Korean Chem. Eng. Res., 56(5), 663-678 (2018)
https://doi.org/10.9713/kcer.2018.56.5.663
PISSN 0304-128X, EISSN 2233-9558

Optical and Acoustic Properties of Binary Mixtures of Butanol Isomers as Oxygenates with Cyclohexane, Benzene and Toluene at 308.15 K

Sweety Verma*, Suman Gahlyan*, Manju Rani† and Sanjeev Maken*,†

Department of Chemical Engineering, Deenbandhu Chhotu Ram University of Science and Technology, Murthal-131 039, India
**Department of Chemistry, Deenbandhu Chhotu Ram University of Science and Technology, Murthal-131 039, India*
(Received 14 May 2018; Received in revised form 11 August 2018; accepted 31 August 2018)

Abstract – Refractive index and speeds of sound for the binary mixture of isomer of butanol (1) + cyclohexane, benzene and toluene (2) were measured at 308.15 K. The measured data were used to calculate deviation in refractive index Δn, ultrasonic speed Δu, isentropic compressibility K_s^E, available volume V_a, excess intermolecular free length L_f and molecular association M_A. All the derived properties were correlated with polynomial equation. Ultrasonic speed data were predicted using various empirical correlations like Nomoto, van Dael, impedance dependence and theoretically with Schaaff's collision factor theory (CFT). Jacobson free length theory (FLT) was used to calculate L_f. The measured refractive index was also correlated with various mixing rules. The deviation in refractive index Δn and ultrasonic speed Δu was used to determine the intermolecular interactions.

Key words: Oxygenates, Hydrocarbon, Refractive index, Speed of sound, Molecular interactions

1. Introduction

Increasing global warming and extinction of fossil fuels is a great current issue. So researchers have shown much interest in the alternative bio-fuels [1,2], which include biodiesel, bioalcohol, vegetable oil and other biomass sources. Bio-fuels are used as an oxygenated compound in motor fuel [3]. The oxygenates are oxygen-containing compounds such as ethers, alkanol and ester which are used as fuel additives. The oxygen present in these oxygenates helps in complete combustion of fuel. These are also good antiknocking agents with high octane number [4]. Oxygenates produced from renewable sources like alkanol (C_3-C_5) may have acceptable properties as gasoline blend components and are considered as potential second generation bio-fuel additives that can be produced by microbial fermentation of biomass (cellulose) [5,6].

Aromatic hydrocarbons are also constituent of motor fuel. However, due to the carcinogenic nature of benzene it needs to be replaced [7, 8] and toluene is a good candidate as it has similar property as benzene but is much less carcinogenic [9]. The aliphatic polar head in mono alcohol has affinity to interact with the delocalized π-electrons of benzene and toluene. Properties like acoustics, optics, transport, surface tension, etc. of these liquid mixtures are of great significance in chemical design and oxygenated fuel formulation [10,11]. Knowledge of the physical properties of binary mixtures is also important in understanding the behavior of mixed liquids [12,13]. The excess/deviation in physical property is a beautiful tool to measure the deviation from ideality and also for understanding of intermolecular interactions in the liquid mixtures. These considerations prompted us to study the refractive index and ultrasonic speed of (A+B) mixtures of butanol isomers with cyclohexane, benzene and toluene at 308.15 K. In this sense, it is an interesting research problem to study the thermos-physical properties of oxygenate with hydrocarbons.

In continuation of our earlier work on the excess properties of oxygenated fuel additives [14-31], we report the refractive index (n_D) and ultrasonic speed (u) data for binary mixtures of butanol isomers with cyclohexane, benzene and toluene. We selected these mixtures because butanol is a second generation fuel additive and its interactions with hydrocarbons would be of great use in fuel formulation. The measured data were used to calculate deviation in refractive index Δn, ultrasonic speed Δu, excess isentropic compressibility K_s^E, excess intermolecular free length L_f^E, available volume V_a and molecular association M_A. All the derived properties were correlated with polynomial equation. Ultrasonic speed data were predicted using various empirical correlations like Nomoto, van Dael, impedance dependence and theoretically with Schaaff's collision factor theory (CFT) [32,33]. Jacobson free length theory (FLT) was applied to calculate L_f^E [34-36]. The measured refractive index was also correlated with various mixing rules. The deviation in refractive index Δn and ultrasonic speed Δu was used to study the intermolecular interactions.

2. Experimental

Benzene and toluene (Merck) were treated with 15% H_2SO_4 in a separating funnel to remove thiophene until the yellow color of acid

† To whom correspondence should be addressed.
E-mail: sanjeevmakin@gmail.com

became colorless [37,38]. The mixtures were kept undisturbed until two layers got separated; after separation in layer the acid was drained. For the neutralization of remaining acid, sodium bicarbonate solution was used. The chemicals were again washed with distilled water and dried over fused $CaCl_2$ for 24 h. After this, the chemicals were purified by fractional distillation and stored over molecular sieves (Merck). Cyclohexane (Merck 99%) was washed several times with a mixture of concentrated nitric acid and concentrated sulfuric acid to nitrate any benzene that may have been present [39]. After repeated washing with $NaHCO_3$ solution and distilled water, it was fractionally distilled over and dried over 0.3 nm molecular sieves (Merck) in an amber colored bottle for several days before use.

The butanol (Fluka Goldie) was stored over fused calcium oxide for absorption of water as impurity in alcohol and then distilled [37,38]. The purity of compound was confirmed by comparing experimentally measured density (ρ), u and n_D with their respective literature values shown in Table 1.

The u values were measured with interferometer (Mittal Enterprises) with frequency generator of 2 MHz and at controlled temperature (308.15±0.01) K. The temperature was controlled by mercury-in-toluene regulator. The detailed procedure for measurement of u has been given earlier [50] and the data are reproducible within ±3%. The n_D values were measured with Abbe refractometer (OSAW, India) having an accuracy of (0.0001 units). The binary mixtures were made using a balance of precision ±0.1 mg (OHAUS, AR224CN) and the uncertainty in mole fraction was $\pm 1 \times 10^{-4}$.

3. Results and Discussion

The properties like Δu and K_s^E shown in Table 2 and Figs. 1 and 2, were calculated from experimental values of u using Eqs. 1 and 2, respectively.

$$\Delta u = u - (\rho^{id} K_s^{id})^{\frac{1}{2}} \quad (1)$$

$$K_s^E = K_s - K_s^{id} \quad (2)$$

$$K_s = (u^2 \rho)^{-1} \quad (3)$$

K_s^{id} was calculated from Equation [51] using α_p [29] [52] and C_p [29,53-55].

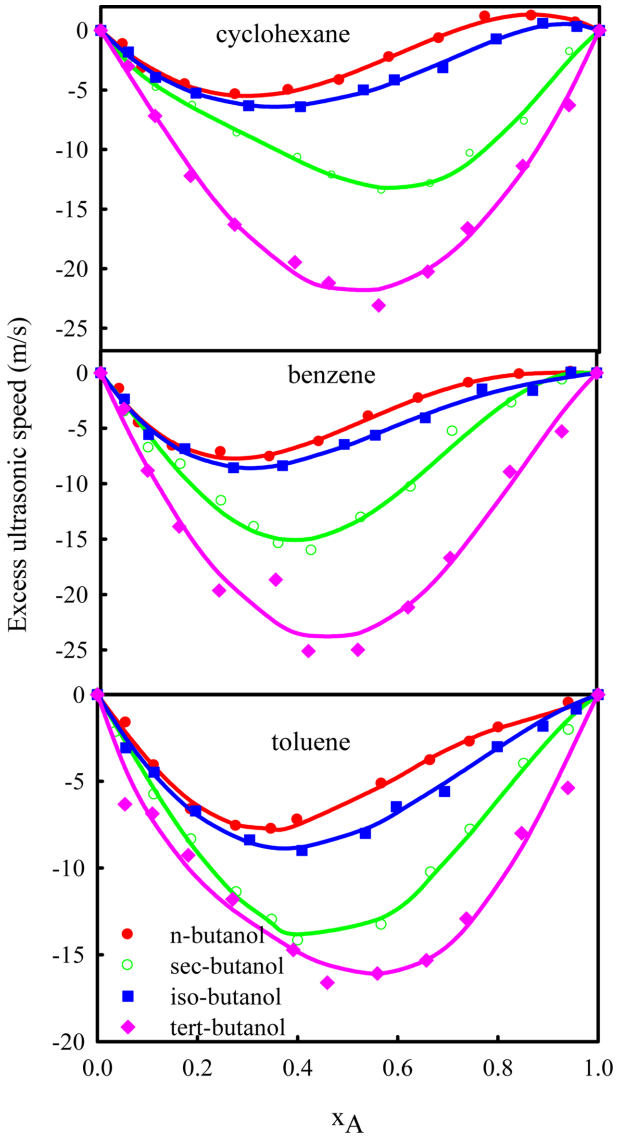

Fig. 1. Deviation in ultrasonic speed of butanol (A) +hydrocarbon (B) mixture as a function of mole fraction of butanol at 308.15 K.

