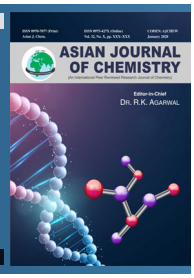
Asian Journal of Chemistry; Vol. 32, No. 2 (2020), 303-310

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2020.22354



Ultrasonic and Optical Studies of Binary Mixtures of Ethanol with Diisopropyl Ether, Cyclohexane or *n*-Alkanes (C_6-C_9) from 298.15 to 318.15 K

PINKI KASHYAP, MANJU RANI* and D.P. TIWARI

Department of Chemical Engineering, Deenbandhu Chhotu Ram University of Science and Technology, Murthal-131039, India

*Corresponding author: E-mail: manjubanwala@gmail.com

Received: 23 July 2019; *Accepted*: 12 September 2019; *Published online*: 30 December 2019; AJC-19717

Ultrasonic speeds (u) and refractive indices (n) of the binary liquid mixtures of ethanol with diisopropyl ether (DIPE) or cyclohexane or *n*-alkane (C_6-C_9) were experimentally measured from 298.15 to 318.15 K over entire composition range. Using these measurements deviation in ultrasonic speed (Δu), deviation in refractive index (Δn), excess intermolecular free length (L_f^E) and excess isentropic compressibility (K_s^E) were calculated and fitted with Redlich-Kister equation. The Δu values are negative for all binary mixture and magnitude of negative deviation for binary mixture of ethanol and *n*-alkane decreases as chain length increases. At equimolar composition, K_s^E follows the order: *n*-hexane > *n*-heptane > *n*-otcane > *n*-nonane > diisopropyl ether > cyclohexane. Experimental results were analyzed to understand the various molecular interactions present in the binary mixtures. The u values for all binary liquid solutions were also correlated using different empirical correlations such as Nomoto, impedence dependence relation and van Dael ideal mixing relation. The u for binary liquid mixtures were also computed theoretically using Schaaff's collision factor theory. Free length theory was used to compute inter-molecular free length (L_f^E). Various correlations *e.g.*, Arago-Biot (A-B), Gladstone-Dale (G-D), Heller (H), Lorentz-Lorentz (L-L), Eyring-John (E-J), Newton (Nw) and Weiner (W) were used for calculating refractive indices of selected systems theoretically.

Keywords: Ultrasonic speed, Refractive index, Ethanol, Diisopropyl ether, Alkanes.

INTRODUCTION

Environmental pollution is a matter of great concern these days due to its adverse effects on all living beings. One of the major causes of pollution is toxic gases and elements released by combustion of fuels. Therefore, there is a need to develop environment friendly fuel such as fuel formulated using oxygenates which have low emission of CO_2 and CO, high octane rating and high fuel efficiency [1-4]. Experimentally measured data of various thermophysical properties for possible mixtures containing oxygenates and components of gasoline such as alkanes, cycloalkanes, aromatics, *etc*. over a wide temperature range is very helpful for formulation of environmental friendly fuel, petrochemical additives, diesel and gasoline [2,5]. The molecular association of alkanols with alkanes has its own great importance due to its various industrial applications. As ethanol and diisopropyl ether are rich oxygenates, highly soluble, self-associating component and therefore useful in petrochemical industries and used as a gasoline stabilizer to increase the efficiency of gasoline engines. Ultrasonic studies of binary mixtures assist in analyzing the non-ideal behavior of mixtures [6] because various significant properties such as isentropic compressibility, intermolecular free length and available volume derived using ultrasonic speed data provides important information about the intermolecular interactions. Refractive index is also a significant physical property, which can play important role in understanding the various interaction between like and unlike molecules in binary mixtures [7,8]. Refractive index relates the speed of light through a given medium to the speed of light in vacuum. Speed of light changes with change in medium. Therefore, refractive index depends on composition of the medium and helps in understanding the non-ideal behaviour of liquid mixtures. In present paper, measured refractive index (n) and ultrasonic speeds (u) values as well as deviation in refractive index (Δn) , deviation in speed of sound (Δu), excess intermolecular free length (L_f^E) and excess isentropic compressibility (K_s^E) calculated using experimental n and u for binary systems of ethanol with diisopropyl ether

or cyclohexane or *n*-alkane (C_6-C_9) have been reported over entire composition set from 298.15 to 318.15 K. The u values for all binary liquid solutions were also correlated using different empirical correlations such as Nomoto, impedence dependence relation and van Dael ideal mixing relation. The u for binary liquid mixtures were also computed theoretically using Schaaff's collision factor theory (CFT). Free length theory (FLT) was used to compute inter-molecular free length. Various correlations Arago-Biot (A-B), Gladstone-Dale (G-D), Heller (H), Lorentz-Lorentz (L-L), Eyring-John (E-J), Newton (Nw) and Weiner (W) were used for calculating refractive indices of selected systems theoretically.

