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Measurement and correlation of thermodynamic properties of ternary mixtures of oxygenated fuel

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Abstract−Oxygenated fuels are of great interest as these are more energy efficient and environment friendly. Therefore, thermodynamic properties like density, ultrasonic speed and refractive indices of diisopropyl ether+benzene+n-hexane mixtures were measured experimentally at 298.15 K, 308.15 K and 318.15 K. Excess properties like volume (V_m^E), isentropic compressibility (K_S^E), intermolecular free length (L_f^E) as well as deviation in ultrasonic speed (Δu) and refractive index (Δn) of these mixtures were derived from experimental data. The V_m^E values were also fitted to the Singh, Cibulka and Nagata equations, and the same were also predicted using Prigogine-Flory-Patterson theory and four geometrical models from constituent binary V_m^E data. The u data were correlated by Nomato, van Dael, impedance dependence correlations and CFT theory at 298.15 K. L_f^E and V_a^E were also calculated using Jacobson free length theory at 298.15 K. The n data were also predicted by Arago-Biot, Gladstone-Dale, Weiner, Heller, Newton, Eyring and John mixing rules.

Keywords: Fuel Oxygenate, Excess Molar Volume, Ultrasonic Speed, Refractive Index, Hydrocarbon, Diisopropyl Ether, PFP Theory

INTRODUCTION

The study of physical properties of liquid-liquid systems has attracted considerable interest in view of its importance to interpret and predict the intermolecular interactions present among mixing components [1-3]. The main problem is the non-availability of data to comprehend the nature of interactions amongst the constituents. The physicochemical properties involving excess thermodynamic functions are found to be relevant to carry out engineering applications in the process industry and designing of separation processes in chemical industries [4-7]. Also the information about the excess thermodynamic functions can be utilized to develop new empirical correlations and to improve the existing theoretical knowledge. Oxygenated motor fuel is a mixture of oxygenate, aromatics and alkanes. In our earlier work, we reported the excess the excess volume [8-17], excess enthalpy [18-29], and vapor-liquid equilibrium data [30-35] of isomers of butanol or propanol with aromatics (benzene, toluene, xylenes and cyclohexane) and interpreted the data in terms of Mecke-Kempter type of association model. This paper is an extension of our past studies associated with various thermodynamic properties of binary mixtures of diisopropyl ether, benzene and n-hexane [17,36,37]. The alcohols and ethers are considered as fuel oxygenate. Excess enthalpy and excess volume of binary mixtures of diisopropyl ether, ethanol, alkane and aromatics were also studied at different temperature over a wide range of temperature [9,19,26,27,38,39]. Transport properties of these binary

Table 1. Purities (wt%), measured densities, ρ (gcm^{-3}), refractive indices n_D and ultrasonic speed u (ms^{-1}) of the pure liquids at 298.15 K

Compound	GC results wt%	ρ/g cm^{-3}		n_D		u	
		This work	Literature [46]	This work	Literature [46]	This work	Literature [46]
DIPE	99.8	0.718522	0.71820	1.3654	1.3655	997.81	998.23
Benzene	99.6	0.873612	0.87355	1.4972	1.4977	1,298.83	1,298
n-Hexane	99.7	0.655296	0.6548	1.3733	1.3736[a][47]	1,080.10	1,077.7

[a][47]; standard uncertainties (u) are u(T)=0.05 K; u(p)=0.001 MPa; u(ρ)=0.5 kg m^{-3}; u(n_D)=0.0005; (u)=0.05 ms^{-1}

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mixtures were also reported to understand the fluid behavior of binary mixtures with oxygenates [40,41-45]. As motor fuel is a mixture of aromatic, alkane and oxygenate, it was considered to undertake the study of ternary liquid mixtures containing alkane and aromatics in association with industrially important solvent diisopropyl ether (DIPE) at various temperatures over the whole range of compositions. After a literature survey we observed that molecular interactions amongst the ternary model fuel systems containing DIPE have not been much explored. A systematic study of thermodynamic properties such as density (ρ), excess molar volume (V_m^E), ultrasonic speed (u) and refractive index (n_D) of ternary diisopropyl ether+benzene+n-hexane system at 298.15 K, 308.15 K and 318.15 K was done. The V_m^E data were interpreted quantitatively in terms of Prigogine-Flory-Patterson (PFP) theory as well as solution models, while other u and n_D properties were also correlated with many correlations.

EXPERIMENTAL

DIPE, benzene and n-hexane (all Merck) were purified [46] and preserved in dark colored bottles with 4A size sieves (Merck). The final clarity of all the purified solvents was confirmed with

Table 2. Experimental density, ρ (gcm^{-3}), ultrasonic speed u (ms^{-1}) and refractive indices n_D along with calculated excess molar volume V_m^E ($cm^3\ mol^{-1}$), deviation in speed of sound Δu (ms^{-1}), excess isentropic compressibility κ_S^E (TPa^{-1}) and deviation in refractive index Δn for the ternary DIPE (1)+benzene (2)+n-hexane (3) system

x_1	x_2	ρ	$V_{exp.}^E$	u	Δu	κ_S^E	n_D	Δn
298.15 K								
0.0177	0.0342	0.661259	0.081	1,078.80	−1.53	4.71	1.3855	−0.0037
0.0212	0.5561	0.754616	0.387	1,158.18	21.45	−32.13	1.4321	−0.0152
0.0214	0.9526	0.860252	0.015	1,279.16	13.2	−14.49	1.4896	−0.0019
0.0268	0.8893	0.840952	0.104	1,254.28	20.65	−24	1.4794	−0.0049
0.047	0.0788	0.669766	0.162	1,079.71	−0.52	3.37	1.3874	−0.0062
0.0578	0.9247	0.855273	−0.061	1,267.83	23.61	−27.92	1.4832	−0.0044
0.0591	0.3608	0.718072	0.344	1,118.94	15.61	−26.63	1.4096	−0.0152
0.0599	0.167	0.684377	0.251	1,088.92	3.91	−5.39	1.3929	−0.0103
0.0987	0.1841	0.690011	0.245	1,088.22	5.63	−9.27	1.3934	−0.0109
0.1024	0.2259	0.69729	0.262	1,093.75	8.20	−14.33	1.3962	−0.0127
0.111	0.3333	0.717001	0.288	1,109.99	15.17	−27.15	1.4046	−0.0161
0.1323	0.5119	0.754161	0.269	1,142.57	26.80	−45.03	1.4220	−0.0181
0.1422	0.8395	0.838054	−0.18	1,234.30	40.72	−55.01	1.4673	−0.0091
0.1468	0.7573	0.814763	0.002	1,206.23	39.69	−57.11	1.4554	−0.0118
0.1643	0.4334	0.740444	0.246	1,125.88	24.91	−44.63	1.4140	−0.0167
0.1768	0.2154	0.701124	0.193	1,086.27	8.71	−16.57	1.3923	−0.0139
0.1855	0.7856	0.826695	−0.196	1,214.43	45.30	−65.40	1.4588	−0.0107
0.2267	0.2655	0.713646	0.154	1,091.89	14.98	−30.10	1.3947	−0.0161
0.2444	0.4765	0.755427	0.178	1,128.75	30.70	−55.47	1.4170	−0.0169
0.2497	0.6887	0.806111	−0.138	1,182.15	47.19	−75.17	1.4446	−0.0128
0.289	0.6072	0.788734	−0.035	1,158.21	44.59	−75.91	1.4330	−0.0145
0.3456	0.3091	0.730299	0.075	1,090.41	21.00	−43.52	1.3970	−0.0162
0.3676	0.6234	0.800945	−0.423	1,159.65	52.29	−92.13	1.4352	−0.0125
0.4373	0.4152	0.757553	0.004	1,106.52	35.57	−71.16	1.4095	−0.0136
0.5016	0.2738	0.734923	−0.014	1,074.66	22.22	−49.15	1.3939	−0.0122
0.5631	0.2116	0.728089	−0.054	1,060.47	17.50	−40.83	1.3867	−0.0112
0.6066	0.1045	0.712478	−0.013	1,039.29	5.56	−13.67	1.3744	−0.0107
0.6701	0.0825	0.712815	0.012	1,031.87	4.04	−9.90	1.3743	−0.007
0.7025	0.1355	0.724121	−0.075	1,038.29	10.61	−26.67	1.3790	−0.0076
0.7302	0.175	0.733102	−0.158	1,043.97	16.54	−41.3	1.3824	−0.008
0.7823	0.0637	0.716824	0.018	1,021.32	2.67	−6.56	1.3730	−0.0039
0.8066	0.0426	0.714708	0.066	1,017.63	1.51	−3.20	1.3710	−0.0031
0.8357	0.1046	0.727763	−0.153	1,025.5	9.24	−24.81	1.3756	−0.0048
0.8862	0.0487	0.721104	−0.033	1,014.57	3.98	−10.72	1.3710	−0.0021
0.9188	0.0342	0.720717	−0.020	1,010.31	2.49	−6.76	1.3692	−0.0017
0.9544	0.0349	0.723332	−0.087	1,007.77	2.42	−7.21	1.3690	−0.0012

