mixture depends on molecular interaction between the components. Components are showing strong interactions results in positive deviations and vice versa. The positive values of viscosity deviations in the ternary mixtures with the lower mole fractions of DEM may due to the presence of interaction between the component molecules of p- dioxane and n-hexane. The viscosity deviations are negative with higher mole fractions of DEM may due to the existence of weak interaction force, where the viscosity predictions may support the excess volume values. The deviation in isothermal compressibility values is both positive and negative at 308.15K, but when the temperature increases from 308.15K to 318.15K, the values changes to negative. The negative values may due to the interstitial accommodation of molecules and the existence of interaction between the molecules at a higher temperature. Low positive values at a lower temperature may due to the presence of weak interactions between the molecules. This value supports the earlier predictions regarding the ternary mixture. The low negative values of deviation in free volume at both 308.15K and 318.15K, even though the value decreases with an increase in temperature, which may support the presence of weak interaction. The calculated excess thermodynamic parameters were fitted to Redlich-Kister polynomial equation to determine the adjustable coefficients and tabulated in Tables 3a and 4b for 308.15K and 318.15K. Figure 3 and 3a represent 3D schematic diagrams of excess volume (V^E) of n-hexane versus mole fractions plots for DEM (X_1) + p-dioxane (X_2) at 308.15K and 318.15K, respectively. Figure 4 and 4b represent 3D schematic diagrams of adiabatic compressibility (ΔK_s) of n-hexane versus volume fractions plots for DEM (ϕ_1) + p-dioxane (ϕ_2) at 308.15K and 318.15K, respectively.

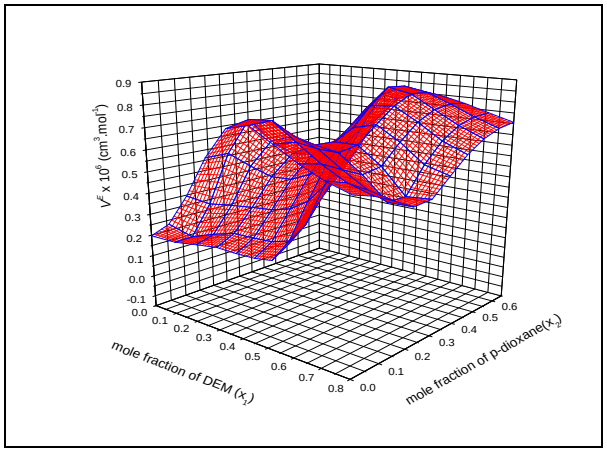

Fig. 3: Mole fraction Vs VE for n-hexane ternary mixture at 308.15K

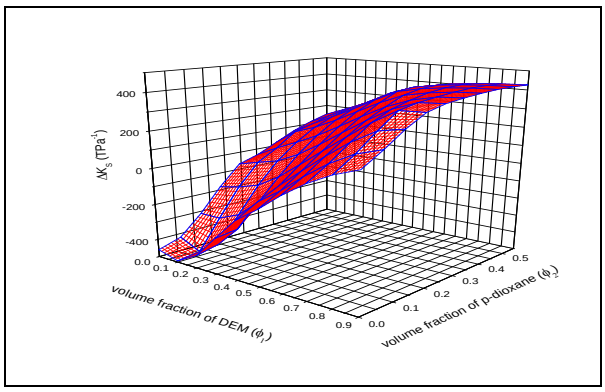

Fig. 3a: Volume fraction Vs ΔKs for n-hexane ternary mixture at 318.15K

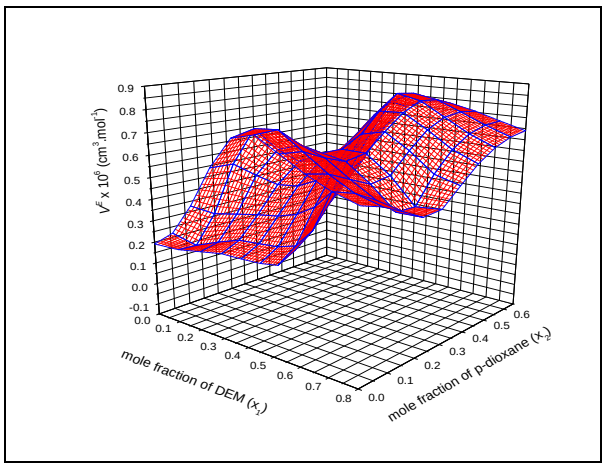

Fig. 4: Mole fraction Vs VE for n-hexane ternary mixture at 318.15K

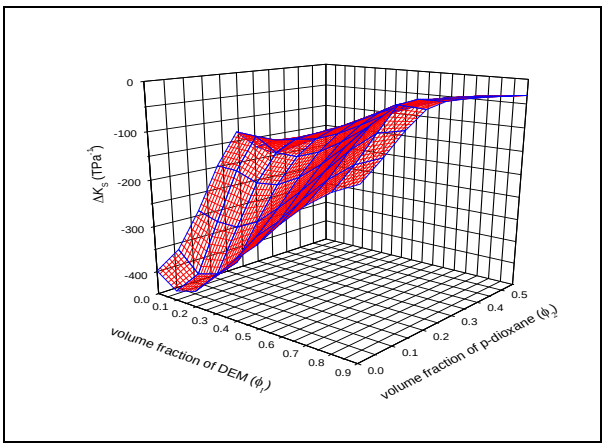

Fig. 4a: Volume fraction Vs ΔKs for n-hexane ternary mixture at 318.15K

4. CONCLUSION

The densities, ultrasonic velocities, viscosities as well as the other excess thermodynamic properties such as excess volume, adiabatic compressibility, deviation in viscosity, free length, isothermal

compressibility, free volume were calculated for the considered two ternary liquid mixtures of dem +1,4-dioxane+ cyclohexane and dem +1,4-dioxane + n-hexane at atmospheric pressures and at the temperature of 308.15K and 318.15K. The thermodynamic excess parameters were calculated with the formulas reported earlier were fitted to Redlich – Kister type polynomial equation to determine the variable coefficients. The behaviour of the ternary liquid mixtures and the deviation from the ideal behaviour has been discussed based on experimental and calculated values. The VE values suggest the existence of intermolecular interactions between the component molecules in the liquid mixtures. Since the excess volume values indicate clearly that the volume contraction results in interactions between the liquid mixtures are a little higher for cyclohexane containing ternary liquid mixture when compared with hexane containing ternary liquid mixtures. The intermolecular interactions may make the dem + 1,4-dioxane +cyclohexane ternary mixture slightly more flexible and compressible, indicated by its ΔKs values than dem +1,4-dioxane + hexane. According to the measured and calculated properties, it can be assumed that strong molecular interactions are possible in dem + 1,4-dioxane + cyclohexane than dem + 1,4-dioxane + n-hexane.

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