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A STUDY ON THERMODYNAMIC PROPERTIES OF BINARY LIQUID MIXTURES OF DIETHYLMALONATE WITH TOLUENE AND CHLOROBENZENE AT 308.15K AND 318.15K

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ABSTRACT

The excess molar volume (V^E), viscosity (η), viscosity deviation (Δη), adiabatic compressibility (ΔK_S) and free volume (V_f) of binary liquid mixtures for Diethylmalonate with toluene and chlorobenzene were measured 308.15K and 318.15K. The intermolecular interactions between the molecules were explained from the above experimental data.

KEYWORDS: Density, viscosity, excess volume, velocity, diethylmalonate, binary mixtures.

INTRODUTION

Thermodynamic behaviors of binary liquid mixtures provide[1-3] information about the molecular interactions. Accurate knowledge of thermodynamic property of binary liquid mixtures has been used in various field of research and the properties are used in to serve many engineering process. Diethylmalonate is used in pharmaceutical industry[4,5] and in the synthesis of chloroquine. It can also be used in various industries, such as pesticides[6,7], paints, etc. The molecular interaction[8] between the binary liquid mixture of diethylmalonate with toluene and chlorobenzene have been explained by calculating thermodynamic properties, such as density, viscosity, ultrasonic velocity at two different temperatures 308.15K & 318.15K over a wide range of different mole fraction. From the above measuring data the acoustical properties, such as excess molar volume (V^E), viscosity (η), viscosity deviation (Δη), Adiabatic compressibility (ΔK_S) and free volume (V_f) have been calculated.

EXPERIMENTAL METHODS

All the organic liquids used in this study were of Analytical grade. Diethylmalonate, toluene, and chlorobenzene were obtained from Merck. The organic liquids[9] were further purified for purity better than 99%, as reported in literature. Liquid mixtures of various compositions were prepared by mass in a 25cm^3 flask using an analytical balance. The average uncertainty in the mole fraction of the mixtures was estimated to be less than ±0.0001. Density and viscosity[10] measurements were carried out using a thermostatically controlled, well-stirred, water-bath to maintain temperature, which was measured with a digital thermometer with an uncertainty of ±0.01K.

Density of pure liquids and their binary liquid mixtures[11] were measured at 308.15K and 318.15K using relative density method. The relative density bottle was calibrated with degassed water and dehumidified air at atmospheric pressure. The uncertainty of the density measurements was estimated to be ±1 x 10$^-$05Kg.m^{-3}. The viscosities (η) of pure organic liquids and their binary mixtures were determined using an Ostwald viscometer which was suspended in a thermostat maintained at 308.15K and318.15K.[12] The uncertainty of calculated absolute viscosities was ± 1x 10^{-4}mPa.s. The ultrasonic velocity of the binary mixture is measured using ultrasonic interferometer (Pico, Chennai) with the output of 2 MHz capacity, where the compressibility of the liquid mixtures are measured.

RESULT AND DISCUSSION

The densities (ρ), viscosities (η), Ultrasonic velocities (U) of binary liquid mixtures of diethylmalonate with toluene and chlorobenzenes were measured at 308.15K and 318.15K as a function of the composition of the corresponding binary mixtures.[14] The Excess volume (V^E), viscosity deviation (Δη), deviation in adiabatic compressibility (ΔK_S) and free volume (V_f) for binary mixtures of diethylmalonate with toluene and chlorobenzene were fitted to the Redlich- Kister's type polynomial equation[16,17] and are given in Table 1, 2,3 and 4 respectively.

From the experimental data, various acoustical parameters were evaluated using the following standard equations:

Density (ρ): $\rho = w \times d_0 / w_0$ ---------- (1)

where w is the mass of sample, w_0 is the mass of the water and d_0 is the density of the water.

Excess molar volume (V^E): $V^E = (X_1M_1+X_2M_2) / \rho - [(X_1M_1/\rho_1) + (X_2M_2/\rho_2)]$ ------ (2)

Where ρ is the density of mixture and X_1, M_1 and ρ_1 and X_2, M_2 and ρ_2 are mole fraction, molar mass and density of pure components 1 and 2 respectively.