Table 2. Continued

x_1	x_2	ρ	$V^E_{exp.}$	u	Δu	κ^E_S	n_D	Δn
308.15 K								
0.0177	0.0342	0.652025	0.077	1,034.07	−1.44	5.07	1.3807	−0.0037
0.0212	0.5561	0.744906	0.346	1,115.13	23.68	−41.78	1.426	−0.0152
0.0214	0.9526	0.8497	−0.006	1,232.33	13.06	−16.42	1.4824	−0.0019
0.0268	0.8893	0.830653	0.066	1,207.97	20.8	−27.84	1.4734	−0.0039
0.0470	0.0788	0.660473	0.142	1,034.76	−0.66	3.9	1.3816	−0.0071
0.0578	0.9247	0.844621	−0.087	1,221.78	24.5	−33.05	1.4771	−0.0034
0.0591	0.3608	0.708769	0.256	1,074.68	16.38	−33.5	1.4046	−0.0145
0.0599	0.1670	0.675113	0.197	1,044.52	4.36	−8.16	1.3872	−0.0108
0.0987	0.1841	0.680719	0.168	1,043.48	5.77	−12.07	1.3868	−0.0122
0.1024	0.2259	0.688038	0.167	1,049.18	8.53	−18.57	1.39	−0.0135
0.111	0.3333	0.707833	0.151	1,065.43	15.66	−34.03	1.3997	−0.0153
0.1323	0.5119	0.745046	0.080	1,097.99	27.69	−55.53	1.4178	−0.0162
0.1422	0.8395	0.827348	−0.232	1,188.96	42.43	−65.59	1.4627	−0.0067
0.1468	0.7573	0.804825	−0.126	1,161.34	41.34	−69.07	1.4513	−0.0091
0.1643	0.4334	0.731409	0.037	1,080.4	24.75	−53.23	1.4081	−0.0167
0.1768	0.2154	0.691826	0.062	1,041.96	9.34	−22.26	1.3865	−0.0143
0.1855	0.7856	0.816087	−0.272	1,169.26	47.06	−78.06	1.4545	−0.0081
0.2267	0.2655	0.704414	−0.031	1,047.23	15.36	−37.68	1.3888	−0.0164
0.2444	0.4765	0.746476	−0.098	1,084.3	31.83	−69.03	1.4122	−0.0155
0.2497	0.6887	0.795946	−0.285	1,137.45	49.05	−90.67	1.4408	−0.0099
0.289	0.6072	0.779049	−0.253	1,113.43	46.04	−91.96	1.4301	−0.0109
0.3456	0.3091	0.72102	−0.182	1,046.13	21.91	−55.16	1.3911	−0.0163
0.3676	0.6234	0.789779	−0.491	1,114.61	53.76	−109.09	1.4296	−0.0115
0.4373	0.4152	0.74801	−0.285	1,062.09	36.74	−87.6	1.4056	−0.0114
0.5016	0.2738	0.725119	−0.266	1,030.65	23.39	−62.41	1.3877	−0.0125
0.5631	0.2116	0.717875	−0.254	1,016.13	18.18	−51.17	1.3803	−0.0118
0.6066	0.1045	0.701769	−0.11	995.4	6.45	−19.48	1.368	−0.0115
0.6701	0.0825	0.701857	−0.065	987.83	4.72	−14.35	1.3682	−0.0076
0.7025	0.1355	0.71314	−0.19	994.29	11.44	−34.5	1.3726	−0.0083
0.7302	0.175	0.721986	−0.282	1,001.06	18.54	−54.65	1.3782	−0.0064
0.7823	0.0637	0.705449	−0.037	977.29	3.28	−10.09	1.3657	−0.0057
0.8066	0.0426	0.703215	0.031	973.36	1.82	−5.12	1.3645	−0.0041
0.8357	0.1046	0.716096	−0.206	981.6	10.05	−31.69	1.3705	−0.0042
0.8862	0.0487	0.709302	−0.06	969.31	3.28	−10.57	1.3646	−0.0029
0.9188	0.0342	0.708809	−0.038	966.27	2.96	−9.5	1.3636	−0.0017
0.9544	0.0349	0.711271	−0.098	964.07	3.2	−10.92	1.3633	−0.0013

gas chromatic analysis and by measuring their densities (ρ), ultrasonic speed (u) and refractive index, (n_D) which are listed in Table 1.

The densities and ultrasonic speed were measured with a precision of $\pm 10^{-3}$ kg m^{-3} and ±0.01 ms^{-1} DSA 5000 M (Anton Paar) instrument. Refractive indices were measured using Abbemat 200 refractometer (Anton Paar) having accuracy up to $\pm 1\times10^{-4}$ with temperature control of ±0.01 K. The measured ρ, u and n_D data of the pure compounds show good agreement with literature values (Table 1). The ternary mixtures were prepared using a weighing balance (OHAUS, AR224CN) having accuracy ±0.1 mg with uncertainty $\pm 1\times10^{-4}$. The measured ρ, u and n_D values of the ternary mixtures are recorded in Table 2.

RESULTS

1. Excess Molar Volume

The V^E_m data (Table 2) were calculated from Eq. (1)

$$V^E_m = \sum_i \frac{x_i M_i}{\rho} - \sum_i \frac{x_i M_i}{\rho_i} \quad (1)$$

where x_i, M_i and ρ_i are the mole fractions, molar masses and density of pure components of the mixture, respectively and ρ is the density of the ternary mixture. The ρ and V^E_m values are listed in Table 2 and V^E_m values are shown in Fig. 1.

The V^E_m for the ternary systems were fitted to the Singh, Cibulka and Nagata [48-50] equations, and the binary contributions (eval-