3-1. Ultrasonic speed

The u data were predicted using various empirical correlations like Nomoto, van Dael and impedance dependence and also theoretically predicted with Schaaff's collision factor theory (CFT) at 308.15 K. The quantitative as well as qualitative comparison of the estimated

Table 1. Comparison of experimental values of refractive index, density and ultrasonic speed of pure liquids at 308.15 K with the corresponding literature values

Compound	n_D		ρ/kg m^{-3}		u/m s^{-1}	
	Exptl.	Literature	Exptl.	Literature	Exptl.	Literature
n-butanol	1.3902	1.3927[40]	798.60	798.25[41]	1205	1205.79[42]
sec-butanol	1.3901	1.3907[43]	794.45	793.72[41]	1180	1174.89[42]
iso-butanol	1.3899	1.3899[44]	789.69	789.66[41]	1154	1153.86[42]
tert-butanol	1.3780	1.3766[45]	770.20	770.39[41]	1090	1084.3[41]
cyclohexane	1.4180	1.4174[46]	762.50	762.46[47]	1212	1212[47]
benzene	1.4912	1.4910[48]	862.93	862.95[47]	1256	1260[49]
toluene	1.4882	1.4881[48]	852.88	852.85[47]	1265	1262[47]

Table 2. Speed of sound and excess speed of sound (m/s), excess molar isentropic compressibility, K_s^E ($\times 10^{-12}$ Nm s^{-2}), excess refractive index for binary mixtures

x_1	u	u^E	K_s^E	n_D	n_D^E
n-butanol (1) + cyclohexane (2)					
0.0447	1208.6	-1.6	2.48	1.4151	-0.0015
0.0831	1204.8	-2.7	6.10	1.4131	-0.0024
0.1695	1200	-4.6	9.16	1.4100	-0.0036
0.2702	1196	-5.5	11.22	1.4061	-0.0045
0.3767	1194	-5.2	11.05	1.4022	-0.0051
0.4790	1193.5	-4.0	9.76	1.3991	-0.0055
0.5787	1195	-2.3	6.52	1.3962	-0.0057
0.6786	1197	-0.5	3.62	1.3943	-0.0053
0.7715	1200	0.8	0.27	1.3921	-0.0042
0.8643	1202	1.3	-0.57	1.3911	-0.0026
0.9528	1204	0.8	-0.52	1.3910	-0.0009
n-butanol (1) + benzene (2)					
0.0386	1250.7	-2.2	3.05	1.4860	-0.0013
0.0772	1244	-4.1	5.58	1.4810	-0.0024
0.1452	1236	-6.3	8.83	1.4729	-0.0036
0.2429	1228	-7.7	11.05	1.4619	-0.0048
0.3414	1221.1	-7.4	10.94	1.4512	-0.0055
0.4406	1216.9	-6.0	9.19	1.4405	-0.0062
0.5405	1214.4	-4.1	6.60	1.4300	-0.0066
0.6413	1212	-2.3	3.90	1.4197	-0.0067
0.7428	1210	-0.9	1.74	1.4100	-0.0061
0.8451	1208	-0.1	0.48	1.4013	-0.0046
0.9482	1206	0.0	0.05	1.3936	-0.0018
n-butanol (1) + toluene (2)					
0.0571	1258.8	-2.2	2.78	1.4809	-0.0014
0.1133	1252	-4.2	5.35	1.4746	-0.0026
0.1871	1244	-6.1	8.08	1.4661	-0.0039
0.2772	1236.7	-7.5	10.06	1.4560	-0.0052
0.3478	1232	-7.7	10.51	1.4483	-0.0059
0.3998	1229	-7.5	10.29	1.4425	-0.0063
0.568	1221	-5.2	7.40	1.4258	-0.0068
0.6653	1217	-3.7	5.21	1.4164	-0.0065
0.7443	1214	-2.6	3.65	1.4094	-0.0059
0.8015	1212	-1.9	2.73	1.4046	-0.0052
0.9415	1207	-0.7	0.96	1.3935	-0.0022
sec-butanol (1) + cyclohexane (2)					
0.0562	1204	-2.8	5.84	1.4151	-0.0013
0.1117	1197	-4.6	10.00	1.4127	-0.0021
0.1845	1190	-6.5	14.08	1.4101	-0.0028
0.2739	1182	-8.4	18.09	1.4070	-0.0033
0.3958	1174	-10.9	22.74	1.4032	-0.0038
0.4639	1170	-12.2	24.74	1.4012	-0.0039
0.5639	1166	-13.2	26.14	1.3984	-0.0038
0.6615	1165	-12.8	24.84	1.3962	-0.0034
0.7411	1167	-11.0	21.37	1.3946	-0.0028
0.8498	1170	-6.8	13.32	1.3927	-0.0015
0.9406	1177	-2.4	4.99	1.3913	-0.0005

Table 2. Speed of sound and excess speed of sound (m/s), excess molar isentropic compressibility, K_s^E ($\times 10^{-12}$ Nm s^{-2}), excess refractive index for binary mixtures

x_1	u	u^E	K_s^E	n_D	n_D^E
sec-butanol (1) + benzene (2)					
0.0486	1244.5	-2.8	4.20	1.4849	-0.0014
0.0972	1234	-5.6	8.59	1.4790	-0.0024
0.1624	1223.8	-9.1	14.21	1.4716	-0.0032
0.2442	1211	-12.6	19.98	1.4627	-0.0039
0.3099	1202	-14.3	23.10	1.4555	-0.0044
0.3594	1196	-15.0	24.43	1.4501	-0.0047
0.4257	1255	-15.0	24.79	1.4429	-0.0052
0.5255	1190	-13.2	22.50	1.4323	-0.0058
0.6260	1186	-9.9	17.55	1.4221	-0.0059
0.7103	1183	-6.6	12.30	1.4141	-0.0053
0.8289	1184	-2.3	5.06	1.4040	-0.0034
0.9314	1182	-0.2	0.86	1.3959	-0.0012
sec-butanol (1) + toluene (2)					
0.0375	1265	-1.8	2.54	1.4842	-0.0004
0.1140	1258	-5.5	7.88	1.4757	-0.0014
0.1881	1245	-8.7	12.74	1.4672	-0.0025
0.2786	1234	-11.7	17.59	1.4571	-0.0037
0.3493	1221.4	-13.2	20.21	1.4494	-0.0044
0.4014	1213	-13.8	21.37	1.4440	-0.0049
0.5679	1207	-12.9	20.59	1.4273	-0.0055
0.6668	1194.1	-10.5	17.23	1.4176	-0.0052
0.7456	1189.9	-8.0	13.43	1.4101	-0.0045
0.8528	1187	-4.3	7.47	1.4017	-0.0031
0.9419	1184.1	-1.4	2.65	1.3944	-0.0014
iso-butanol (1) + cyclohexane (2)					
0.0554	1205	-2.0	4.12	1.4151	-0.0015
0.1101	1198	-3.5	7.37	1.4121	-0.0025
0.1910	1190	-5.3	10.94	1.4092	-0.0035
0.2969	1181	-6.6	13.74	1.4057	-0.0042
0.4005	1174	-7.0	14.58	1.4022	-0.0045
0.5268	1168.7	-6.1	13.10	1.3986	-0.0045
0.5887	1165.6	-5.2	11.42	1.3971	-0.0043
0.6861	1162	-3.3	7.78	1.3949	-0.0039
0.7932	1160	-0.9	3.17	1.3928	-0.0030
0.8863	1158	0.6	-0.02	1.3913	-0.0019
0.9549	1155.6	0.7	-0.78	1.3901	-0.0008
iso-butanol (1) + benzene (2)					
0.0484	1245.4	-2.8	4.02	1.4848	-0.0015
0.0969	1234.4	-5.0	7.30	1.4789	-0.0025
0.1700	1222.3	-7.2	10.85	1.4705	-0.0036
0.2680	1207.5	-8.5	13.22	1.4594	-0.0045
0.3668	1196	-8.3	13.34	1.4487	-0.0052
0.4912	1185	-6.7	11.30	1.4360	-0.0058
0.5538	1180	-5.6	9.77	1.4291	-0.0060
0.6546	1173	-3.8	7.10	1.4188	-0.0060
0.7688	1167	-2.0	4.32	1.4081	-0.0051
0.8711	1160	-0.9	2.31	1.3997	-0.0034
0.9483	1157	-0.4	0.97	1.3937	-0.0015

Table 2. Speed of sound and excess speed of sound (m/s), excess molar isentropic compressibility, K_s^E ($\times 10^{-12}$ Nm s^{-2}), excess refractive index for binary mixtures

x_1	u	u^E	K_s^E	n_D	n_D^E
iso-butanol (1) + toluene (2)					
0.0572	1254	-2.6	3.56	1.4814	-0.0012
0.1135	1245	-4.6	6.56	1.4749	-0.0022
0.1964	1232	-6.9	9.98	1.4653	-0.0034
0.3041	1217	-8.5	12.68	1.4539	-0.0046
0.4088	1204.1	-8.7	13.51	1.4425	-0.0055
0.5354	1191	-7.8	12.50	1.4297	-0.0061
0.5970	1186	-6.9	11.37	1.4231	-0.0062
0.6934	1177	-5.3	9.01	1.4141	-0.0058
0.7988	1169.3	-3.3	5.92	1.4054	-0.0046
0.8897	1162	-1.7	3.14	1.3979	-0.0029
0.9563	1157	-0.6	1.19	1.3927	-0.0012
tert-butanol (1) + cyclohexane (2)					
0.0548	1202	-3.6	6.56	1.4151	-0.0006
0.109	1191	-7.2	13.20	1.4124	-0.0013
0.1806	1177	-11.6	21.73	1.4088	-0.0020
0.2686	1162	-16.2	31.09	1.4045	-0.0027
0.3895	1144	-20.4	40.65	1.3994	-0.0030
0.4573	1134	-21.6	43.89	1.3968	-0.0029
0.5574	1120	-21.7	45.49	1.3932	-0.0025
0.6556	1111	-20.1	43.11	1.3898	-0.0019
0.7359	1105	-17.4	38.10	1.3871	-0.0015
0.8464	1097	-11.8	26.41	1.3833	-0.0008
0.9391	1091	-5.3	12.00	1.3801	-0.0004
tert-butanol (1) + benzene(2)					
0.0473	1240.3	-4.5	6.38	1.4849	-0.0010
0.0949	1222.9	-8.6	12.65	1.4787	-0.0017
0.1588	1203	-13.3	20.66	1.4709	-0.0024
0.2393	1180	-18.1	29.73	1.4611	-0.0029
0.3533	1159	-22.5	39.68	1.4474	-0.0038
0.4192	1141	-23.7	43.37	1.4395	-0.0043
0.5189	1125	-23.5	45.48	1.4275	-0.0050
0.6198	1114	-21.0	42.91	1.4159	-0.0051
0.7048	1107	-17.2	37.06	1.4068	-0.0046
0.8251	1100	-10.2	23.87	1.3948	-0.0029
0.9296	1092	-3.6	9.58	1.3851	-0.0010
tert-butanol (1)+ toluene(2)					
0.0552	1248	-4.2	5.9	1.4818	-0.0006
0.1098	1237	-7.2	10.5	1.4749	-0.0012
0.1817	1221	-10.0	15.6	1.4661	-0.0021
0.2701	1202	-12.4	20.7	1.4550	-0.0032
0.3913	1177	-14.7	26.6	1.4408	-0.0045
0.4592	1163	-15.6	29.1	1.4329	-0.0049
0.5593	1146	-16.1	31.4	1.4212	-0.0052
0.6573	1130	-15.3	31.1	1.4107	-0.0049
0.7374	1119	-13.4	28.4	1.4029	-0.0042
0.8474	1106	-8.8	20.2	1.3923	-0.0026
0.9396	1094	-3.6	9.2	1.3836	-0.0010