Adiabatic compressibility (K_S): $K_S = 1/ (U^2\rho)$ ---------- (3)

where U is the speed of sound and ρ is the density of liquid.

Deviation in adiabatic compressibility (ΔK_S): $\Delta K_S = K_S - (\phi_1 K_{S1} + \phi_2 K_{S2})$ ---------- (4)

where K_S is [13]adiabatic compressibility of mixture,ϕ_1, K_{S1} and ϕ_2, K_{S2} are volume fraction, and adiabatic compressibility of pure components 1 and 2 respectively.

Viscosity (η): $\eta = [A \times t - B/t] \rho$ ---------- (5)

Where ρ is the density of mixture, t is the time flow in seconds and A&B characteristic constant of the viscometer at the given temperature.[14]

Excess viscosity ($\Delta\eta$): $\Delta\eta = \eta_{mix} - (X_1\eta_1 + X_2\eta_2)$----------(6)

Where η_{mix} is a viscosity of mixtures, X_1,η_1 and X_2, η_2 are mole fractions and viscosity of pure components 1 and 2 respectively.

Effective molecular weight (Meff): $Meff = X_1M_1+X_2M_2 / (X_1 +X_2)$----------(7)

where X_1 and X_2 are the mole fraction and M_1 and M_2 are molecular weight of component 1 and 2 respectively.

Free volume (V_f): $V_f = [(MU) / (K\eta)]^{3/2}$ ---------- (8)

Where M is the effective molecular weight, U is ultrasonic velocity, K is Jacobson's constant (4.28×10^9) and η is the viscosity.

All the calculated excess parameters were fitted to ***Redlich- Kister's[15] type polynomial equation***

$AE = [X_1X_2(a+b(X_1 - X_2)+c(X_1 - X_2))]$ ----------(9)

by the method of least squares to derive the adjustable parameters a, b, c. From the theortetical values for all excess parameters were calculated and the standard deviation values were calculated using the relation

$\sigma = [(A_{exp} - A_{cal})^2 / (n-m)^{1/2}]$ ----------(10)

Table 1: Thermodynamic parameters for the binary liquid mixture of Diethylmalonate + Toluene at 308.15 K.

Mole fraction X_1	Density (ρ) (10^3 kg m^{-3})	Excess volume (V^E) (10^3 m^3 mol^{-1})	Volume Fraction ϕ_1	Ultrasonic velosity U (ms^{-1})	Adiabatic compressibility ΔKs (TPa^{-1})	viscosity η (cP)	M_{eff}	Free volume V_f (10^{-09} m^3mol^{-1})	Excess viscosity Δη (cP)
0.0856	0.8598	0.1718	0.1188	1249	1.4784	0.4923	97.97	1.8320	0.8494
0.1791	0.8818	0.4045	0.2436	1250	2.9527	0.5458	104.33	1.8803	0.7359
0.2772	0.9022	0.7847	0.3668	1252	4.1479	0.6131	111.00	1.8954	0.6281
0.3652	0.9208	0.9063	0.4700	1254	5.0741	0.6622	116.98	1.9446	0.5202
0.4632	0.9407	0.9695	0.5760	1256	5.4713	0.7272	123.65	1.9687	0.4101
0.5731	0.9635	0.7544	0.6840	1260	3.1803	0.7866	131.13	2.0398	0.2735
0.6646	0.9818	0.5093	0.7651	1263	1.4696	0.8624	137.35	2.0277	0.1858
0.7652	1.0034	-0.1322	0.8456	1264	-0.3276	0.9379	144.20	2.0372	0.0816
0.8765	1.0234	-0.4694	0.9240	1266	-1.4677	1.0279	151.77	2.0300	-0.0270

Table 2: Thermodynamic parameters for the binary liquid mixture of Diethylmalonate + Toluene at 318.15K.