Table 2. Continued

x_1	x_2	ρ	$V^E_{exp.}$	u	Δu	κ^E_S	n_D	Δn
318.15 K								
0.0177	0.0342	0.642616	0.077	989.63	−1.4	5.72	1.3757	−0.0037
0.0212	0.5561	0.734998	0.318	1,071.78	25.32	−51.94	1.4204	−0.0142
0.0214	0.9526	0.838987	−0.012	1,187.22	13.87	−19.82	1.4747	−0.0019
0.0268	0.8893	0.820078	0.055	1,163.72	22.33	−34.15	1.4669	−0.0029
0.047	0.0788	0.650878	0.161	990.38	−0.55	4.35	1.3764	−0.0071
0.0578	0.9247	0.833953	−0.104	1,176.51	25.28	−38.81	1.4694	−0.0034
0.0591	0.3608	0.698773	0.275	1,030.5	16.91	−39.79	1.3986	−0.0145
0.0599	0.167	0.665314	0.23	1,000.18	4.55	−9.66	1.3818	−0.0108
0.0987	0.1841	0.670627	0.241	999.03	5.86	−13.39	1.3816	−0.0119
0.1024	0.2259	0.677833	0.246	1,005.04	8.97	−21.82	1.3854	−0.0125
0.111	0.3333	0.697488	0.22	1,021.73	16.65	−41.11	1.3937	−0.0153
0.1323	0.5119	0.734766	0.082	1,053.86	28.57	−65.82	1.4113	−0.0162
0.1422	0.8395	0.816788	−0.27	1,143.71	43.25	−76.46	1.4553	−0.0067
0.1468	0.7573	0.794645	−0.197	1,116.58	42.34	−81.42	1.4441	−0.0091
0.1643	0.4334	0.720952	0.079	1,036.07	25.3	−62.14	1.4018	−0.0167
0.1768	0.2154	0.681052	0.227	998.47	10.41	−26.94	1.3812	−0.0139
0.1855	0.7856	0.805678	−0.331	1,124.47	48.23	−91.76	1.4472	−0.0081
0.2267	0.2655	0.693343	0.153	1,002.47	15.22	−40.95	1.3834	−0.0159
0.2444	0.4765	0.736305	−0.139	1,040.36	32.89	−82.41	1.4068	−0.0145
0.2497	0.6887	0.785999	−0.405	1,092.91	50.19	−107.29	1.4340	−0.0096
0.289	0.6072	0.769429	−0.416	1,069.55	47.57	−110.51	1.4240	−0.0101
0.3456	0.3091	0.710008	−0.062	1,001.49	21.95	−62.37	1.3850	−0.0163
0.3676	0.6234	0.779303	−0.56	1,069.84	54.54	−127.57	1.4236	−0.0105
0.4373	0.4152	0.738342	−0.45	1,017.87	37.43	−104.56	1.4001	−0.0104
0.5016	0.2738	0.714475	−0.246	986.83	24.15	−74.07	1.3823	−0.0118
0.5631	0.2116	0.706926	−0.173	972.78	19.28	−61.62	1.3754	−0.0108
0.6066	0.1045	0.69044	0.078	950.98	6.31	−19.87	1.3624	−0.0115
0.6701	0.0825	0.690722	0.076	943.44	4.55	−14.4	1.3629	−0.0072
0.7025	0.1355	0.702306	−0.142	949.26	10.68	−36.86	1.3667	−0.0083
0.7302	0.175	0.711451	−0.314	955.77	17.58	−60.59	1.3722	−0.0064
0.7823	0.0637	0.694616	0.019	933.47	3.58	−12.11	1.361	−0.0047
0.8066	0.0426	0.69247	0.072	929.94	2.49	−7.90	1.359	−0.0039
0.8357	0.1046	0.705451	−0.222	938.06	10.65	−39	1.3656	−0.0032
0.8862	0.0487	0.698615	−0.059	924.69	2.7	−10.14	1.3592	−0.0026
0.9188	0.0342	0.698109	−0.038	921.82	2.51	−9.41	1.3578	−0.0017
0.9544	0.0349	0.70056	−0.108	920.79	3.91	−15.34	1.3575	−0.0013

uated by Redlich-Kister equation) required for these equations are reported in our previous work [17,37].

Singh Equation [48]:

$$V^E_m = V^E_{12} + V^E_{23} + V^E_{31} + x_1x_2x_3\sum_{i=1}^{4} A^{(i)}\{x_1(x_2-x_3)\}^{(i-1)} \quad (2)$$

Cibulka Equation [49]:

$$V^E_m = V^E_{12} + V^E_{23} + V^E_{31} + x_1x_2x_3\{A^{(1)} + A^{(2)}x_1 + A^{(3)}x_2\} \quad (3)$$

Nagata Equation [50]:

$$V^E_m = V^E_{12} + V^E_{23} + V^E_{31} + x_1x_2x_3A^{(1)} \quad (4)$$

where $A^{(i)}$ are the characteristics parameters. These parameters for Eqs. (2)-(4) along with their respective standard deviations are tabulated in Table 3. The V^E_m values were also predicted by following thermodynamic solution models and tabulated in Table 4. These models use excess volume of constituents binary mixtures reported earlier [17,37].

Tsao-Smith Model [51]:

$$V^E_m = \frac{V^E_{12}x_2}{1-x_1} + \frac{V^E_{31}x_3}{1-x_1} + V^E_{23}(1-x_1) \quad (5)$$

Jacob-Fitzner Model [52]:

$$V^E_m = \frac{V^E_{12}x_1x_2}{[(x_1+x_3/2)(x_2+x_3/2)]} + \frac{V^E_{23}x_2x_3}{[(x_2+x_1/2)(x_3+x_1/2)]}$$

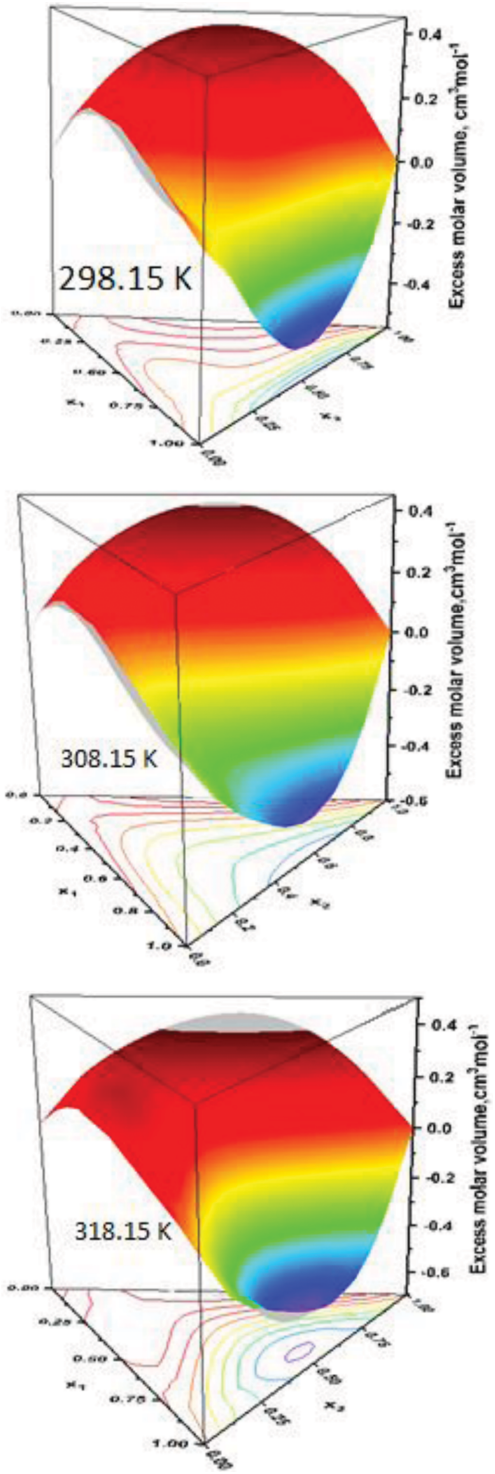


Fig. 1. Excess molar volume as a function of mole fractions (x_1, x_2 and x_3) for the ternary DIPE (1)+benzene (2)+n-hexane (3) system.

$$+\frac{V_{31}^{E}x_3x_1}{[(x_3+x_2/2)(x_1+x_2/2)]} \quad (6)$$

Kohler model [53]:

$$V_m^E = V_{12}^E(x_1+x_2)^2 + V_{23}^E(x_2+x_3)^2 + V_{31}^E(x_3+x_1)^2 \quad (7)$$

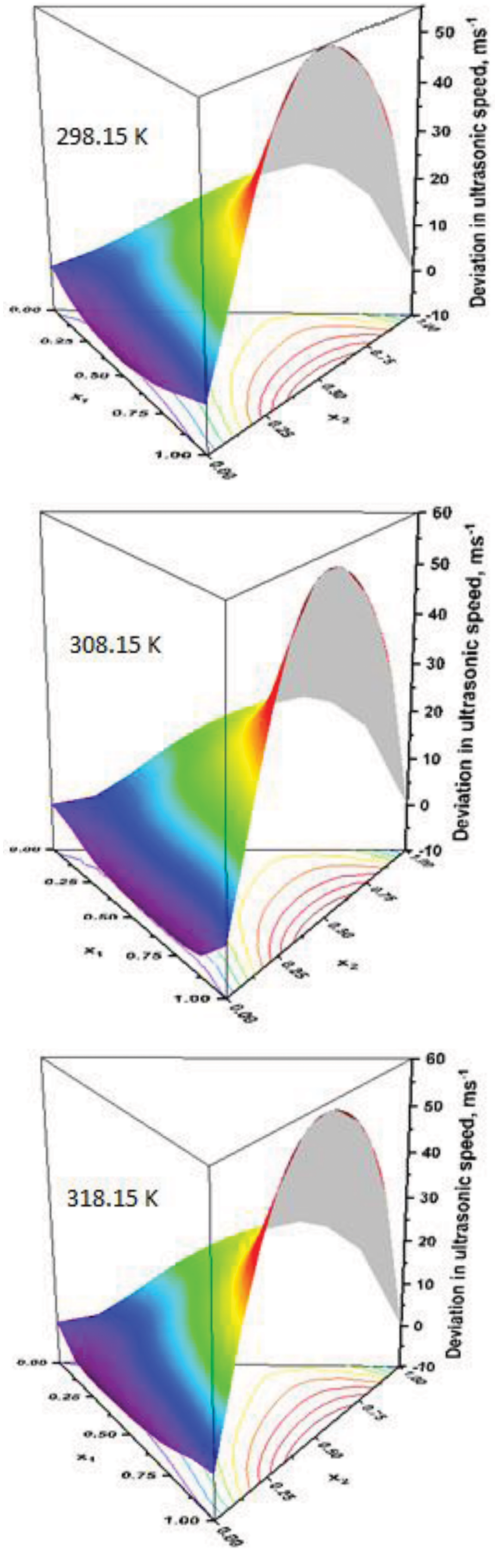


Fig. 2. Deviation in ultrasonic speed as a function of mole fractions (x_1, x_2 and x_3) for the ternary DIPE (1)+benzene (2)+n-hexane (3) system.