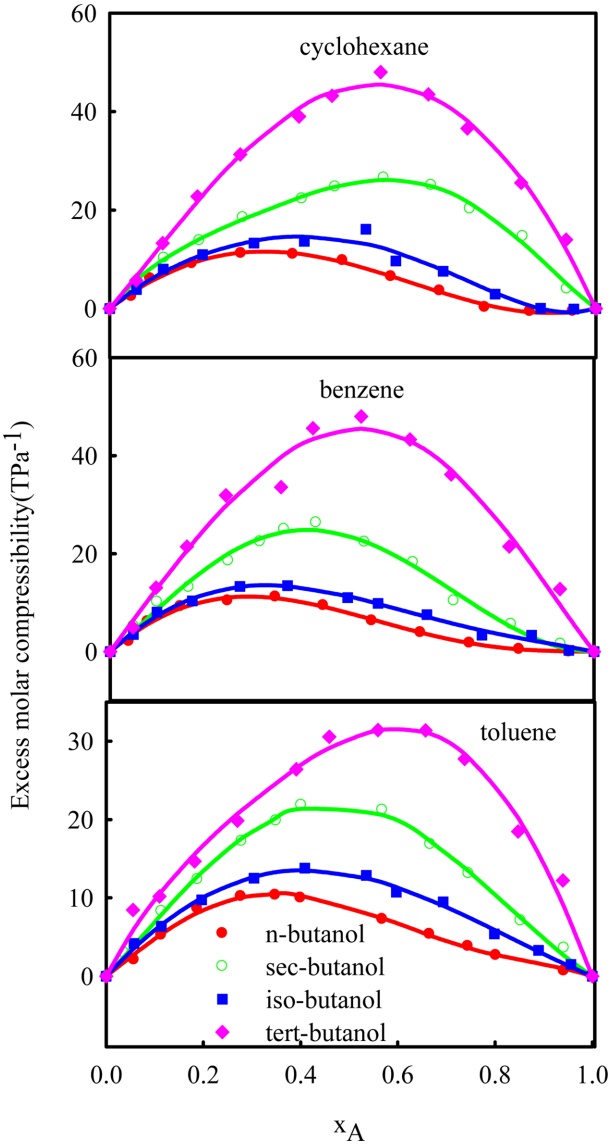

Fig. 2. Values of excess isentropic compressibility of butanol (A) + hydrocarbon (B) mixture as a function of mole fraction of butanol.

correlations values with experimental values is given in terms of standard deviation in Table 3 and Fig. 3 (a,b,c), respectively. Jacobson free length theory (FLT) was used to calculate the L_f^E.

3-1-1. *Schaaffs' collision factor theory (CFT)* [32,33]

According to CFT,

$$u_{mix} = \frac{u_\infty (x_1 S_1 + x_2 S_2)(x_1 b_1 + x_2 b_2)}{V_{mix}} \quad (4)$$

where u_∞ is 1600 ms^{-1} and b and S are the geometric volume and collision factor, respectively.

The actual geometric volume per mol of the liquids was computed as

$$b = \frac{4\Pi r^3 N_A}{3} \quad (5)$$

and the value of collision factor S was calculated as

$$S = \frac{uV_T}{bu_\infty} \quad (6)$$

These theoretically calculated *u* values are compared with experimental values in Fig. 3, and quantitative comparison is given in terms of standard deviation in Table 4.

Among all correlations and theoretical approaches for *u* as from Fig. 3, the value predicted by van Dael relation is best for binary mixtures of tert-butanol (A) + benzene (B) and all butanol (A) + toluene (B) systems. Schaaff's collision factor theory (SCF) is good for n-butanol or sec-butanol (A) + cyclohexane (B) and all butanol (A) + benzene (B) systems. Nomoto and impedance relation deviation are larger than all other correlations for all systems, as can be seen from Table 4. So these correlations are not predicting the experimental data.

3-1-2. *Jacobson free length theory* [34-36]

This theory was used to calculate the L_f^E. The L_f for ideal solution was calculated using molar volume and surface area using following equation:

$$L_f = \frac{2V_a}{Y} \quad (7)$$

$$V_a = V_T - V_o \quad (8)$$

$$Y = (36\Pi N_A V_o^2)^{1/3} \quad (9)$$

Table 3. Standard deviations in ultrasonic velocity predicted by various correlations

Binary mixture	Nomoto	Van Deal	Impedance	CFT
n-butanol (1) + cyclohexane (2)	0.922	0.744	0.899	0.648
n-butanol (1)+ benzene(2)	0.966	0.885	1.052	0.831
n-butanol (1) + toluene (2)	0.872	0.163	0.810	0.681
sec-butanol (1) + cyclohexane (2)	1.872	1.548	1.769	1.356
sec-butanol (1) + benzene (2)	1.971	1.829	2.131	1.609
sec-butanol (1) + toluene (2)	1.594	0.577	1.526	1.172
iso-butanol (1) + cyclohexane (2)	1.007	0.551	0.845	0.618
iso-butanol (1) + benzene (2)	1.261	1.056	1.500	1.141
iso-butanol (1) +toluene (2)	1.125	0.171	1.069	0.798
tert-butanol (1) + cyclohexane (2)	1.726	0.786	1.497	1.035
tert-butanol (1) + benzene (2)	2.598	2.141	3.209	2.448
tert-butanol (1) + toluene (2)	1.599	0.337	1.702	1.062

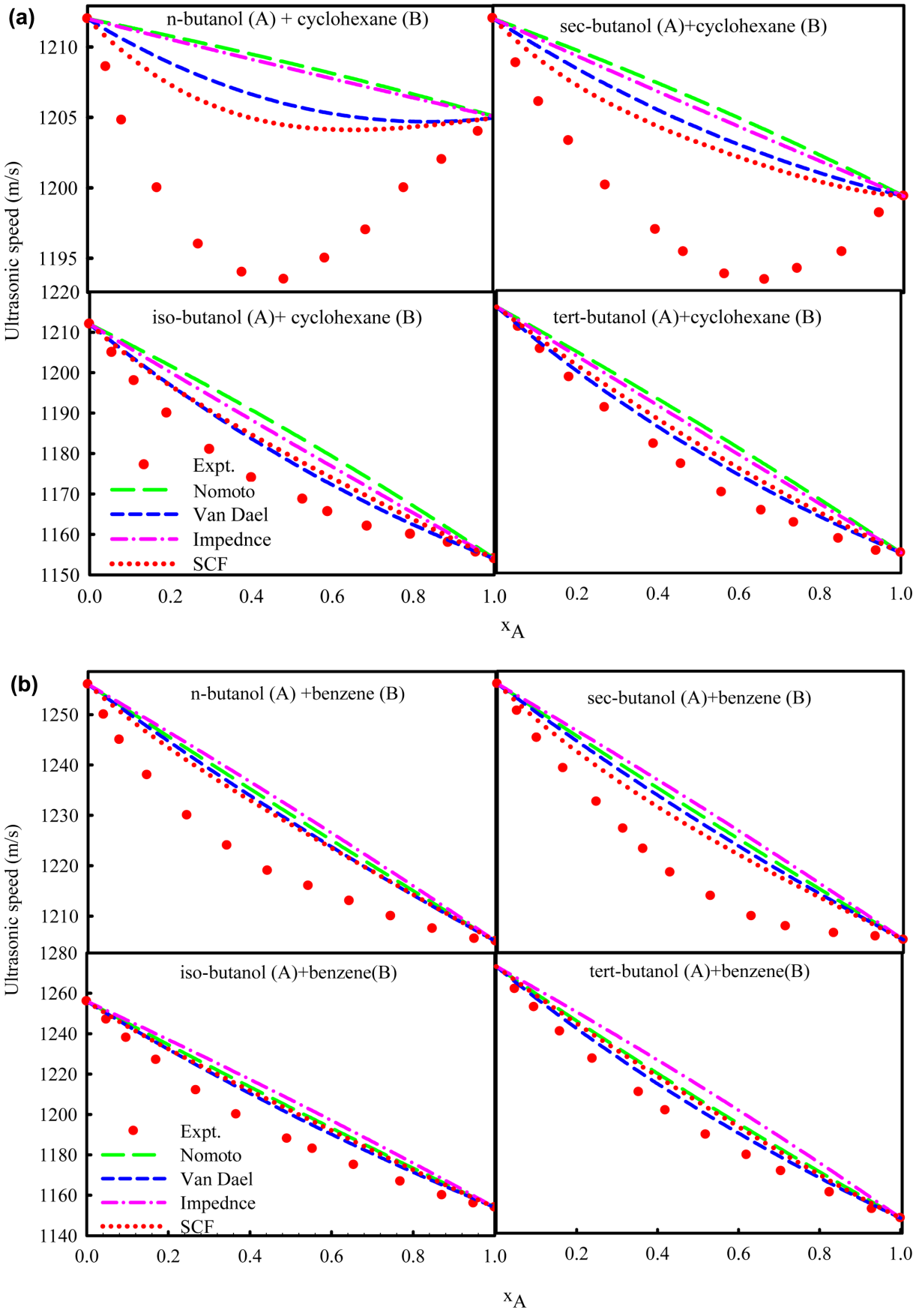

Fig. 3. (a) Ultrasonic speed of butanol (A) + cyclohexane (B) as predicted by various correlations. (b). Ultrasonic speed of butanol (A) + benzene (B) as predicted by various correlations. (c) Ultrasonic speed of butanol (A) + toluene (B) as predicted by various correlations.

