THERMODYNAMIC PARAMETERS OF A TERNARY LIQUID MIXTURE AT 308.15K AND 318.15K

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ABSTRACT

Densities, viscosities and ultrasonic velocities were measured for ternary liquid mixtures of diethylmalonate with toluene andbenzaldehyde at 308.15K and 318.15K. The thermodynamic properties such as V^E, ΔK_s,etc., were calculated and applied to Redlich - Kister polynomial equation to determine the appropriate coefficients. The intermolecular interactions between the components present in the ternary liquid mixtures were explained from the above experimental data.

INDEX TERMS: ultrasonic velocity, ternary liquid mixture, diethylmalonate, molecular interaction.

I.INTRODUCTION

Currently, the measurement of ultrasonic velocity has been successfully employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures. These physical properties are easily measuredandtabulated. The data thus allow indirect determination of the composition of ternary mixtures[1,2]. 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[3,4]. Therefore the detailed study of the thermodynamic and transport properties of the ternary mixtures of diethylmalonate with toluene and benzaldehyde at 308.15K and 318.15K hence form the main scope of the present work. Diethylmalonate is used in pharmaceutical industryand in the synthesis of chloroquine[5]. It is also used in various industries, such as pesticides, paints, etc.

II. MATERIALS AND METHODS

All the organic liquids used in this study were of Analytical grade. Diethylmalonate, toluene, benzaldehyde were obtained from Merck. The organic liquids[6] 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[7] 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 ternary liquid mixtures[8] 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 ternary liquid mixtures were determined using an Ostwald viscometer which was suspended in a thermostat maintained at 308.15K and318.15K. The ultrasonic velocity of the ternary mixture is measured using ultrasonic interferometer (Pico, Chennai) with the output of 2 MHz capacity, from which the compressibility of the liquid mixtures are measured.

III.RESULT AND DISCUSSION

The densities (ρ), viscosities (η), Ultrasonic velocities (U) of ternary liquid mixtures of diethylmalonate with toluene and benzaldehyde were measured at 308.15K and 318.15K as a function of the composition of the corresponding ternary mixtures.[9] The Excess volume (V^E), viscosity deviation ($\Delta\eta$), deviation in adiabatic compressibility (ΔK_S) and free volume (V_f) for binary mixtures of diethylmalonate with toluene and benzaldehyde were fitted to the Redlich- Kister's type polynomial equation[10,11] .

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

Density *(ρ)* = $w \times d_0 / w_0$

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

Viscosity (η): = (A x t – B/ t) x ρ

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.

Excess molar volume (V^E):

$V^E = [(X_1M_1+X_2M_2)+(X_3M_3) / \rho_{mix}] – [(X_1M_1/\rho_1) + (X_2M_2/\rho_2)+ (X_3M_3/\rho_3)]$

Where ρ is the density of mixture and X_1, M_1 and ρ_1 , X_2, M_2 and ρ_2 and X_3, M_3 and ρ_3 are mole fraction, molar mass and density of pure components 1, 2 and3 respectively.

Adiabatic compressibility *(K_S):* $Ks = 1 / U^2\rho$

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

Deviation in adiabatic compressibility (ΔK_S): $\Delta K_S = K_S – (\varphi_1K_{S1}+ \varphi_2K_{S2}+\varphi_3K_{S3})$

Where K_S is adiabatic compressibility of mixture, ϕ_1, K_{S1}, ϕ_2, $K_{S2}$and φ_3, $K_{S3}$are volume fraction, and adiabatic compressibility of pure components 1, 2 and 3 respectively.

Calculated thermodynamic parameters for the ternary liquid mixtures of diethylmalonate,toluene and benzaldehyde at 308.15K and 318.15Kare represented in the following tables.