Rastogi model [54]:

$$V_m^E = \frac{V_{12}^E(x_1+x_2)+V_{23}^E(x_2+x_3)+V_{31}^E(x_3+x_1)}{2} \quad (8)$$

Table 3. Coefficient $A^{(n)}$ (n=1−4) of Singh, Cibulka and Nagata equations for smoothening of calculated V_m^E, Δu, κ_S^E and Δn properties along with their standard deviations for the ternary DIPE (1)+benzene (2)+n-hexane (3) system

Property	Equation	T/K	$A^{(1)}$	$A^{(2)}$	$A^{(3)}$	$A^{(4)}$	σ
	Singh	298.15	0.2371	46.3194	3.9163	1.5931	0.0328
		308.15	−6.8224	19.4884	3.8500	1.6454	0.0278
		318.15	−4.1652	−52.4707	2.9523	4.7892	0.0305
	Cibulka	298.15	−9.1002	5.9357	23.5384		0.0342
		308.15	−11.0332	2.3239	11.3173		0.0258
		318.15	4.8394	−7.2588	−20.071		0.0424
	Nagata	298.15	0.6969				0.0602
		308.15	−6.4960				0.0350
		318.15	−4.2331				0.0587
Δu	Singh	298.15	−236.495	−1,049.932	755.213	1,419.077	3.40
		308.15	−249.927	−1,220.246	961.502	1,824.829	3.84
		318.15	−309.235	−710.166	1,031.522	544.391	3.97
κ_S^E	Singh	298.15	292.48	1,809.38	−1,347.21	−2,319.12	6.79
		308.15	345.39	1,389.90	−2,902.63	−1,548.13	10.18
		318.15	543.12	21.420	−2,811.16	−463.65	12.17
Δn	Singh	298.15	−0.0840	1.0397	−0.2089	0.0197	0.0007
		308.15	−0.0903	1.5101	−0.1024	0.3701	0.0006
		318.15	−0.1176	1.5491	−0.1874	−0.0329	0.0007

Table 4. Molar volume, V ($cm^3\ mol^{-1}$), isobaric expansivity, α (K^{-1}), and isothermal compressibility, κ_T ($cm^3\ J^{-1}$), characteristic pressure, P* ($J\ cm^{-3}$), characteristic molar volume, V* ($cm^3\ mol^{-1}$), and characteristic temperature, T* (K), obtained from Flory theory for the pure liquids

Compound	T/K	V	$10^3\ \alpha$	$10^6\ \kappa_T$	P*	V*	T*
DIPE	298.15	141.89	1.435	1,817.0	417.00	106.64	4,368
	308.15	144.32	1.490	1,987.7	420.25	107.00	4,378
	318.15	146.55	1.540	2,255.0	405.54	107.27	4,400
Benzene	298.15	89.41	1.213	978.0	615.19	69.32	4,728
	308.15	90.52	1.250	1,051.8	623.34	69.38	4,739
	318.15	91.67	1.266	1,138.0	612.49	69.68	4,791
n-Hexane	298.15	131.51	1.391	1,728.2	419.85	99.42	4,430
	308.15	133.38	1.430	1,864.7	423.13	99.67	4,457
	318.15	135.33	1.468	2,049.0	417.47	100.00	4,488

Radojkovic model [55]:

$$V_m^E = V_{12}^E + V_{23}^E + V_{31}^E \tag{9}$$

The V_m^E values of the present ternary systems were also analyzed by PFP theory [56-59].

Prigogine-Flory-Patterson Theory

In this theory, V_{ijk}^E for a ternary system is given by [56-59]

$$V_m^E = V_{123(\text{interaction})}^E - V_{123(\textit{free}\ \text{volume})}^E + V_{123(\textit{P*}\ \textit{effect})}^E \tag{10}$$

where $V_{123(\text{interaction})}^E$, $V_{123(\text{free volume})}^E$ and $V_{123(P^*\ \text{effect})}^E$ were calculated using following relations:

$$\frac{V_{123(\text{interaction})}^E}{\sum_{i=1}^{3} x_i V_i^*} = \sum_{\substack{i,j=1 \\ i\neq j}}^{3} \frac{(\tilde{V}^{1/3}-1)\tilde{V}^{2/3}\psi_i\theta_j\chi_{ij}^*}{((4/3)\tilde{V}^{-1/3}-1)P_i^*} \tag{11}$$

$$\frac{V_{123(\textit{free}\ \text{volume})}^E}{\sum_{i=1}^{3} x_i V_i^*} = \sum_{\substack{i,j=1 \\ i\neq j}}^{3} \frac{(\tilde{V}_i-\tilde{V}_j)^2\{(14/9)\tilde{V}^{-1/3}-1\}\psi_i\psi_j}{\{(4/3)\tilde{V}^{-1/3}-1\}\tilde{V}} \tag{12}$$

$$\frac{V_{123(\textit{P*}\ \text{effect})}^E}{\sum_{i=1}^{3} x_i V_i^*} = \sum_{\substack{i,j=1 \\ i\neq j}}^{3} \frac{(\tilde{V}_i-\tilde{V}_j)(P_i^*-P_j^*)\psi_i\psi_j}{P_i^*\psi_j + P_j^*\psi_i} \tag{13}$$

In these equations all the terms have their usual meaning described elsewhere [60, 61] and the values of these parameters (P_i^*, V_i^*, T_i^*, α_i, κ_{T_i}) are given in Table 4. Calculation of V_m^E from Eq. (10) requires a knowledge of Flory interaction parameters χ_{ij}^*. The interaction parameter (χ_{ij}^*) was calculated by method described earlier [59]. These PFP predicted V_m^E values are shown in Table 5. The V_m^E values from PFP theory are in good agreement with experimental data for the binary systems [17,37] but for the ternary systems, the

Table 5. Comparison of excess molar volume, V_m^E ($cm^3\ mol^{-1}$) with its predicted values using various thermodynamic solution models and PFP theory along with standard deviation for the ternary DIPE (1)+benzene (2)+n-hexane (3) system