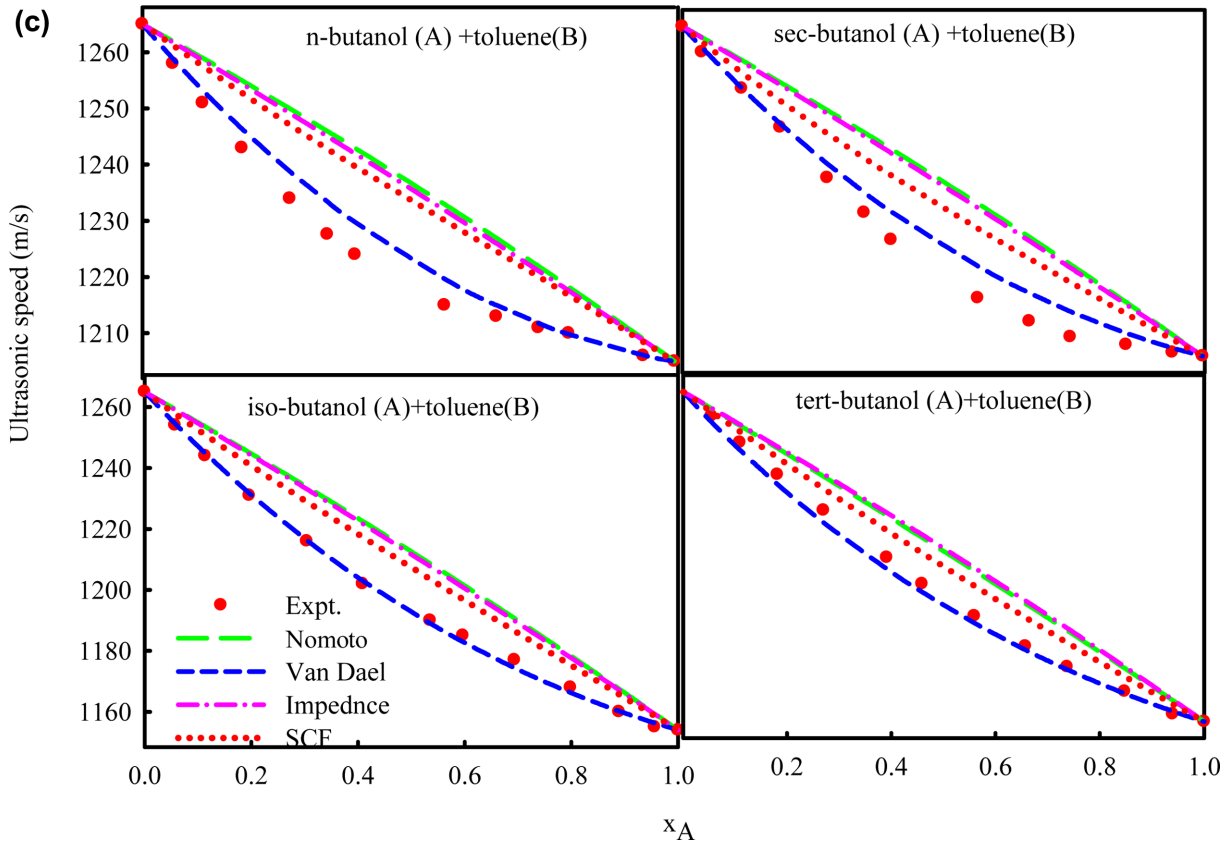

Fig. 3. (a) Ultrasonic speed of butanol (A) + cyclohexane (B) as predicted by various correlations. (b). Ultrasonic speed of butanol (A) + benzene (B) as predicted by various correlations. (c) Ultrasonic speed of butanol (A) + toluene (B) as predicted by various correlations.

Table 4. Values of available volume (×10^{-6}, m^{3}mol^{-1}), free length, excess free length (Å) and molecular association

x_1	V_a	L_f	L_f^E	M_A
n-butanol(1) + cyclohexane(2)				
0.0447	23.72	0.599	0.002	-0.010
0.0831	23.57	0.598	0.004	-0.019
0.1695	23.22	0.597	0.007	-0.027
0.2702	22.80	0.595	0.010	-0.035
0.3767	22.35	0.591	0.011	-0.042
0.4790	21.91	0.586	0.011	-0.045
0.5787	21.48	0.580	0.010	-0.046
0.6786	21.04	0.573	0.008	-0.043
0.7715	20.64	0.567	0.006	-0.036
0.8643	20.23	0.560	0.004	-0.025
0.9528	19.85	0.553	0.001	-0.008
n-butanol(1) + benzene(2)				
0.0386	19.22	0.548	0.002	-0.013
0.0772	19.25	0.550	0.003	-0.028
0.1452	19.29	0.551	0.004	-0.043
0.2429	19.35	0.553	0.006	-0.059
0.3414	19.39	0.554	0.006	-0.063
0.4406	19.43	0.554	0.006	-0.075
0.5405	19.47	0.553	0.005	-0.075
0.6413	19.51	0.552	0.004	-0.067
0.7428	19.55	0.552	0.003	-0.055
0.8451	19.59	0.551	0.002	-0.034
0.9482	19.62	0.550	0.001	-0.018

Table 4. Values of available volume (×10^{-6}, m^{3}mol^{-1}), free length, excess free length (Å) and molecular association

x_1	V_a	L_f	L_f^E	M_A
n-butanol(1) + toluene(2)				
0.0571	21.30	0.5364	0.001	-0.012
0.1133	21.21	0.5378	0.001	-0.014
0.1871	21.10	0.5396	0.002	-0.020
0.2772	20.95	0.5415	0.002	-0.026
0.3478	20.83	0.5426	0.003	-0.032
0.3998	20.74	0.5433	0.002	-0.036
0.568	20.44	0.5447	0.001	-0.036
0.6653	20.26	0.5455	0.001	-0.034
0.7443	20.11	0.5462	0.000	-0.030
0.8015	20.01	0.5469	0.000	-0.019
0.9415	19.75	0.5489	0.000	-0.012
sec-butanol(1) + cyclohexane(2)				
0.0562	23.79	0.603	0.005	-0.005
0.1117	23.67	0.607	0.009	-0.013
0.1845	23.50	0.610	0.012	-0.020
0.2739	23.27	0.612	0.014	-0.025
0.3958	22.95	0.613	0.015	-0.028
0.4639	22.76	0.612	0.015	-0.027
0.5639	22.47	0.611	0.014	-0.023
0.6615	22.18	0.609	0.012	-0.018
0.7411	21.94	0.607	0.010	-0.013
0.8498	21.60	0.604	0.007	-0.008
0.9406	21.31	0.600	0.003	-0.003
sec-butanol(1) + benzene(2)				
0.0486	19.31	0.553	0.004	-0.009
0.0972	19.42	0.558	0.007	-0.019
0.1624	19.56	0.564	0.010	-0.026
0.2442	19.73	0.571	0.012	-0.034
0.3099	19.83	0.575	0.013	-0.037
0.3594	19.93	0.578	0.014	-0.034
0.4257	20.05	0.582	0.014	-0.032
0.5255	20.24	0.586	0.013	-0.027
0.6260	20.42	0.589	0.012	-0.018
0.7103	20.58	0.591	0.009	-0.012
0.8289	20.79	0.593	0.006	-0.004
0.9314	20.98	0.595	0.002	-0.009
x_1	V_a	L_f	L_f	M_A
sec-butanol(1) + toluene(2)				
0.0375	21.39	0.539	0.001	-0.004
0.1140	21.40	0.546	0.004	-0.010
0.1881	21.39	0.552	0.006	-0.016
0.2786	21.38	0.559	0.007	-0.019
0.3493	21.37	0.564	0.008	-0.019
0.4014	21.35	0.567	0.008	-0.019
0.5679	21.30	0.576	0.007	-0.016
0.6668	21.26	0.581	0.005	-0.013
0.7456	21.23	0.585	0.004	-0.010
0.8528	21.18	0.590	0.003	-0.008
0.9419	21.14	0.594	0.001	-0.002
iso-butanol(1) + cyclohexane(2)				
0.0554	23.75	0.601	0.004	-0.005
0.1101	23.59	0.602	0.006	-0.013
0.1910	23.35	0.603	0.009	-0.022
0.2969	23.01	0.602	0.010	-0.029
0.4005	22.67	0.600	0.010	-0.035
0.5268	22.25	0.596	0.009	-0.038
0.5887	22.04	0.594	0.008	-0.042
0.6861	21.71	0.590	0.007	-0.037
0.7932	21.34	0.586	0.005	-0.030
0.8863	21.02	0.582	0.003	-0.021
0.9549	20.78	0.579	0.001	-0.012