Mole fraction X_1	Density (ρ) (10^3 kg m^{-3})	Excess volume (V^E) (10^3 m^3 mol^{-1})	Volume Fraction ϕ_1	Ultrasonic velosity U (ms^{-1})	Adiabatic compressibility ΔKs (TPa^{-1})	viscosity η (cP)	M_{eff}	Free volume V_f (10^{-09} m^3mol^{-1})	Excess viscosity Δη (cP)
0.0856	0.8551	0.1418	0.1188	1222	0.6718	0.4400	97.97	1.9370	-0.0999
0.1791	0.8769	0.3848	0.2437	1223	1.8159	0.4975	104.33	1.9653	-0.1114
0.2772	0.8979	0.6674	0.3670	1224	3.8565	0.5785	111.00	1.9265	-0.1027
0.3651	0.9161	0.8285	0.4701	1226	4.8030	0.6133	116.98	2.0157	-0.1328
0.4632	0.9355	0.9448	0.5761	1228	5.2424	0.6728	123.65	2.0478	-0.1456
0.5730	0.9585	0.6801	0.6842	1232	3.0428	0.7363	131.13	2.1022	-0.1632
0.6645	0.9775	0.3151	0.7653	1234	1.1645	0.7981	137.35	2.1195	-0.1690
0.7652	0.9971	-0.0589	0.8455	1237	-0.8835	0.8852	144.20	2.0894	-0.1561
0.8764	1.0169	-0.3853	0.9239	1238	-1.2350	0.9978	151.77	2.0168	-0.1255

Table 3: Thermodynamic parameters for the binary liquid mixture of Diethylmalonate + Chlorobenzene at 308.15 K.

Mole fraction X_1	Density (ρ) (10^3 kg m^{-3})	Excess Volume (V^E) (10^3 m^3 mol^{-1})	Volume Fraction ϕ_1	Ultrasonic velosity U (ms^{-1})	Adiabatic compressibility ΔKs (TPa^{-1})	Viscosity η (cP)	M_{eff}	Free volume V_f (10^{-07} m^3mol^{-1})	Excess viscosity Δη (cP)
0.1035	1.0847	0.0881	0.1470	0.7245	1231.00	4.3850	117.48	1.2112	1.2473
0.2151	1.0770	0.1231	0.2904	0.7629	1236.50	5.8478	122.80	1.4082	0.9990
0.3074	1.0715	0.1258	0.3985	0.7994	1243.50	4.0759	127.19	1.6057	0.7985
0.4000	1.0667	0.0913	0.4989	0.8588	1252.50	-0.0799	131.60	1.9022	0.6200
0.4982	1.0624	0.0101	0.5972	0.9207	1259.00	-2.0473	136.28	2.2422	0.4298
0.5918	1.0588	-0.0951	0.6840	0.9965	1265.50	-4.5594	140.73	2.6701	0.2652
0.6896	1.0548	-0.1386	0.7684	1.0831	1271.00	-5.8987	145.39	3.1981	0.1007
0.8006	1.0501	-0.1319	0.8571	1.1833	1275.50	-5.8551	150.67	3.8731	-0.0842
0.9057	1.0458	-0.0879	0.9348	1.2973	1277.50	-3.8657	155.67	4.6805	-0.2399

Table 4: Thermodynamic parameters for the binary liquid mixture of Diethylmalonate + Chlorobenzene at 318.15K.

Mole fraction X_1	Density (ρ) (10^3 kg m^{-3})	Excess volume (V^E) (10^3 m^3 mol^{-1})	Volume Fraction ϕ_1	Ultrasonic velosity U (ms^{-1})	Adiabatic compressibility ΔKs (TPa^{-1})	Viscosity η (cP)	M_{eff}	Free volume V_f (10^{-07} m^3mol^{-1})	Excess viscosity Δη (cP)
0.1035	1.0710	0.0769	0.1470	0.7120	1209.00	3.9639	117.48	1.1485	1.2220
0.2151	1.0634	0.1082	0.2904	0.7424	1212.00	4.9399	122.80	1.3118	0.9988
0.3074	1.0580	0.1057	0.3986	0.8135	1215.50	4.2484	127.19	1.5931	0.8603
0.4000	1.0531	0.0831	0.4989	0.8737	1221.50	0.6494	131.60	1.8798	0.7100
0.4982	1.0486	0.0203	0.5972	0.9357	1227.50	-3.1308	136.28	2.2116	0.5489
0.5918	1.0449	-0.0657	0.6841	1.0063	1232.00	-5.7204	140.73	2.6028	0.4069
0.6896	1.0409	-0.1143	0.7684	1.0681	1234.00	-5.5973	145.39	2.9961	0.2465
0.8006	1.0365	-0.1262	0.8571	1.2001	1235.00	-4.1370	150.67	3.7691	0.1263
0.9057	1.0322	-0.0867	0.9348	1.2778	1235.00	-1.7296	155.67	4.3489	-0.0346