x_1	x_2	$V^E_{exp.}$	V^E_{Tao}	V^E_{Jacob}	V^E_{Kohler}	$V^E_{Rastogi}$	V^E_{Radoj}	V^E_{PFP}
298.15 K								
0.0177	0.0342	0.081	0.019	0.032	0.072	0.037	0.074	0.166
0.0212	0.5561	0.387	−0.005	0.013	0.368	0.186	0.377	1.035
0.0214	0.9526	0.015	−0.043	−0.026	0.008	0.004	0.008	0.074
0.0268	0.8893	0.104	−0.045	−0.015	0.098	0.049	0.099	0.301
0.047	0.0788	0.162	0.045	0.077	0.147	0.077	0.158	0.338
0.0578	0.9247	−0.061	−0.109	−0.095	−0.078	−0.039	−0.077	−0.041
0.0591	0.3608	0.344	0.018	0.053	0.314	0.166	0.342	0.906
0.0599	0.167	0.251	0.048	0.083	0.229	0.122	0.252	0.591
0.0987	0.1841	0.245	0.068	0.120	0.229	0.127	0.266	0.578
0.1024	0.2259	0.262	0.060	0.113	0.244	0.135	0.285	0.648
0.111	0.3333	0.288	0.030	0.088	0.256	0.142	0.300	0.762
0.1323	0.5119	0.269	−0.045	0.027	0.186	0.101	0.220	0.723
0.1422	0.8395	−0.18	−0.229	−0.217	−0.203	−0.102	−0.202	−0.196
0.1468	0.7573	0.002	−0.187	−0.137	−0.076	−0.038	−0.068	0.144
0.1643	0.4334	0.246	−0.024	0.053	0.174	0.098	0.217	0.669
0.1768	0.2154	0.193	0.081	0.158	0.204	0.119	0.258	0.495
0.1855	0.7856	−0.196	−0.269	−0.252	−0.234	−0.117	−0.232	−0.207
0.2267	0.2655	0.154	0.053	0.137	0.166	0.099	0.223	0.451
0.2444	0.4765	0.178	−0.104	−0.027	0.031	0.022	0.065	0.460
0.2497	0.6887	−0.138	−0.294	−0.265	−0.238	−0.120	−0.233	−0.113
0.289	0.6072	−0.035	−0.272	−0.233	−0.201	−0.101	−0.191	0.038
0.3456	0.3091	0.075	−0.028	0.049	0.04	0.029	0.082	0.265
0.3676	0.6234	−0.423	−0.415	−0.412	−0.409	−0.205	−0.408	−0.527
0.4373	0.4152	0.004	−0.225	−0.194	−0.188	−0.096	−0.177	0.050
0.5016	0.2738	−0.014	−0.090	−0.052	−0.075	−0.037	−0.055	0.034
0.5631	0.2116	−0.054	−0.048	−0.017	−0.049	−0.025	−0.031	−0.041
0.6066	0.1045	−0.013	0.061	0.094	0.053	0.028	0.072	−0.040
0.6701	0.0825	0.012	0.057	0.079	0.046	0.024	0.060	−0.034
0.7025	0.1355	−0.075	−0.024	−0.015	−0.04	−0.021	−0.030	−0.116
0.7302	0.1750	−0.158	−0.101	−0.105	−0.117	−0.061	−0.112	−0.214
0.7823	0.0637	0.018	0.028	0.035	0.017	0.008	0.024	−0.035
0.8066	0.0426	0.066	0.041	0.047	0.032	0.016	0.038	0.012
0.8357	0.1046	−0.153	−0.051	−0.056	−0.063	−0.032	−0.059	−0.207
0.8862	0.0487	−0.033	0.000	0.000	−0.007	−0.004	−0.004	−0.074
0.9188	0.0342	−0.020	0.002	0.002	−0.002	−0.001	0.000	−0.052
0.9544	0.0349	−0.087	−0.015	−0.016	−0.016	−0.008	−0.015	−0.11
Standard deviation (σ)			0.1676	0.1370	0.0652	0.1005	0.0613	0.2558

comparison between experimental V_m^E values and values calculated from PFP theory is not very impressive, as evident from the standard deviation (Table 5). This may be due to the addition of n-hexane to this binary mixture, as this would break the n-π interaction between DIPE and benzene, and internal accommodation of n-hexane is also very poor due to steric factor at 298.15 K. This contributes to increase in magnitude of free volume contribution ($V^E_{123(free\ volume)}$) factor from negative to positive that should be negative instead of positive. Thus, the positive magnitude of $V^E_{123(free\ volume)}$ contribution makes PFP theory inadequate for analyzing the V_m^E data of present ternary system. Patterson and co-workers also postulated that the discrepancies between theory and experimental values arise from additional factors that occur during mixing [62] since PFP theory does not consider all the possible interactions existing in the component molecules.

2. Ultrasonic Speed

The measured u and derived Δu and κ_S^E are given in Table 2 and shown in Fig. 2 and 3, respectively. The Δu and κ_S^E values were calculated using the experimentally measured ρ and u data.

$$\Delta u = u - (\rho^{id}\kappa_S^{id})^{1/2} \tag{14}$$

$$\kappa_S^E = \kappa_S - \kappa_S^{id} \tag{15}$$

Table 5. Continued

x_1	x_2	$V^E_{exp.}$	V^E_{Tao}	V^E_{Jacob}	V^E_{Kohler}	$V^E_{Rastogi}$	V^E_{Radoj}	V^E_{PFP}
308.15 K								
0.0177	0.0342	0.077	0.018	0.033	0.075	0.038	0.077	0.162
0.0212	0.5561	0.346	−0.007	0.014	0.385	0.195	0.392	1.005
0.0214	0.9526	−0.006	−0.042	−0.026	0.006	0.003	0.006	0.057
0.0268	0.8893	0.066	−0.046	−0.015	0.094	0.047	0.096	0.268
0.047	0.0788	0.142	0.044	0.077	0.148	0.078	0.159	0.319
0.0578	0.9247	−0.087	−0.112	−0.097	−0.082	−0.041	−0.082	−0.062
0.0591	0.3608	0.256	0.015	0.053	0.315	0.166	0.34	0.828
0.0599	0.167	0.197	0.046	0.082	0.227	0.121	0.249	0.542
0.0987	0.1841	0.168	0.064	0.118	0.226	0.125	0.26	0.506
0.1024	0.2259	0.167	0.056	0.111	0.241	0.133	0.278	0.559
0.111	0.3333	0.151	0.026	0.087	0.256	0.141	0.295	0.634
0.1323	0.5119	0.080	−0.055	0.025	0.191	0.103	0.219	0.546
0.1422	0.8395	−0.232	−0.252	−0.238	−0.226	−0.114	−0.226	−0.237
0.1468	0.7573	−0.126	−0.210	−0.155	−0.094	−0.048	−0.090	0.028
0.1643	0.4334	0.037	−0.032	0.051	0.176	0.098	0.214	0.471
0.1768	0.2154	0.062	0.075	0.154	0.200	0.116	0.250	0.368
0.1855	0.7856	−0.272	−0.302	−0.283	−0.266	−0.134	−0.266	−0.270
0.2267	0.2655	−0.031	0.047	0.134	0.163	0.097	0.216	0.273
0.2444	0.4765	−0.098	−0.116	−0.033	0.028	0.019	0.056	0.197
0.2497	0.6887	−0.285	−0.329	−0.298	−0.271	−0.137	−0.269	−0.245
0.289	0.6072	−0.253	−0.300	−0.257	−0.224	−0.114	−0.219	−0.164
0.3456	0.3091	−0.182	−0.033	0.047	0.038	0.027	0.079	0.017
0.3676	0.6234	−0.491	−0.450	−0.447	−0.444	−0.222	−0.444	−0.577
0.4373	0.4152	−0.285	−0.230	−0.198	−0.191	−0.098	−0.181	−0.223
0.5016	0.2738	−0.266	−0.093	−0.053	−0.077	−0.039	−0.058	−0.208
0.5631	0.2116	−0.254	−0.054	−0.023	−0.056	−0.029	−0.041	−0.234
0.6066	0.1045	−0.110	0.051	0.083	0.039	0.020	0.052	−0.137
0.6701	0.0825	−0.065	0.046	0.065	0.029	0.013	0.035	−0.112
0.7025	0.1355	−0.190	−0.039	−0.033	−0.063	−0.035	−0.060	−0.228
0.7302	0.175	−0.282	−0.122	−0.13	−0.145	−0.076	−0.146	−0.330
0.7823	0.0637	−0.037	0.015	0.018	−0.01	−0.007	−0.011	−0.090
0.8066	0.0426	0.031	0.029	0.032	0.008	0.002	0.007	−0.025
0.8357	0.1046	−0.206	−0.085	−0.096	−0.111	−0.058	−0.114	−0.255
0.8862	0.0487	−0.060	−0.019	−0.026	−0.044	−0.024	−0.046	−0.100
0.9188	0.0342	−0.038	−0.014	−0.020	−0.035	−0.018	−0.036	−0.070
0.9544	0.0349	−0.098	−0.045	−0.050	−0.055	−0.028	−0.056	−0.119
Standard deviation (σ)			0.1218	0.1211	0.0994	0.1240	0.1172	0.2613

$$\kappa_S = (u^2\rho)^{-1} \tag{16}$$

κ_S^{id} was calculated as:

$$\kappa_S^{id} = \sum_{i=1}^{3}\phi_i\kappa_{S,i} + T\left\{\sum_{i=1}^{3}\frac{\phi_i V_i(\alpha_i)^2}{C_{p,i}}\right\} - T\left(\sum_{i=1}^{3}x_i V_i\right)\frac{\left(\sum_{i=1}^{3}\phi_i\alpha_i\right)^2}{\left(\sum_{i=1}^{3}x_i C_{p,i}\right)} \tag{17}$$