Table 4. Values of available volume (×10^{-6}, m^{3}mol^{-1}), free length, excess free length (Å) and molecular association

x_1	V_a	L_f	L_f^E	M_A
iso-butanol(1) + benzene(2)				
0.0484	19.28	0.551	0.003	-0.012
0.0969	19.36	0.554	0.005	-0.023
0.1700	19.48	0.558	0.006	-0.032
0.2680	19.62	0.562	0.007	-0.042
0.3668	19.76	0.565	0.007	-0.049
0.4912	19.93	0.568	0.007	-0.052
0.5538	20.02	0.570	0.007	-0.054
0.6546	20.16	0.572	0.006	-0.049
0.7688	20.31	0.574	0.005	-0.042
0.8711	20.45	0.576	0.003	-0.030
0.9483	20.55	0.577	0.001	-0.018
iso-butanol(1) + toluene(2)				
0.0572	21.36	0.539	0.002	-0.007
0.1135	21.33	0.543	0.003	-0.012
0.1964	21.28	0.547	0.004	-0.018
0.3041	21.21	0.552	0.004	-0.023
0.4088	21.13	0.556	0.004	-0.025
0.5354	21.03	0.561	0.003	-0.024
0.5970	20.98	0.563	0.003	-0.021
0.6934	20.90	0.566	0.002	-0.018
0.7988	20.80	0.570	0.002	-0.012
0.8897	20.72	0.573	0.001	-0.007
0.9563	20.66	0.575	0.000	-0.003
tert-butanol(1) + cyclohexane(2)				
0.0548	23.91	0.605	0.003	-0.006
0.1090	23.92	0.612	0.006	-0.013
0.1806	23.93	0.619	0.009	-0.018
0.2686	23.94	0.628	0.012	-0.023
0.3895	23.93	0.639	0.015	-0.025
0.4573	23.92	0.644	0.015	-0.021
0.5574	23.89	0.650	0.015	-0.021
0.6556	23.85	0.656	0.014	-0.017
0.7359	23.81	0.659	0.012	-0.010
0.8464	23.74	0.662	0.008	-0.004
0.9391	23.66	0.664	0.003	-0.002
tert-butanol(1) + benzene(2)				
0.0473	19.40	0.555	0.003	-0.005
0.0949	19.60	0.563	0.006	-0.013
0.1588	19.87	0.574	0.008	-0.020
0.2393	20.22	0.586	0.011	-0.025
0.3533	20.71	0.602	0.014	-0.028
0.4192	21.00	0.610	0.015	-0.027
0.5189	21.44	0.623	0.015	-0.023
0.6198	21.89	0.634	0.015	-0.018
0.7048	22.28	0.643	0.014	-0.013
0.8251	22.83	0.654	0.011	-0.008
0.9296	23.30	0.661	0.005	-0.003
tert-butanol(1) + toluene(2)				
0.0552	21.51	0.544	0.002	-0.004
0.1098	21.62	0.552	0.003	-0.010
0.1817	21.78	0.563	0.005	-0.016
0.2701	21.97	0.576	0.007	-0.019
0.3913	22.23	0.593	0.008	-0.019
0.4592	22.38	0.603	0.008	-0.019
0.5593	22.60	0.616	0.008	-0.016
0.6573	22.82	0.628	0.008	-0.013
0.7374	23.00	0.637	0.007	-0.010
0.8474	23.26	0.649	0.005	-0.008
0.9396	23.47	0.659	0.002	-0.002

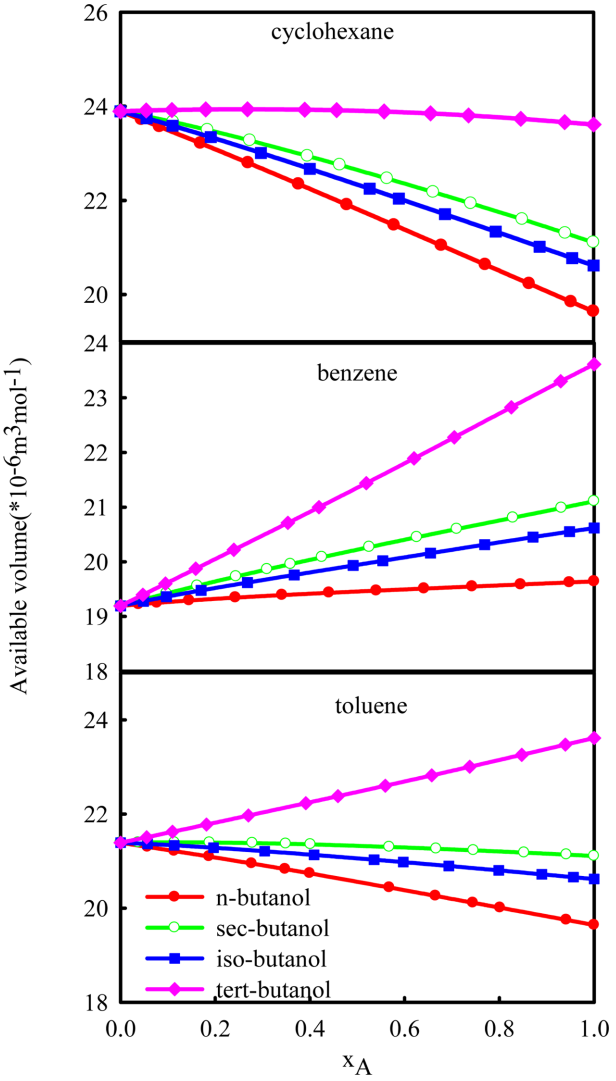

Fig. 4. Available volume of butanol (A) + hydrocarbon (B) mixture.

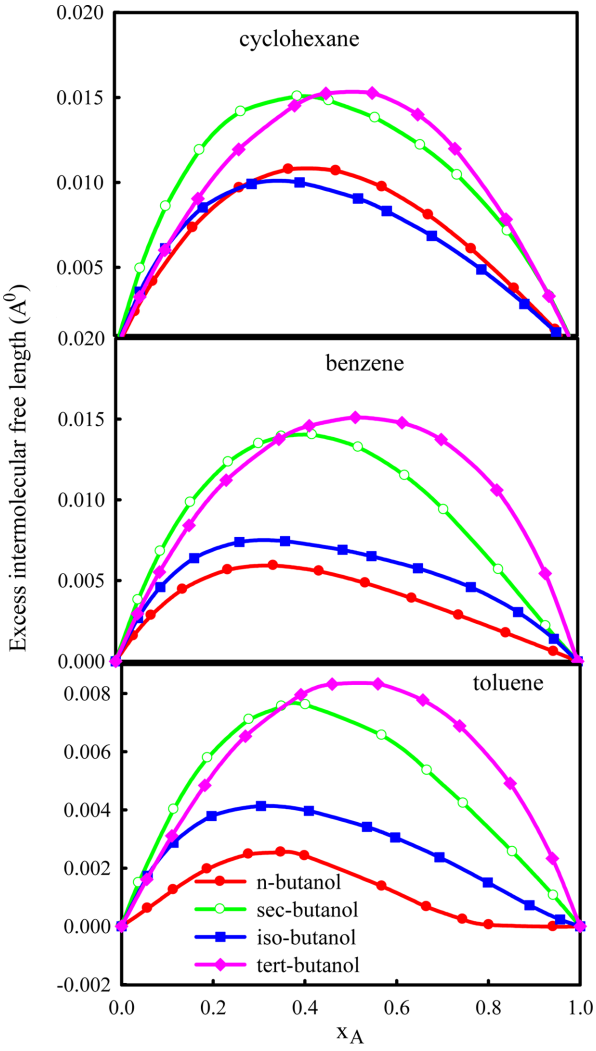

Fig. 5. Excess intermolecular free length of butanol (A) + hydrocarbon (B) mixture as a function of mole fraction of butanol at 308.15 K.

Each term in above equation has the usual meaning [34-36] and L_f^E of mixtures was calculated using Eq. (10):

$$u_{mix} = \frac{K}{L_{f(mix)}\rho_{mix}^{1/2}} \tag{10}$$

where K, Jacobson constant, varies from 618 to 642 at temperature 293.15 K to 313.15 K.

The L_f^E values were calculated as:

$$X_m^E = X_m - x_1X_1^o - x_2X_2^o \tag{11}$$

The available volume calculated from Eq. (8) is shown in Fig. 4 for all respective mixtures. The L_f^E calculated using Eq. (11) with mole fraction of component A of binary mixture is shown in Figs. 5. The calculated values of L_f^E and V_a are also given in Table 4.

Molecular association (M_A) value has also been calculated as:

$$M_A = \left(\frac{u_{mix}}{x_1u_1 + x_2u_2}\right)^2 - 1 \tag{12}$$

These values are given in Table 4 and Fig. 6. The variation of molecular association with composition gives a direct measure of the non-ideality of the binary mixture because of the intermolecular association of the two components. Its value becomes less negative as the strength of intermolecular interactions between the component molecules increases.

3-2. Refractive Index

The deviation in n_D was calculated from Eq. (11), which is given in Table 2 and Fig. 7 along with experimental n_D values for all binary mixtures. For the theoretical estimation of n_D the Arago-Biot (A-B), Gladstone-Dale (G-D), Lorentz-Lorentz (L-L); Heller (H), Weiner (W), Newton (Nw), and Eyring-John (E-J) mixing rules were used. All mixing rules are discussed in detail in our earlier paper [17]. The comparison between predicted values of all mixing rules and experimental values is very good. The quantitative comparison is given in terms of standard deviation and reported in Table 5.