TABLE -1: Thermodynamic parameters for the ternary liquid mixtures of diethylmalonate + toluene+ Benzaldehyde at 308.15K

Mole fraction X_1	Mole fraction X_2	Density (ρ) (10^3kg m^{-3})	Excess volume (V^E) (10^3 m^3mol^{-1})	Ultrasonic velosity U (ms^{-1})	Volume fraction Φ_1	Volume fraction Φ_2	Isentropic compressibility $\Delta Ks(TPa^{-1})$
0.0520	0.4964	0.9334	0.2845	1300	0.0736	0.5009	14.8158
0.0667	0.4800	0.9364	0.3889	1300	0.0938	0.4816	15.8634
0.0754	0.4652	0.9376	0.6310	1300	0.1058	0.4652	19.1859
0.0871	0.4709	0.9389	0.4212	1290	0.1214	0.4682	24.9408
0.1003	0.4773	0.9399	0.2396	1280	0.1389	0.4715	30.3323
0.1094	0.4373	0.9432	0.7859	1260	0.1512	0.4313	59.0443
0.1241	0.5131	0.9337	0.3347	1240	0.1696	0.5001	63.8465
0.1362	0.5154	0.9342	0.2990	1270	0.1851	0.4996	28.7444
0.1488	0.3427	0.9635	0.6617	1260	0.2033	0.3340	67.6939
0.1620	0.3432	0.9613	0.9741	1310	0.2200	0.3324	18.7278
0.1747	0.3475	0.9612	0.9510	1316	0.2359	0.3346	9.6994
0.2013	0.4224	0.9495	0.8640	1310	0.2673	0.4000	-2.3485

0.1510	0.4337	0.9453	0.8511	1300	0.2050	0.4197	12.7025
0.2256	0.3900	0.9628	0.0665	1290	0.2970	0.3661	14.8364
0.2432	0.3979	0.9631	-0.0623	1290	0.3175	0.3704	9.4321
0.2569	0.3595	0.9656	0.5287	1312	0.3342	0.3335	-3.5179
0.2708	0.3420	0.9665	0.8598	1330	0.3506	0.3157	-17.3835
0.2919	0.3558	0.9687	0.3760	1340	0.3741	0.3252	-33.8379
0.3156	0.2902	0.9762	0.9569	1300	0.4020	0.2636	13.2445
0.3358	0.3838	0.9677	0.0799	1290	0.4218	0.3438	-0.6807
0.3483	0.2568	0.9828	0.9687	1280	0.4385	0.2306	33.1658
0.3627	0.3716	0.9678	0.4495	1270	0.4508	0.3293	19.5298
0.3807	0.3739	0.9757	-0.5399	1260	0.4696	0.3289	21.8926
0.4048	0.1888	0.9998	0.4598	1280	0.4998	0.1662	33.1837

TABLE -2

Thermodynamic parameters for the ternary liquid mixtures of diethylmalonate + toluene+ benzaldehyde at 318.15K

Mole fraction X_1	Mole fraction X_2	Density (ρ) (10^3kg m^{-3})	Excess volume (V^E) (10^3 m^3mol^{-1})	Ultrasonic velocity U (ms^{-1})	Volume fraction Φ_1	Volume fraction Φ_2	Isentropic compressibility $\Delta Ks(TPa^{-1})$
0.0520	0.4964	0.9298	0.2114	1260	0.0737	0.5015	32.0939
0.0667	0.4800	0.9332	0.2667	1270	0.0939	0.4822	22.3225
0.0754	0.4652	0.9366	0.2494	1260	0.1059	0.4658	35.8973
0.0871	0.4709	0.9400	-0.2173	1270	0.1216	0.4688	21.2551
0.1003	0.4773	0.9434	-0.6930	1250	0.1391	0.4720	37.2049
0.1094	0.4373	0.9468	-0.1518	1260	0.1514	0.4318	35.8750
0.1241	0.5131	0.9502	-2.1752	1240	0.1698	0.5006	38.2625
0.1362	0.5154	0.9536	-2.5682	1250	0.1853	0.5000	24.8754
0.1488	0.3427	0.9570	0.9301	1230	0.2036	0.3345	78.4118
0.1620	0.3432	0.9604	0.5709	1230	0.2203	0.3328	77.1638

0.1747	0.3475	0.9638	0.1207	1270	0.2362	0.3350	31.7562
0.2013	0.4224	0.9672	-1.8378	1300	0.2676	0.4003	-17.8647
0.1510	0.4337	0.9706	-2.6674	1290	0.2052	0.4202	-2.1789
0.2256	0.3900	0.9740	-1.8457	1270	0.2973	0.3664	11.7478
0.2432	0.3979	0.9774	-2.3670	1260	0.3178	0.3708	15.8096
0.2569	0.3595	0.9808	-1.8895	1290	0.3346	0.3338	-7.3680
0.2708	0.3420	0.9842	-1.8735	1300	0.3510	0.3160	-14.0243
0.2919	0.3558	0.9876	-2.5263	1310	0.3745	0.3255	-31.2253
0.3156	0.2902	0.9910	-1.4501	1260	0.4024	0.2639	26.1449
0.3358	0.3838	0.9944	-3.8473	1270	0.4220	0.3440	-6.5542
0.3483	0.2568	0.9978	-1.4806	1250	0.4389	0.2308	39.3353
0.3627	0.3716	1.0012	-4.3452	1250	0.4511	0.3295	14.5167