Δu and κ_S^E data were fitted to Eq. (18) [48]:

$$X_{123}(X = \Delta u,\ \kappa_S^E,\ \Delta n) = X_{12} + X_{23} + x_{31} + x_1x_2x_3\left[\sum_{i=1}^{4}A^{(i)}\{x_1(x_2 - x_3)\}\right] \tag{18}$$

The standard deviation for Δu and κ_S^E along with $A^{(i)}$ coefficients for ternary systems have been reported in Table 3. Following theoretical relations were employed for estimation of u of ternary systems:

Nomoto's relation [63]:

$$u = \left(\frac{R_m}{V_{mix}}\right)^3 = \left[\frac{\sum x_i R_i}{\sum x_i V_i}\right]^3 \tag{19}$$

Table 5. Continued

x_1	x_2	$V^E_{exp.}$	V^E_{Tao}	V^E_{Jacob}	V^E_{Kohler}	$V^E_{Rastogi}$	V^E_{Radoj}	V^E_{PFP}
318.15 K								
0.0177	0.0342	0.077	0.016	0.034	0.077	0.039	0.079	0.158
0.0212	0.5561	0.318	−0.009	0.014	0.396	0.200	0.402	0.964
0.0214	0.9526	−0.012	−0.045	−0.028	−0.002	−0.001	−0.002	0.053
0.0268	0.8893	0.055	−0.05	−0.017	0.084	0.042	0.084	0.257
0.047	0.0788	0.161	0.041	0.078	0.150	0.079	0.161	0.330
0.0578	0.9247	−0.104	−0.122	−0.106	−0.094	−0.047	−0.095	−0.072
0.0591	0.3608	0.275	0.013	0.053	0.319	0.168	0.341	0.835
0.0599	0.167	0.230	0.043	0.082	0.228	0.122	0.249	0.564
0.0987	0.1841	0.241	0.061	0.118	0.226	0.124	0.257	0.566
0.1024	0.2259	0.246	0.052	0.110	0.241	0.133	0.275	0.626
0.111	0.3333	0.22	0.021	0.087	0.258	0.141	0.292	0.693
0.1323	0.5119	0.082	−0.063	0.023	0.192	0.102	0.213	0.545
0.1422	0.8395	−0.270	−0.278	−0.263	−0.253	−0.127	−0.254	−0.258
0.1468	0.7573	−0.197	−0.231	−0.172	−0.115	−0.059	−0.117	−0.031
0.1643	0.4334	0.079	−0.040	0.049	0.177	0.097	0.207	0.508
0.1768	0.2154	0.227	0.070	0.152	0.198	0.114	0.243	0.521
0.1855	0.7856	−0.331	−0.332	−0.312	−0.297	−0.15	−0.299	−0.309
0.2267	0.2655	0.153	0.039	0.131	0.160	0.094	0.206	0.447
0.2444	0.4765	−0.139	−0.130	−0.040	0.022	0.014	0.041	0.160
0.2497	0.6887	−0.405	−0.360	−0.326	−0.300	−0.153	−0.304	−0.343
0.289	0.6072	−0.416	−0.325	−0.280	−0.247	−0.127	−0.249	−0.307
0.3456	0.3091	−0.062	−0.043	0.041	0.031	0.022	0.064	0.135
0.3676	0.6234	−0.560	−0.485	−0.482	−0.478	−0.24	−0.479	−0.613
0.4373	0.4152	−0.450	−0.245	−0.211	−0.205	−0.106	−0.200	−0.372
0.5016	0.2738	−0.246	−0.104	−0.063	−0.088	−0.046	−0.075	−0.184
0.5631	0.2116	−0.173	−0.065	−0.033	−0.068	−0.037	−0.059	−0.154
0.6066	0.1045	0.078	0.04	0.071	0.025	0.012	0.031	0.036
0.6701	0.0825	0.076	0.037	0.056	0.016	0.005	0.016	0.014
0.7025	0.1355	−0.142	−0.049	−0.045	−0.078	−0.044	−0.081	−0.181
0.7302	0.175	−0.314	−0.139	−0.148	−0.166	−0.088	−0.17	−0.354
0.7823	0.0637	0.019	0.011	0.012	−0.021	−0.014	−0.026	−0.044
0.8066	0.0426	0.072	0.029	0.031	0.001	−0.002	−0.003	0.004
0.8357	0.1046	−0.222	−0.103	−0.117	−0.135	−0.071	−0.140	−0.267
0.8862	0.0487	−0.059	−0.024	−0.033	−0.057	−0.030	−0.061	−0.101
0.9188	0.0342	−0.038	−0.018	−0.025	−0.045	−0.024	−0.047	−0.071
0.9544	0.0349	−0.108	−0.060	−0.067	−0.073	−0.037	−0.074	−0.126
Standard deviation (σ)			0.1285	0.1140	0.0872	0.1447	0.0936	0.2568

$$R_m = \left[\frac{(M_i u_i^{1/3})}{\rho_i^*}\right] \tag{20}$$

van-Dael ideal mixing relation [64]:

$$\frac{1}{(\sum(x_i M_i))u^2} = \sum\left(\frac{x_i}{M_i u_{id}^2}\right) \tag{21}$$

where x_i and M_i are the mole fraction molar mass of the ith component and u_{id}^2 is the ultrasonic speed of the ideal mixture.

Impedance dependence relation [65]:

$$u = \frac{\sum(x_i Z_i)}{\sum(x_i \rho_i^*)} \tag{22}$$

where $Z_i = \mu_i \rho_i^*$ is specific acoustic impedance of the component *i*.

Schaaff's Collision Factor theory (CFT) [66-68]:

According to CFT

$$u_{mix} = \frac{u_\infty (x_1 S_1 + x_2 S_2 + x_3 S_3)(x_1 b_1 + x_2 b_2 + x_3 b_3)}{V_{mix}} \tag{23}$$

$$b = \frac{4\Pi r^3 N_A}{3} \tag{24}$$

and

$$S = \frac{u V_T}{b u_\infty} \tag{25}$$

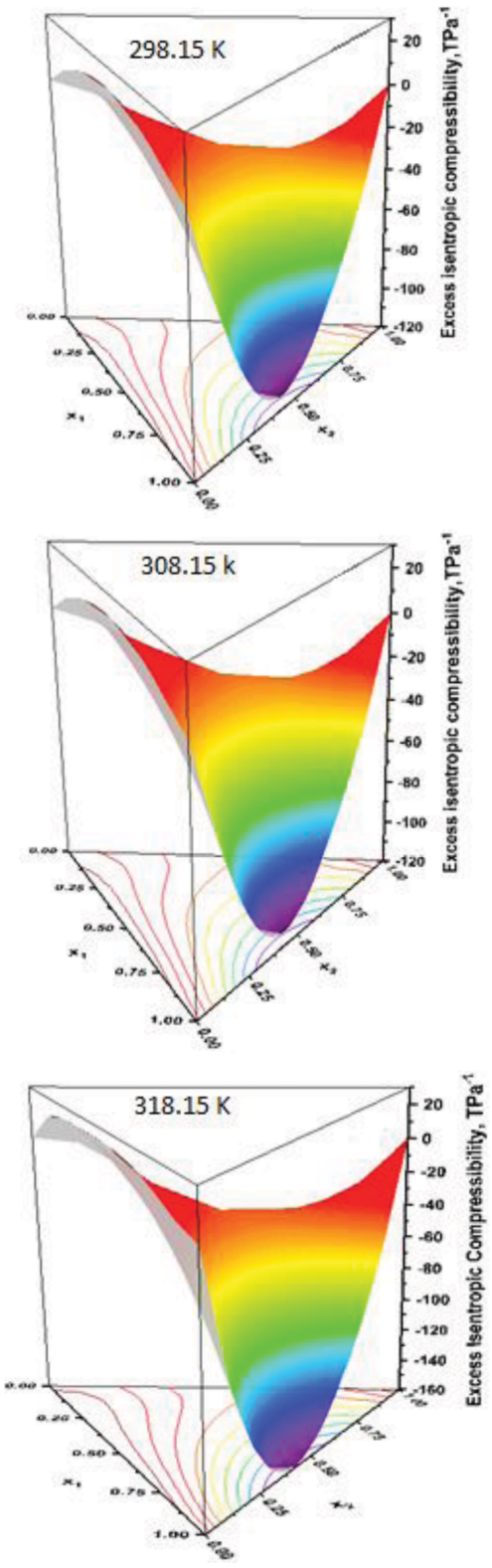


Fig. 3. Excess isentropic compressibility as a function of mole fractions (x_1, x_2 and x_3) for the ternary DIPE (1)+benzene (2)+n-hexane (3) system.