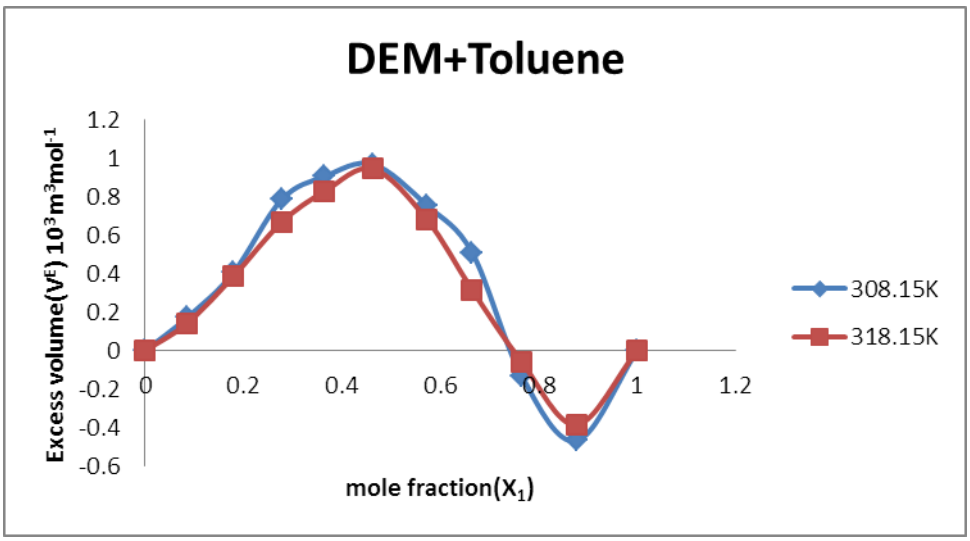

Fig 1: Excess volume for the binary mixture of Diethylmalonate +Toluene at 308.15K and 318.15K.

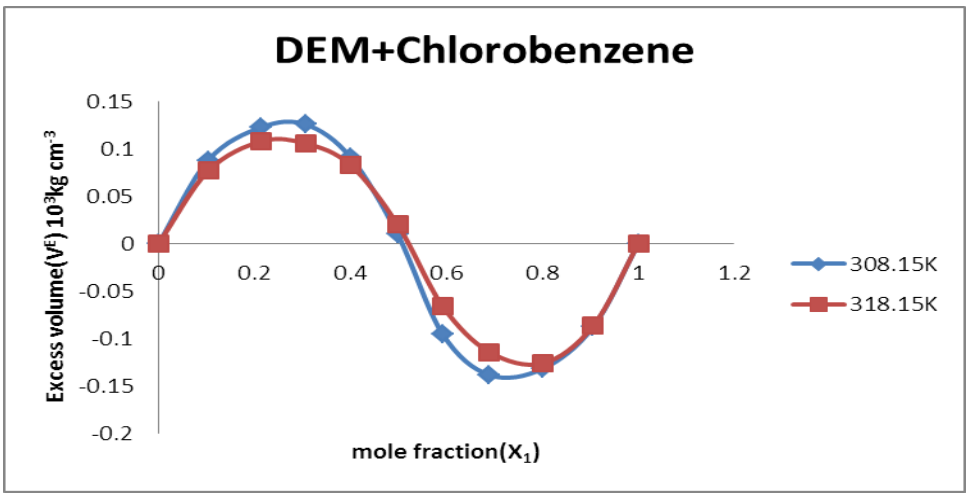

Fig 2: Excess volume for the binary mixture of Diethylmalonate +Chlorobenzene at 308.15K and 318.15K.