Redlich-Kister equation was used to correlate the above calcu-

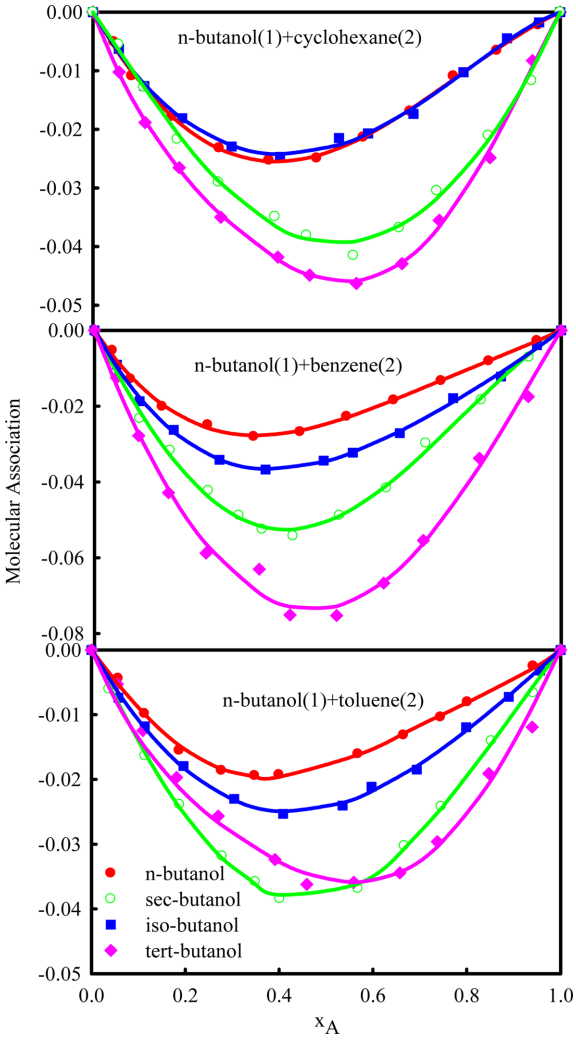

Fig. 6. Molecular association of butanol (A) + hydrocarbon (B) mixture as a function of mole fraction of butanol at 308.15 K.

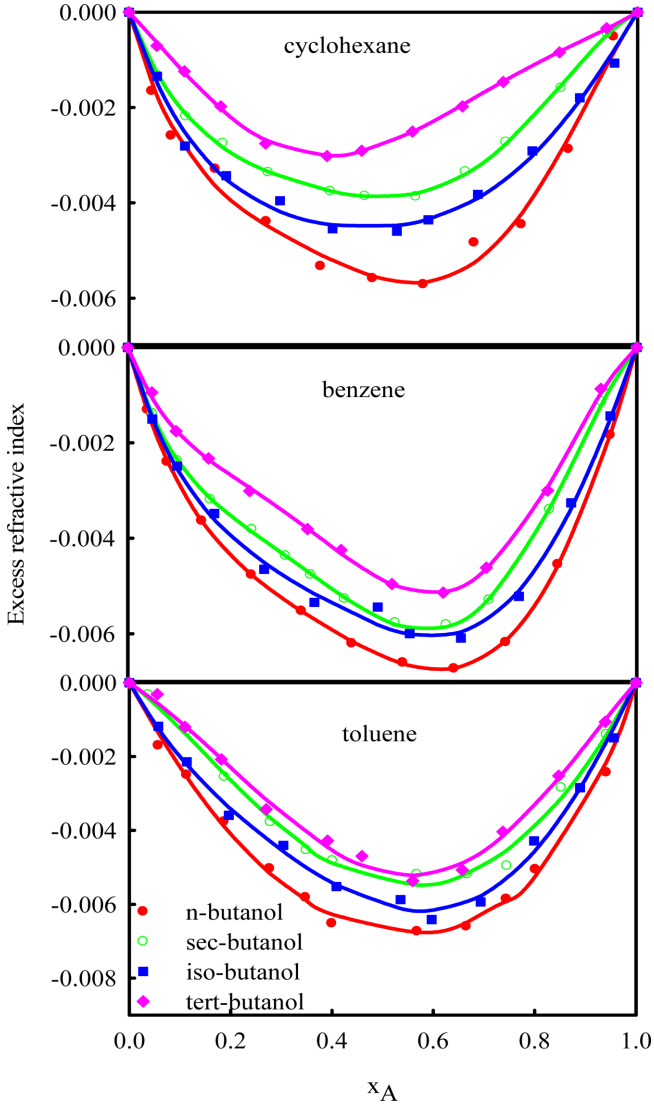

Fig. 7. Excess refractive index of butanol (A) + hydrocarbon (B) mixture as a function of mole fraction of butanol at 308.15 K.

lated excess or deviation in properties values:

$$X_m^E = x_1(1-x_1)\left[\sum_{n=1}^{4} A_n(2x_1-1)^{(n-1)}\right] \quad (13)$$

The standard deviation $\sigma(X_m^E)$ along with A_n parameters of Eq. (13) are reported in Table 6. The $X_m^E(X_m = u, K_s, L_f$ and $n_D)$ values calculated using Eq. (13) along with experimental values are shown in Figs. 1, 2, 5 and 7.

The Δu values for the present systems shown in Fig. 1 are negative at all composition and vary as: n-butanol > iso butanol > sec-

Table 5. Value of standard deviations of calculated values of refractive index using various correlations

System	AB	GD	LL	Weiner	Heller	Newton	Erying
n-butanol(1)+cyclohexane(2)	0.019	0.019	0.019	0.021	0.018	0.019	0.019
n-butanol(1)+benzene(2)	0.017	0.017	0.015	0.042	0.014	0.017	0.017
n-butanol(1)+toluene(2)	0.030	0.030	0.028	0.054	0.027	0.032	0.029
sec-butanol(1)+cyclohexane(2)	0.014	0.014	0.014	0.016	0.014	0.014	0.014
sec-butanol(1)+benzene(2)	0.014	0.014	0.012	0.040	0.011	0.017	0.013
sec-butanol(1)+toluene(2)	0.024	0.024	0.021	0.048	0.020	0.026	0.023
iso-butanol(1)+cyclohexane(2)	0.016	0.016	0.016	0.018	0.016	0.016	0.016
iso-butanol(1)+benzene(2)	0.015	0.015	0.012	0.039	0.011	0.017	0.013
iso-butanol(1)+toluene(2)	0.026	0.026	0.023	0.048	0.023	0.028	0.025
tert-butanol(1)+cyclohexane(2)	0.011	0.011	0.011	0.015	0.011	0.012	0.011
tert-butanol(1)+benzene(2)	0.008	0.008	0.005	0.040	0.004	0.011	0.007
tert-butanol(1)+toluene(2)	0.022	0.022	0.019	0.052	0.017	0.025	0.020

Table 6. Coefficient A_n of Redlich-Kister equation and standard deviations

System	A_1	A_2	A_3	A_4	σ
n-butanol (1) + cyclohexane (2)					
$\Delta u/ms^{-1}$	-14.54	31.96	6.20	-1.51	0.314
k_s^E/TPa^{-1}	35.51	-53.26	-9.14	4.34	0.466
$L_f^E/Å$	0.042	-0.015	0.001	0.000	0.000
Δn	-0.022	-0.005	-0.005	0.016	0.000
n-butanol (1) + benzene (2)					
$\Delta u/ms^{-1}$	-19.73	38.24	-11.92	-6.12	0.436
k_s^E/TPa^{-1}	30.79	-53.39	12.69	11.08	0.536
$L_f^E/Å$	0.021	-0.015	0.0077	-0.001	0.000
Δn	-0.026	-0.009	-0.013	0.010	0.000
n-butanol (1) + toluene(2)					
$\Delta u/ms^{-1}$	-25.26	29.13	-2.34	-16.84	0.335
k_s^E/TPa^{-1}	35.38	-38.59	-0.96	24.60	0.396
$L_f^E/Å$	0.008	-0.014	-0.002	0.009	0.000
Δn	-0.027	-0.005	-0.007	-0.004	0.000
sec-butanol (1) + cyclohexane (2)					
$\Delta u/ms^{-1}$	-50.69	-24.68	3.76	37.61	0.521
k_s^E/TPa^{-1}	101.99	35.03	-3.42	-59.84	0.823
$L_f^E/Å$	0.058	-0.019	0.023	-0.001	0.000
Δn	-0.0155	0.0002	-0.0010	0.0113	0.000
sec-butanol (1) + benzene (2)					
$\Delta u/ms^{-1}$	-55.27	44.72	30.88	-14.17	1.032
k_s^E/TPa^{-1}	93.52	-61.32	-53.45	19.77	1.450
$L_f^E/Å$	0.054	-0.021	0.004	-0.008	0.000
Δn	-0.023	-0.010	-0.001	0.021	0.000
sec-butanol (1) + toluene (2)					
$\Delta u/ms^{-1}$	-55.13	16.92	20.96	-3.42	0.431
k_s^E/TPa^{-1}	86.88	-17.27	-33.71	4.54	0.622
$L_f^E/Å$	0.029	-0.015	0.002	0.0033	0.000
Δn	-0.022	-0.006	0.003	-0.003	0.000
iso-butanol (1) + cyclohexane (2)					
$\Delta u/ms^{-1}$	-25.76	19.73	18.36	12.92	0.881
k_s^E/TPa^{-1}	54.55	-35.84	-28.77	-21.49	1.432
$L_f^E/Å$	0.037	-0.019	0.013	-0.005	0.000
Δn	-0.018	0.001	-0.007	0.005	0.000
iso-butanol (1) + benzene (2)					
$\Delta u/ms^{-1}$	-26.03	34.01	-9.64	-5.70	0.508
k_s^E/TPa^{-1}	44.41	-46.68	11.25	11.25	0.743
$L_f^E/Å$	0.027	-0.0118	0.020	-0.006	0.000
Δn	-0.023	-0.008	-0.010	0.011	0.000
iso-butanol (1) + toluene (2)					
$\Delta u/ms^{-1}$	-32.62	19.92	1.32	-2.33	0.359
k_s^E/TPa^{-1}	51.90	-22.96	-5.37	2.68	0.502
$L_f^E/Å$	0.014	-0.010	0.006	-0.006	0.000
Δn	-0.024	-0.008	-0.003	0.006	0.017
tert-butanol (1) + cyclohexane (2)					
$\Delta u/ms^{-1}$	-87.52	-5.66	7.87	-9.61	0.877
k_s^E/TPa^{-1}	180.20	38.08	-14.91	11.25	1.624
$L_f^E/Å$	0.062	0.002	-0.002	-0.007	0.000
Δn	-0.011	0.008	0.002	-0.005	0.007
tert-butanol (1) + benzene (2)					
$\Delta u/ms^{-1}$	-94.94	18.54	23.48	9.48	1.989
k_s^E/TPa^{-1}	181.69	14.46	-49.11	-17.98	3.235
$L_f^E/Å$	0.060	0.005	0.019	0.008	0.000
Δn	-0.020	-0.011	0.002	0.020	0.000
tert-butanol (1) + toluene(2)					
$\Delta u/ms^{-1}$	-63.70	-12.86	-10.96	28.54	1.221
k_s^E/TPa^{-1}	121.27	50.22	20.01	-28.06	1.825
$L_f^E/Å$	0.034	0.001	0.003	0.006	0.000
Δn	-0.021	-0.007	0.008	0.003	0.013