The comparison between these predicted and experimental u values is shown in Fig. 4 in terms of percentage standard deviations.

Table 6. Values of available volume (V_a), excess available volume (V_a^E) ($\times 10^{-6}$, m^3 mol^{-1}), free length (L_f), excess intermolecular free length (L_f^E) (Å) and molecular association M_A at 298.15 K for the ternary DIPE (1)+benzene (2)+n-hexane (3) system

x_1	x_2	V_a	V_a^E	L_f	L_f^E
0.0177	0.0342	30.246	−0.046	0.691	0.0031
0.0212	0.5561	23.406	−0.359	0.616	0.0203
0.0214	0.9526	18.713	−0.086	0.529	0.0029
0.0268	0.8893	19.449	−0.16	0.545	0.0078
0.047	0.0788	29.719	−0.105	0.687	0.0065
0.0578	0.9247	19.096	−0.166	0.535	0.0026
0.0591	0.3608	25.970	−0.359	0.649	0.0179
0.0599	0.1670	28.547	−0.213	0.677	0.0114
0.0987	0.1841	28.424	−0.242	0.676	0.0118
0.1024	0.2259	27.868	−0.286	0.670	0.0134
0.111	0.3333	26.464	−0.371	0.655	0.0164
0.1323	0.5119	24.228	−0.436	0.626	0.0183
0.1422	0.8395	20.243	−0.349	0.554	0.0035
0.1468	0.7573	21.242	−0.393	0.575	0.0102
0.1643	0.4334	25.304	−0.443	0.640	0.0173
0.1768	0.2154	28.212	−0.306	0.673	0.0118
0.1855	0.7856	20.970	−0.431	0.566	0.0050
0.2267	0.2655	27.666	−0.378	0.667	0.0124
0.2444	0.4765	24.96	−0.496	0.634	0.0167
0.2497	0.6887	22.29	−0.525	0.589	0.0089
0.289	0.6072	23.403	−0.555	0.609	0.0124
0.3456	0.3091	27.405	−0.464	0.663	0.0121
0.3676	0.6234	23.331	−0.669	0.600	0.0034
0.4373	0.4152	26.245	−0.579	0.648	0.0131
0.5016	0.2738	28.311	−0.484	0.672	0.0098
0.5631	0.2116	29.34	−0.425	0.683	0.0073
0.6066	0.1045	31.00	−0.243	0.701	0.0045
0.6701	0.0825	31.519	−0.197	0.707	0.0042
0.7025	0.1355	30.829	−0.322	0.699	0.0044
0.7302	0.175	30.329	−0.414	0.692	0.004
0.7823	0.0637	32.14	−0.158	0.713	0.0036
0.8066	0.0426	32.54	−0.099	0.718	0.0037
0.8357	0.1046	31.665	−0.288	0.706	0.0015
0.8862	0.0487	32.675	−0.136	0.718	0.0017
0.9188	0.0342	32.996	−0.097	0.721	0.0013
0.9544	0.0349	33.082	−0.114	0.721	−0.0001

The Nomoto and impedance dependence correlations predict very well the experimental ultrasonic speed data.

Jacobson free length theory [69-71]:

The free length (L_f), available volume (V_a) values, excess available volume (V_a^E) and excess intermolecular free length (L_f^E) were calculated using Eqs. (26)-(28) as per this theory and given in Table 6.

$$L_f = \frac{2V_a}{Y} = \frac{2\left[V_T - \sum_i x_i V_{0i}\right]}{\sum_i x_i Y_i} \quad (26)$$

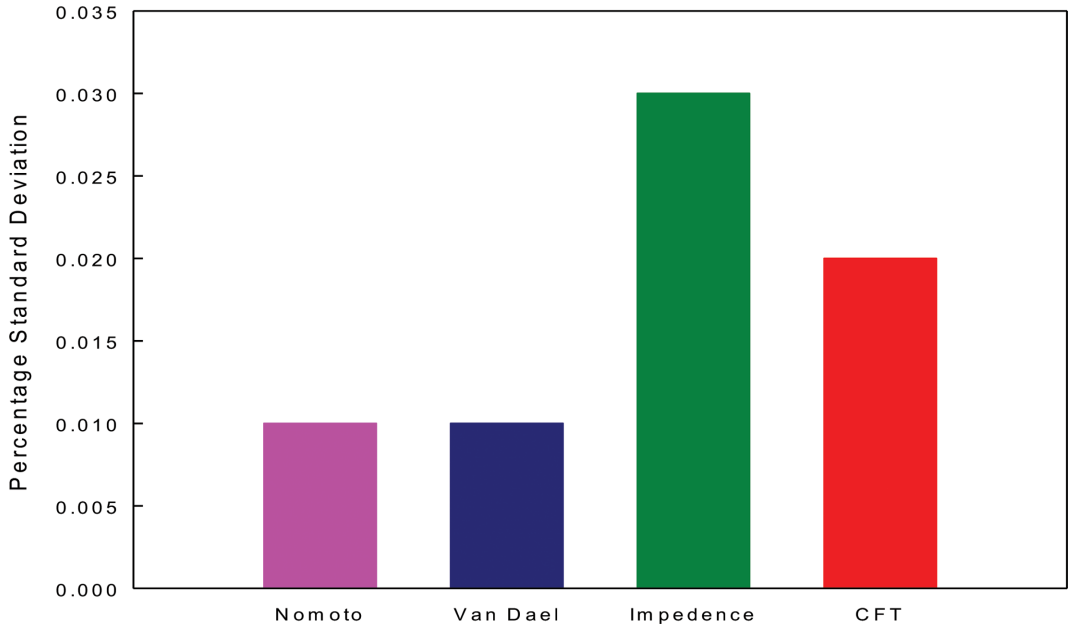


Fig. 4. Percentage standard deviations (σ in %) in ultrasonic speed predicted by various correlations for DIPE (1)+benzene (2)+n-hexane (3) system at 298.15 K.

$$u_{mix} = \frac{K}{L_{f(mix)}\rho_{mix}^{1/2}} \tag{27}$$

$$X_m^E(L_f \text{ and } V_a) = X_m - \sum_{i=1}^{3} x_i M_i^o$$

where K is Jacobson constant and its value is 618 to 642 at T= 293.15 K to 313.15 K.

3. Refractive Index

The Δn values (Table 2 and Fig. 5) were calculated using Eq. (28), and these Δn values were fitted to Eq. (18) whose parameters are given in Table 3.

$$\Delta n = n - \sum_i x_i n_i \tag{28}$$

Various correlations used for quantitative determination of n_D of ternary systems are the following:

Arago-Biot (A-B):

$$n = \sum_i n_i \phi_i \tag{29}$$

Gladstone-Dale (G-D):

$$n - 1 = \sum_i (n_i - 1)\phi_i \tag{30}$$

Lorentz-Lorentz (L-L):

$$\frac{n^2-1}{n^2+2} = \sum_i \left(\frac{n_i^2-1}{n_i^2+2}\right)\phi_i \tag{31}$$

Weiner (W):

$$\frac{n^2-n_1^2}{n^2+2n_1^2} = \sum_{i\neq 1}\left(\frac{n_i^2-n_1^2}{n_i^2+2n_2^2}\right)\phi_i \tag{32}$$

Heller (H):

$$\frac{n-1}{n} = \frac{3}{2}\sum_{i\neq 1}\left(\frac{\left(\frac{n_i}{n_1}\right)^2-1}{\left(\frac{n_i}{n_1}\right)^2+2}\right)\phi_i \tag{33}$$

Newton (Nw):

$$n^2 - 1 = \sum_i (n_i^2 - 1)\phi_i \tag{34}$$

Eyring and John (E-J):

$$n = \sum_i n_i \phi_i^2 + 2\sum_{i\neq j}(n_i n_j)^{1/2}\phi_i\phi_j \tag{35}$$

In all the above correlations, n represents the refractive index of the mixture; n_i and ϕ_i represent the refractive index and volume fraction of the ith component, respectively.