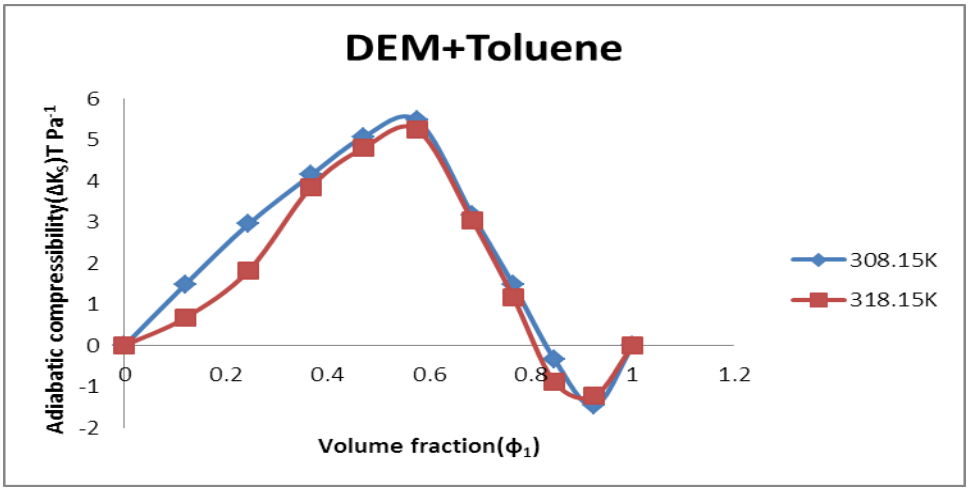

Fig 3: Adiabatic compressibility for the binary mixture of Diethylmalonate +Toluene at 308.15K and 318.15K.

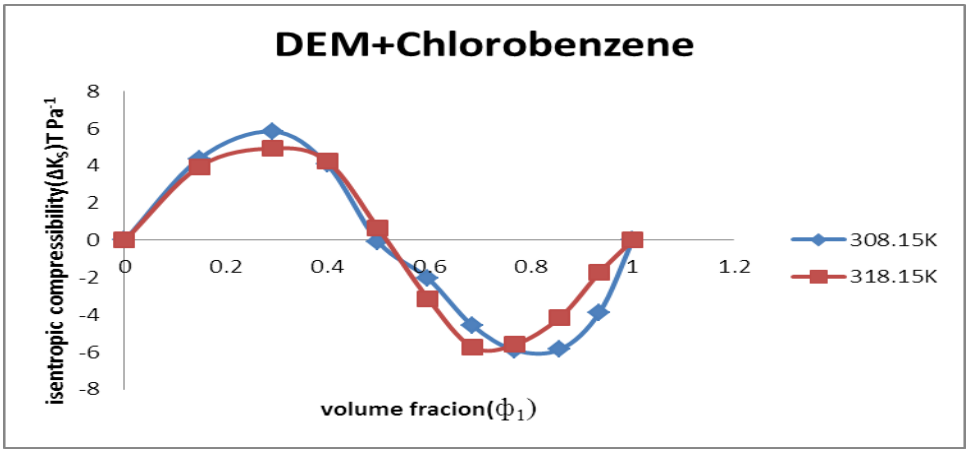

Fig 4: Adiabatic compressibility for the binary mixture of Diethylmalonate +Chlorobenzene at 308.15K and 318.15K.

Diethylmalonate +toluene: The excess volume of the binary mixture of Diethylmalonate and toluene shows positive values for the maximum mole fractions except the last two where the mole fraction of diethylmalonate is high.[16] The positive values of the excess volume increases up to equimolar mole fraction and then decreases and reaches negative values, where the mole fractions of the diethylmalonate are higher. Similarly the isentropic compressibility values show a similar tendency like excess volume values,[17] which increases up to equimolar mole fractions and then decreases, reaches negative deviation.