butanol > tert-butanol. Negative Δu value indicates the specific interactions among unlike molecules. As expected, the values of Δu become more negative with the branching of alkyl group due to weak H-bonding, which leads to easy dissociation. Thus, the branched chain alcohols result in larger reduction of u from ideal values. Among binary mixture of butanol isomers with cyclohexane, benzene or toluene, the magnitude of Δu varies in the order: toluene > benzene > cyclohexane (the $\Delta\eta$ values are negative for all of these systems). Δu for isomers of butanol (A) + cyclohexane (B) system was found negative because cyclohexane is a non-polar liquid, and due to its cyclic structure it occupies more space and also causes rupture of hydrogen bond as well as dipole-dipole interaction of monomer and polymer of isomers of butanol or cohesive forces in cyclohexane [56]. While aromatic hydrocarbon, due to π-electron donor-acceptor specific interactions with butanol, the aromatic hydrocarbon breaks the hydrogen bonds to large extent [57-59]. This leads to higher Δu values than that for cyclohexane. Toluene interacts with alcohols more strongly than the benzene due to presence of methyl group, which increases the electron density on the ring.

If the above assumptions for interaction of molecules are correct, then it should be reflected in K_s^E values for the binary systems. The K_s^E value depends on the interactional strength between unlike components and available volume of mixture. The greater is the available volume, the greater will be the compressibility. Order of K_s^E shown in Fig. 2 for butanol (A) + hydrocarbon (B) is: n-butanol < isobutanol < sec-butanol < tert-butanol.

Weak interactions between unlike molecules are responsible for positive deviation in K_s^E values. The greater is the available volume, the greater will be the compressibility. The V_a values in Fig. 4 confirm that tert-butanol has greater available volume in comparison to other butanol isomer, so K_s^E values are larger for tert-butanol system. The K_s^E values are more positive for cyclohexane in comparison to toluene and benzene in all systems due to its non-polar nature and its structure, which leads to a positive contribution. The K_s^E values for toluene are larger than benzene system with all butanol due to greater π-electron donor-acceptor specific interactions in comparison to benzene. L_f^E is the distance between two adjacent molecules, which is dependent on the type of packing and extent of association in given liquids. Order for L_f^E is shown in Fig. 5, which is positive for all the systems. More compressibility means more available volume, which in turn leads to more intermolecular length. Thus, the order for L_f^E and V_a again supports our earlier predictions about intermolecular interactions in the binary mixtures.

As n_D is a speed of light dependent property, the lower is the density, the greater is the speed of light, which leads to a decrease in refractive index. Hence, for tert-butanol the Δn is largest while lowest for n-butanol. The Δn value for toluene is largest among all systems with hydrocarbon.

4. Conclusion

Refractive index and speeds of sound of cyclohexane, benzene and toluene with butanol were measured over the whole composition range at 308.15 K. From the measured data the deviation in refractive index Δn, ultrasonic speed Δu, isentropic compressibility K_s^E, available volume V_a, excess intermolecular free length L_f^E and molecular association M_A were calculated. Jacobson free length theory (FLT) was used to calculate L_f^E. The measured refractive index and ultrasonic speed properties were correlated using various empirical relations. Van Dael relation is best for predicting the experimental values for all systems. Toluene due to π-electron donor-acceptor specific interactions with butanol break the hydrogen bonds to large extent in comparison to benzene and cyclohexane.

Acknowledgment

Ms. Sweety Verma acknowledges TEQIP Phase 3, Government of India, for financial assistance.

References

1. Hajbabaei, M., Karavalakis, G., Johnson, K. C., Guthrie, J., Mitchell, A. and Durbin, T. D., "Impacts of Biodiesel Feedstock and Additives on Criteria Emissions from a Heavy-duty Engine," *Fuel Process Technol*., **126**, 402-414(2014).
2. Kim, K. H., Choi, I. S., Kim, H. M., Wi, S. G. and Bae, H.-J., "Bioethanol Production from the Nutrient Stress-induced Microalga Chlorella Vulgaris by Enzymatic Hydrolysis and Immobilized Yeast Fermentation," *Bioresource Technol.*, **153**, 47-54(2014).
3. Surisetty, V. R., Dalai, A. K. and Kozinski, J., "Alcohols as Alternative Fuels: An Overview," *Applied Catalysis A: General*, **404**, 1-11(2011).
4. Karabektas, M., Ergen, G. and Hosoz, M., "The Effects of Using Diethylether as Additive on the Performance and Emissions of a Diesel Engine Fuelled with CNG," *Fuel*, **115**, 855-860(2014).
5. Ezeji, T. C. and Blaschek, H. P., Butanol Production from Lignocellulosic Biomass, in: H. P. Blaschek, T. C. Ezeji, J. Sheffran (Eds.), Biofuels from Agricultural Wastes and Byproducts, Wiley-Blackwell, Oxford, UK (2010).
6. Luque, R., Menendez, J. A., Arenillas, A. and Cot, J., "Microwave-assisted Pyrolysis of Biomass Feedstocks: the Way Forward," *Energy & Environl. Sci.*, **5**, 5481-5488(2012).
7. Regulation 715/2007 of the European Parliament ad of the Council on type approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) (2007).
8. Directive 2009/30/EC of the European Parliament ad of the Council on the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions (2009).
9. Dees, C., Askari, M. and Henley, D., "Carcinogenic Potential of Benzene and Toluene When Evaluated Using Cyclin-dependent Kinase Activation and p53-DNA Binding," *Environ. Health Persp.*, **104**, 1289-1292(1996).
10. Belda, R., Herraez, J. V. and Diez, O., "Rheological Study and Thermodynamic Analysis of the Binary System (water/ethanol): Influence of Concentration," *Phys. Chem. Liq.*, **42**, 467-479(2004).
11. Belda, R., Herraez, J. V. and Diez, O., "A Study of the Refractive