DISCUSSION

In the studied ternary DIPE (1)+benzene (2)+n-hexane (3) system V_m^E, Δu and κ_S^E values are positive as well as negative. It may be explained on the basis of contributing binary systems.

The V_m^E values may be supposed to be the resultant of two opposing factors/contributions. The positive contribution is due to disruption in orientation order of the pure component and also due to steric effects that prevent the proximity of pure components. The negative contribution arises due to the specific n-π interaction between lone pair of electrons present on oxygen atom of DIPE with delocalized π-electron cloud of the benzene ring as in case of DIPE (1)+benzene (2) system which have negative V_m^E [17,37]. For another binary mixture of DIPE (1)+n-hexane (2), it is observed that there is no specific interaction between the component molecules and V_m^E is due to disorder in the orientation of the hydrocarbons or breaking of cohesion forces between straight chain of n-

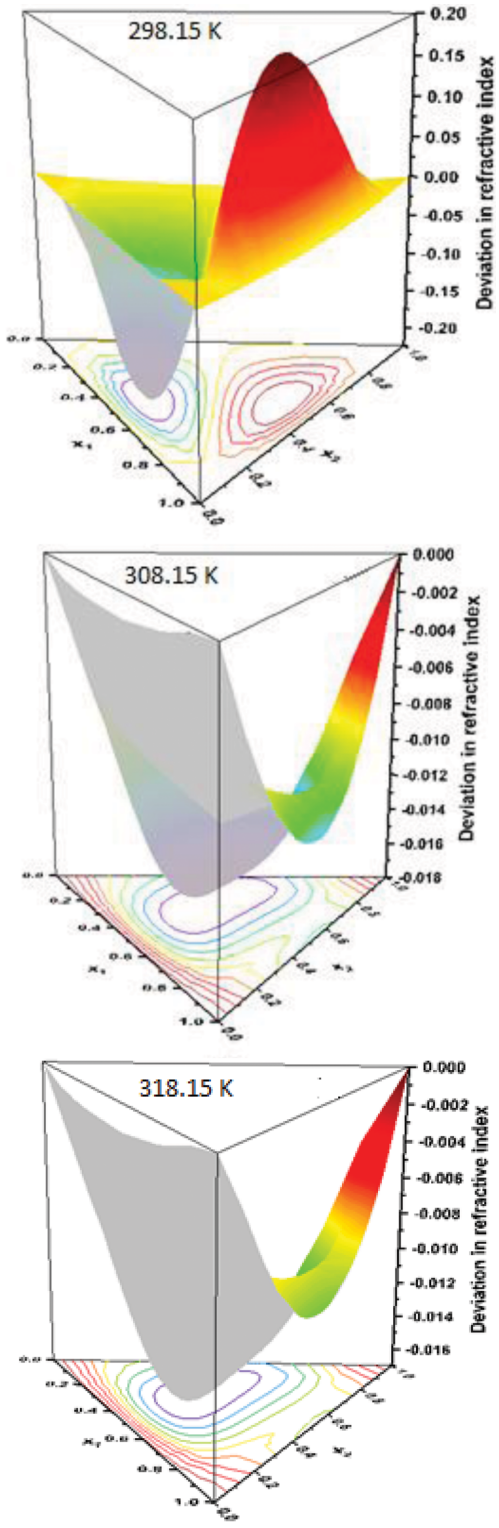


Fig. 5. Deviation in refractive index as a function of mole fractions (x_1, x_2 and x_3) for the ternary DIPE (1)+benzene (2)+n-hexane (3) system.

hexane, which leads to positive contribution to V_m^E. Thus, addition of n-hexane to DIPE (1)+benzene (2) binary system results in breaking of n-π interaction, which leads to the positive values of V_m^E and shifts V_m^E values from their qualitative behavior, which can be observed from Fig. 1. If the above interpretation for behavior of molecules is correct, then it should also be reflected in other measured properties, which are indeed found.

The excess isentropic compressibility (κ_S^E) depends on the interactional strength between unlike components of mixture [43,44,72]. The positive as well as negative κ_S^E values in Fig. 2 for the studied system over whole composition range indicate the specific n-π interaction and disorder in the orientation of the n-hexane or breaking of cohesion forces between straight chain molecules.

The ultrasonic waves require a medium for propagation; therefore, denser the medium due to specific interactions between unlike molecules, the ultrasonic speed would be higher; while in case of refractive index studies, the refractive index is inversely proportional to specific interactions between unlike molecules. Thus the positive and negative Δu and Δn values from Figs. 3 and 4 also support the above argument.

All the V_m^E, Δu, κ_S^E and Δn values are temperature dependent. With increase in temperature from 298.15 K to 318.15 K, deviation from ideality increases in positive or negative direction as reflected in Figs. 1-3 and 5. The deviation in/excess property is a function of strength of intermolecular interactions consequently on density of mixtures. This may be due to the weakening of intermolecular forces at higher temperature, leading to increase in randomness at higher temperature and consequently decrease in density of the mixtures. Thus if value of deviation in/excess property shows negative deviation from ideality, it becomes more negative, and if it is positive it become more positive with increase in temperature. This is indeed true in our case for Δu and Δn (Table 3), as these decrease with decrease in density and for κ_S^E which increases with decrease in density But the same is not true for V_m^E. This may be due to the fitting of n-hexane molecule in between benzene and DIPE molecule due to available space at higher temperature as volume is a packing effect.

The solution models prediction of ternary V_m^E was good for this system as seen from their standard deviations reported in Table 5. These models present the advantage of prediction of ternary V_m^E data from exclusive use of binary data [17,37]. Deviations presented by Singh, Cibulka and Nagata equations for V_m^E are also small, but among all three equations applied the Singh equation is best fitted to present ternary mixtures. The same was also reported for other ternary mixtures [73,74].

The Δu and κ_S^E for ternary systems against composition are shown in Figs. 2 and 3 at various temperatures in the form of ternary surface plots along with the contour lines; it can be concluded that the overall behavior of the ternary systems towards Δu and κ_S^E is between the corresponding binary components [17,37]. The increase in temperature results in volume expansion and hence κ_S^E values also increases (Fig. 3) for the ternary mixtures.

The Δn values are all positive for this ternary system as shown in Fig. 5. Different correlations expressed in Eq. (29)-(35) predict the Δn data very well (Table 7).

CONCLUSION

Density, ultrasonic speed and refractive indices of the ternary

Table 7. Value of standard deviation of calculated values of refractive index using various correlations for the ternary DIPE (1)+benzene (2)+n-hexane (3) system

T/K	AB	GD	LL	Weiner	Heller	Newton	Eyring
298.15	0.0037	0.0037	0.0042	0.0035	0.0035	0.0042	0.0034
308.15	0.0040	0.0040	0.0044	0.0039	0.0041	0.0044	0.0039
318.15	0.0040	0.0040	0.0043	0.0039	0.0040	0.0043	0.0039

DIPE (1)+benzene (2)+n-hexane (3) mixtures were reported at 298.15 K to 318.15 K. Experimental data were used to derive V_m^E, Δu, κ_S^E, L_f^E and Δn of ternary mixtures. Among all Singh, Cibulka and Nagata equations, the Singh equation is best fitted to the present ternary mixtures. The V_m^E data have also been interpreted using PFP theory. Various geometrical solution models like Tsao-Smith model, Jacob-Fitzner model, Kohler model, Rastogi model, Radojkovic model were found to predict well the V_m^E values for the ternary mixtures using their constituent binary excess volume data. Various correlations like Nomoto, van Dael and impedance dependence relation and CFT theory were applied to correlate ultrasonic speed data at 298.15 K. The Δu, κ_S^E and Δn values were also fitted to the Singh equation. Various correlations like Arago-Biot and Weiner were used to correlate Δn values of the studied ternary mixtures.

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