When temperature is increase from 308.15K to 318.15K the values of the calculated thermodynamic parameters reduces but the trend is as similar as 308.15K. The values may clearly indicate the weak interaction between the unlike molecules. The value of viscosity

supports the other calculated thermodynamic parameters. But the nature of self- association results the presence of like molecular interactions are shown by negative values.

Diethylmalonate + chlorobenzene

For the binary liquid mixtures of diethylmalonate with chlorobenzene the excess volume (V^E) and deviation of isentropic compressibility (ΔK_S) values shift from positive to negative, shows that increasing of interaction[18] between unlike molecules with increasing mole fraction of diethylmalonate. This may be due to breaking the intermolecular association of diethylmalonate by chlorobenzene and decreasing molecular order in low mole fraction of diethylmalonate.[19] But when increase the mole fraction of diethylmalonate it associate strongly, hence the trend goes towards negative value. When two $–COO^-$ residue approach close to one another there is an extra attractive force arising from the interaction between the dipoles in these two groups.

The interaction exists between the binary mixture can be represented as,

Diethylmalonate + Chlorobenzene > Diethylmalonate +Toluene.

Table 5: Adjustable parameters a, b, c and standard deviation values for the excess acoustical values. Diethylmalonate + Toluene at 308.15K.

Parameters	A	B	C	Σ
$V^E(10^3 m^3 mol^{-1})$	3.799	-3.7485	-8.2473	0.0182
$\Delta Ks(T\ Pa^{-1})$	21.356	-8.1126	-34.9867	0.1083
η (cP)	2.7443	2.074	6.8235	0.0156
Δη (cP)	1.25	-3.7061	0.2758	0.0780
$V_{f(10^{-09} m^3 mol^{-1})}$	7.1381	6.0153	1.712	0.127

Table 6: Adjustable parameters a, b, c and standard deviation values for the excess acoustical values. Diethylmalonate + Toluene at 318.15K.

Parameters	A	B	C	Σ
$V^E(10^3 m^3 mol^{-1})$	3.3909	-3.401	-7.2607	0.0577
$\Delta Ks(T\ Pa^{-1})$	20.4040	-4.6021	-42.7956	0.1208
η (cP)	2.5441	2.0633	6.5106	0.0175
Δη (cP)	-0.5746	-0.2226	-0.7859	0.0016
$V_{f(10^{-09} m^3 mol^{-1})}$	7.584	4.1793	1.7392	0.1356

Table 7: Adjustable parameters a,b,c and standard deviation values for the excess acoustical values. Diethylmalonate + chlorobenzene at 308.15K.

Parameters	a	B	C	Σ
$V^E(10^5 m^3 mol^{-1})$	-0.006181	-1.4544	-0.06909	9.6133
$\Delta Ks(T\ Pa^{-1})$	3.21599	-61.0156	-15.2908	0.41981
η (cP)	3.32105	2.46854	9.82437	0.00465
Δη (cP)	1.53137	-6.09944	4.85254	0.00162
$V_{f(10^{-07} m^3 mol^{-1})}$	7.8500	1.4200	3.1000	1.5404

Table 8: Adjustable parameters a, b, c and standard deviation values for the excess acoustical values. Diethylmalonate + chlorobenzene at 318.15K.

Parameters	a	B	C	Σ
$V^E(10^5 m^3 mol^{-1})$	0.03893	-1.27567	-0.2577	0.00014
$\Delta Ks(T\ Pa^{-1})$	0.642013	-56.3186	-1.3692	0.353577
η (cP)	3.37883	2.48063	9.52827	0.004848
Δη (cP)	1.969	-5.09544	5.56813	0.002073
$V_{f(10^{-07} m^3 mol^{-1})}$	7.76	1.34	2.85	1.4056

CONCLUSION

The experimental data and the calculated thermodynamic parameters clearly indicate the presence of the molecular interaction between the component molecules in the binary liquid mixtures. The experimental values clearly indicate that the interaction exists between diethylmalonate with toluene is comparatively low when compared with chlorobenzene as one of binary liquid mixtures.

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