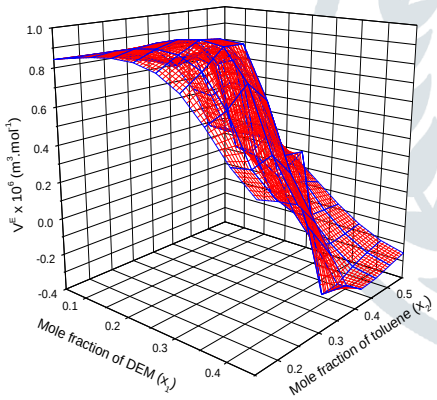

Fig. 1a: Mole fraction Vs V^E for DME ternary mixture at 308.15K

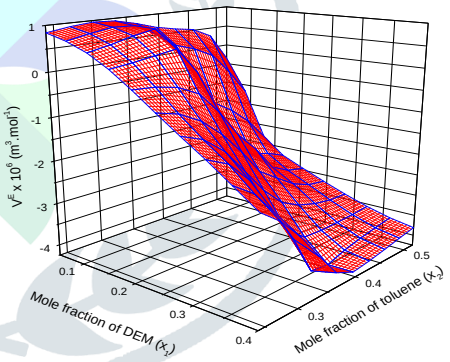

Fig. 1b: Mole fraction VsV^E for DEM ternary mixture at 318.15K

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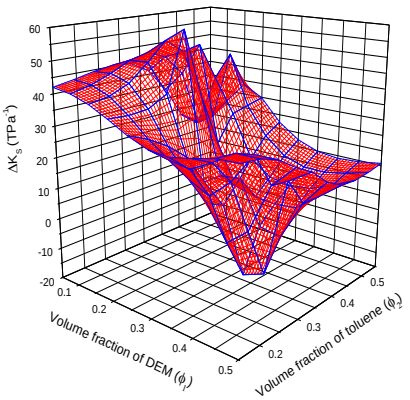

Fig. 2a: Volume fraction Vs ΔKs for DEM ternary mixture at 308.15K

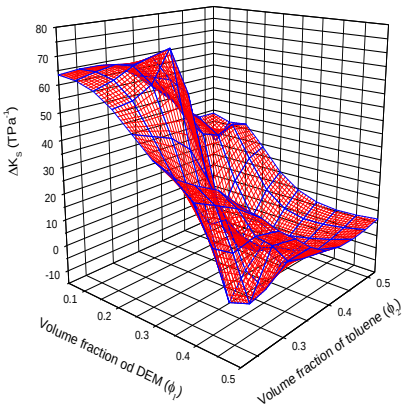

Fig. 2b: Volume fraction Vs ΔKs for DEM ternary mixture at318.15K

Ternary Mixture – Diethylmalonate+toluene+benzaldehyde

The ternary liquid mixtures of diethylmalonate, toluene and Benzaldehyde shows positive deviations for both the parameters such as excess volume and adiabatic compressibility[12,13]. The results of calculated thermodynamic parameters clearly indicate the absence of molecular interactions between the component molecules in the ternary liquid mixtures[14].

A few negative values randomly shown by both the excess volume and adiabatic compressibility parameters are due to the presence of self- associative nature of the component molecules[15]. When the temperature varies from 308.15K to 318.15K the values are decreased but the movement of component molecules are similar to lower temperature[16]. The values clearly indicates the presence of weak interactions between the unlike molecules of ternary mixtures, when benzaldehyde concentration is higher.

IV.CONCLUSION

The experimental data and the calculated thermodynamic parameters clearly indicate the presence of the molecular interaction between the component molecules in the ternary liquid mixtures. The experimental values clearly indicate that the interaction exists between diethylmalonate with toluene and benzaldehyde.

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