Index and Surface Tension Synergy of the Binary Water/Ethanol: Influence of Concentration," *Phys. Chem. Liq*., **43**, 91-101(2005).
12. Adhikhari, A. B., Rahman, I. M. M., Uddin, M. A., Hasegawa, H. and Majid, M. A., "Volumetric Behavior of the Binary Mixtures of Methyl Ethyl Ketone with n-Hexane, Cyclohexane, and Benzene at T = (303.15, 313.15, and 323.15) K," *J. Chem Eng. Data*, **54**, 1138-1141(2009).
13. Al-Jimaz, A. S., Al-Kandary, J. A. and Abdul-Latif, A.-H.M., "Densities and Viscosities for Binary Mixtures of Phenetole with 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol at Different Temperatures," *Fluid Phase Equilibri.*, **218**, 247-260(2004).
14. Gahlyan, S., Rani, M., Lee, I., Moon, I. and Maken, S., "Measurement and Correlation of Excess Molar Volumes for Mixtures of 1-propanol and Aromatic Hydrocarbons," *Korean J. Chem. Eng*., **32**, 168-177(2015).
15. Gahlyan, S., Rani, M. and Maken, S., "Excess Molar Volume of Binary Mixtures Containing an Oxygenate," *J. Mol. Liq*., **199**, 42-50(2014).
16. Gahlyan, S., Verma, S., Rani, M. and Maken, S., "Application of Flory-Treszczanowicz-Benson Model and Prigogine-Flory-Patterson Theory to Excess Molar Volumes of Isomers of Propanol with Cyclohexane or n-hexane," *Korean Chem. Eng. Res*., **56**(2018). In press.
17. Gahlyan, S., Rani, M., Maken, S., Kwon, H., Tak, K. and Moon, I., "Modeling of Thermodynamic Properties of An Oxygenate +aromatic Hydrocarbon: Excess Molar Enthalpy," *J. Ind. Eng. Chem*., **23**, 299-306(2015).
18. Gahlyan, S., Verma, S., Rani, M. and Maken, S., "Ultrasonic Speed and Isentropic Compressibility of 2-propanol with Hydrocarbons at 298.15 and 308.15 K," *Korean Chem Eng. Res*., **55**, 668-678(2017).
19. Gahlyan, S., Verma, S., Rani, M. and Maken, S., "Viscometric Studies of Molecular Interactions in Binary Mixtures of Formamide with Alkanol at 298.15 and 308.15 K," *Korean Chem Eng. Res.*, **55**, 520-529(2017).
20. Gahlyan, S., Verma, S., Rani, M. and Maken, S., "Volumetric Studies of Isomers of Propanol and Butanol with n-decane: Flory-Treszczanowicz-Benson Model and Prigogine-Flory-Patterson Theory," *J. Mol. Liq*., **244**, 233-240(2017).
21. Gahlyan, S., Verma, S., Rani, M. and Maken, S., "Excess Molar Enthalpy of Oxygenate+hydrocarbon Mixtures: Application of Flory-Treszczanowicz-Benson Model and Graph Theoretical Approach," *J. Mol. Liq*., **258**, 142-146(2018).
22. Gahlyan, S., Verma, S., Rani, M. and Maken, S., "Viscometric and FTIR Studies of Molecular Interactions in 2-propanol+hydrocarbons Mixtures at 298.15 and 308.15 K," *Korean J. Chem. Eng*., **35**(2018).
23. Gahlyan, S., Verma, S., Rani, M. and Maken, S., "Measurements and Modeling of Excess Molar Enthalpy of Binary Mixtures of Oxygenate and Hydrocarbons," *Asian J. Chem*., **30**, 731-735(2018).
24. Partibha, Kumar, K., Gahlyan, S., Rani, M. and Bhankar, V., "Measurement and Correlation of Thermodynamic Properties of Amine and Esters," *J. Mol. Liq*., **259**, 167-178(2018).
25. Rani, M., Agarwal, S., Lahot, P. and Maken, S., "Excess Molar Enthalpies of Binary Mixtures of Formamide with Butanol at 298.15 K: Application of Prigogine-Flory-Patterson Theory and Treszczanowicz-Benson Association Model," *J. Ind. Eng. Chem*., **19**, 1715-1721(2013).
26. Rani, M., Gahlyan, S., Gaur, A. and Maken, S., "Ultrasonic Study on Molecular Interactions in Binary Mixtures of Formamide with 1-propanol or 2-propanol," *Chinese J. Chem Eng*., **23**, 689-698 (2015).
27. Kashyap, P., Rani, M., Gahlyan, S., Tiwari, D. P. and Maken, S., "Volumetric, Acoustic and Optical Properties of Binary Mixtures of 2-propanol with n-alkanes (C6-C10) from 293.15 K to 303.15 K," *J. Mol. Liq*., **268**, 304-314(2018).
28. Rani, M. and Maken, S., "Topological Studies of Molecular Interactions of Formamide with Propanol and Butanol at 298.15 K," *J. Ind. Eng. Chem*., **18**, 1694-1704(2012).
29. Gahlyan, S., Rani, M. and Maken, S., "Ultrasonic Speeds, Viscosities, Refractive Indices and FT-IR Spectroscopic Studies of an Oxygenate with Aliphatic and Aromatic Hydrocarbons at 298.15 K and 308.15 K," *J. Mol. Liq*., **219**, 1107-1123(2016).
30. Rani, M., Gahlyan, S., Om, H., Verma, N. and Maken, S., "Ultrasonic Studies of Molecular Interactions in Binary Mixtures of Formamide with Some Isomers of Butanol at 298.15 K and 308.15 K," *J. Mol. Liq*., **194**, 100-109(2014).
31. Gahlyan, S., Verma, S., Rani, M. and Maken, S., "Transport Properties and Modeling of Viscosity for Binary Mixtures of Butanol Isomers + Hydrocarbons," *Arab. J. Sci.CI Eng*., https://doi.org/10.1007/s13369-018-3276-1R.
32. Schaaffs, W., Molekularakustik, Springer-Verlag, 1963.
33. Schaaffs, W., "Das Problem Der Theoretischen Bereehnung Der Schallgeschwindigkeit in Binaren Flussigkeitsmischungen," *Acustica*, **33**, 272-276(1975).
34. Jacobson, B., "Association Numbers in Liquid Systems from Intermolecular Free Length Relationships," *Acta. Chem. Scand*., **9**, 997-1008(1955).
35. Jacobson, B., "Ultrasonic Velocity in Liquids and Liquid Mixtures," *J. Chem. Phys*., **20**, 927-928(1952).
36. Jacobson, B., "Intermolecular Free Lengths in the Liquid State. I. Adiabaic and Isothermal Compressibilities," *Acta. Chem. Scand*., **6**, 1485-1498(1952).
37. Riddick, J. A., Bunger, W. B. and Sakano, T. K., "Organic Solvents. Physical Properties and Methods of Purification," 4th ed., Wiley, New York(1986).
38. Vogel, A. I., "A Text Book of Practical Organic Chemistry, 4th ed.," ELBS Longman, London(1978).
39. Barta, L., Kooner, Z. S., Hepler, L. G., Roux-Desgranges, G. and Grolier, J. P. E., "Thermodynamics of Complex Formation in Chloroform + 1,4-dioxane," *Can. J. Chem*., **67**, 1225-1229(1989).
40. de Cominges, B. E., Piñeiro, M. M., Mosteiro, E., Mascato, E., Mato, M. M., Iglesias, T. P. and Legido, J. L., "Temperature Dependence of Thermophysical Properties of Octane+1-butanol System," *J. Therm. Anal. Calorim*., **70**, 217-227(2002).
41. Nain, A. K., Srivastava, T., Pandey, J. D. and Gopal, S., "Densities, Ultrasonic Speeds and Excess Properties of Binary Mixtures of Methyl Acrylate with 1-butanol, or 2-butanol, or 2-methyl-1-propanol, or 2-methyl-2-propanol at Temperatures from 288.15 to 318.15K," *J. Mol. Liq*., **149**, 9-17(2009).
42. Troncoso, J., Tovar, C. A., Cerdeiriña, C. A., Carballo, E. and Romaní, L., "Temperature Dependence of Densities and Speeds of Sound of Nitromethane + Butanol Isomers in the Range (288.15−308.15) K," *J. Chem.& Eng. Data*, **46**, 312-316(2001).

43. Chandra Sekhar, M., Madhu Mohan, T., Vijaya Krishna, T., Venkatesulu, A. and Siva Kumar, K., "Density, Refractive Index, Speed of Sound and Computational Studies of Intermolecular Interactions in Binary Mixtures of 2-Chloroaniline with Butanols (1-Butanol, 2-Butanol) at T = (303.15–318.15) K," *J. Sol.Chem*, **44**, 237-263(2015).
44. Sastry, N. V. and Patel, S. R., " Excess Volumes and Dielectric Properties for (methyl methacrylate + a branched alcohol) at T= 298.15 K and T = 308.15 K," *J. Chem. Thermodyn*., **32**, 1669-1682(2000).
45. Kijevčanin, M. L., Radović, I. R., Djordjević, B. D., Tasić, A. Ž. and Šerbanović, S. P., "Experimental Determination and Modeling of Densities and Refractive Indices of the Binary Systems Alcohol+dicyclohexylamine at T = (288.15–323.15)K," *Thermochim Acta*, **525**, 114-128(2011).
46. Ghanadzadeh Gilani, A., Paktinat, N. and Moghadam, P. M., "Relative Permittivity Data of Binary Mixtures Containing 2-butanol, 2-butanone, and cyclohexane," *J. Chem. Thermodyn*., **43**, 569-575(2011).
47. George, J. and Sastry, N. V., "Densities, Excess Molar Volumes, Viscosities, Speeds of Sound, Excess Isentropic Compressibilities, and Relative Permittivities for C_mH_{2m}+1$(OCH_2CH_2)_nOH$ (m = 1 or 2 or 4 and n = 1) + benzene, + toluene, + (o-, m-, and p-) xylenes, + ethylbenzene, and + cyclohexane," *J. Chem. Eng. Data*, **48**, 977-989(2003).
48. Nayak, J. N., Aralaguppi, M. I. and Aminabhavi, T. M., "Density, Viscosity, Refractive Index, and Speed of Sound in the Binary Mixtures of Ethyl Chloroacetate with Aromatic Liquids at 298.15, 303.15, and 308.15 K," *J. Chem. Eng. Data*, **47**, 964-969(2002).
49. Sastry, N. V., Patel, M. C. and Patel, S. R., "Ultrasonic Behaviour of Methyl Methacrylate+hydrocarbon Mixtures at 298.15 and 308.15 K," *Fluid Phase Equilib*, **155**, 261-276(1999).
50. Nayak, J. N., Aralaguppi, M. I. and Aminabhavi, T. M., "Density, Viscosity, Refractive Index, and Speed of Sound for the Binary Mixtures of Ethyl Chloroacetate with n-alkanes (C6 to C12) at (298.15, 303.15, and 308.15) K," *J. Chem.Eng. Data*, **46**, 891-896(2001).
51. Kiyohara, O. and Benson, G. C., "Ultrasonic Speeds and Isentropic Compressibilities of n-alkanol + n-heptane Mixtures at 298.15 K," *J. ChemThermodyn*., **11**, 861-873(1979).
52. Troncoso, J., Carballo, E., Cerdeiriña, C. A., González, D. and Romaní, L., "Systematic Determination of Densities and Speeds of Sound of Nitroethane + isomers of Butanol in the Range (283.15−308.15) K," *J. Chem. Eng. Data*, **45**, 594-599(2000).
53. Sharma, V. K., Dua, R., Dimple and Jangra, S. K., "Heat Capacities of Binary and Ternary Mixtures Containing o-chlorotoluene, Cyclic Ether and Aromatic Hydrocarbons," *Fluid Phase Equilib*., **378**, 83-92(2014).
54. Troncoso, J. and Valencia, J. L., Souto-Caride, M., González-Salgado, D. and Peleteiro, J., "Thermodynamic Properties of Dodecane + 1-butanol and + 2-butanol Systems," *J. Chem Eng. Data*, **49**, 1789-1793(2004).
55. Páramo, R., Zouine, M. and Casanova, C., "New Batch Cells Adapted to Measure Saturated Heat Capacities of Liquids," *J. Chem. Eng. Data*, **47**, 441-448(2002).
56. Oswal, S. L., Prajapati, K. D., Oswal, P., Ghael, N. Y. and Ijardar, S.P., "Viscosity of Binary Mixtures of 1-alkanol+cyclohexane, 2-alkanol+cyclohexane and 1-alkanol + methylcyclohexane at 303.15 K," *J. Mol. Liq.*, **116**, 73-82(2005).
57. Bhardwaj, U., Maken, S. and Singh, K. C., "MExcess Volumes of 1-butanol, 2-butanol, 2-methylpropan-1-ol, and 2-methylpropan-2-ol with Xylenes at 308.15 K," *J. Chem. Eng. Data*, **41**, 1043-1045 (1996).
58. Bhardwaj, U., Maken, S. and Singh, K. C., "Molar Excess Enthalpies and Molar Excess Volumes of all Isomers of Butanol with Cyclohexane at 308.15 K in terms of an Associated Model with a Flory Contribution Term," *Indian J. Chem*., **37A**, 316-322(1998).
59. Bhardwaj, U., Maken, S. and Singh, K. C., "Excess Molar Volumes of (an isomer of butanol+ benzene or toluene) at the Temperature 308.15 K," *J. Chem. Thermodyn*., **28**, 1173-1177(1996).