EXPERIMENTAL

Ethanol, cyclohexane, *n*-alkane (C_6, C_7, C_8) were supplied by Merck while nonane and diisopropyl ether were supplied by Sigma-Aldrich and Loba Chemicals, respectively and their complete specifications are mentioned in Table-1. Ethanol and alkanes were simply distilled and their middle fraction was collected. Diisopropyl ether was purified by using standard methods [9]. Then all the chemicals were kept over molecular sieves (4 Å) for more than 72 h. Purities of compounds were ensured by measuring and comparing their physical properties like ρ, u and n with literature data [10-34] as given in Table-2.

For measurement of u and ρ, Anton Paar DSA-5000 M was used with uncertainty of ± 0.1 m s^{-1} and ± 10^{-6} g cm^{-3}, respectively. The n values were measured by using Anton Paar refractometer (Abbemat-200) with temperature controlled within ± 0.01 K with precision up to ± 1 × 10^{-4}. All samples were prepared by using weighing balance (OHAUS, AR224CN) having ± 0.1 mg accuracy and the uncertainty in mole fraction was ± 1 × 10^{-4}. The Δu and Δn were calculated using experimental u and n values.

RESULTS AND DISCUSSION

The experimental u and n values along with calculated Δu and Δn values using eqn. 1 are reported in Table-3.

$$\Delta X = X_m - x_1X_1^o - x_2X_2^o \quad (1)$$

where ΔX, X_m and X_i^o symbolises the deviation in thermodynamic property, mixture property and pure component property respectively in the binary mixture. The calculated data was fitted with Redlich-Kister equation [35].

TABLE-1
CHEMICALS SPECIFICATIONS

Sample	CAS No.	Make	Mass fraction purity	Purification method
Ethanol	64-17-5	Merck	0.999	Distillation
Diisopropyl ether	108-20-3	Loba	0.985	Distillation
n-Hexane	110-54-3	Merck	0.985	Distillation
Cyclohexane	110-82-7	Merck	0.990	Distillation
n-Heptane	142-82-5	Merck	0.990	Distillation
n-Octane	111-65-9	Merck	0.990	Distillation
n-Nonane	111-84-2	Sigma-Aldrich	0.990	Distillation

TABLE-2
PURITIES, MEASURED DENSITIES (ρ, 10^3 × g cm^{-3}), ULTRASONIC SPEEDS (u, m s^{-1}) AND REFRACTIVE INDICES (n_D) OF THE PURE COMPONENTS

Compound	Temp. (K)	ρ		u		n_D	
		This work	Literature	This work	Literature	This work	Literature
Ethanol	298.15	787.08	786.60 [12]	1147.91	1146.20 [13]	1.3612	1.3593 [14]
	308.15	778.41	777.94 [12]	1114.18	1109.40 [15]	1.3566	1.3553 [16]
	318.15	769.57	769.15 [12]	1080.72	1075.67 [17]	1.3520	1.3512 [16]
Diisopropyl ether	298.15	720.12	719.17 [10]	1001.24	998.00 [18]	1.3654	1.3652 [11]
	308.15	709.51	708.12 [11]	956.85	962.00 [18]	1.3598	1.3596 [19]
	318.15	698.71	–	912.95	–	1.3541	–
n-Hexane	298.15	655.56	655.13 [20]	1077.01	1077.21 [21]	1.3733	1.3732 [22]
	308.15	646.40	646.07 [20]	1032.16	1031.8 [23]	1.3679	1.3672 [24]
	318.15	637.12	636.79 [20]	987.62	988.00 [25]	1.3628	–
Cyclohexane	298.15	773.97	773.92 [20]	1253.00	1253.71 [21]	1.4237	1.4235 [21]
	308.15	764.49	764.51 [20]	1204.43	1205.00 [25]	1.4180	1.4175 [26]
	318.15	754.89	754.85 [20]	1156.74	1157.00 [25]	1.4123	–
n-Heptane	298.15	679.58	679.78 [23]	1129.74	1131.10 [23]	1.3846	1.3852 [23]
	308.15	671.02	671.27 [23]	1086.87	1088.40 [23]	1.3793	1.3800 [23]
	318.15	662.34	662.50 [27]	1044.49	–	1.3740	–
n-Octane	298.15	698.72	698.60 [28]	1171.72	1172.70 [29]	1.3953	1.3951 [30] 1.3955 [12]
	308.15	690.60	690.42 [29]	1130.67	1131.70 [29]	1.3902	1.3906 [12]
	318.15	682.38	682.19 [12]	1089.97	1096.00 [31]	1.3853	1.3849 [12]
n-Nonane	298.15	713.97	713.96 [32]	1205.98	1203.70 [32] 1209.00 [33]	1.4032	1.4030 [32]
	308.15	706.15	706.01 [34]	1165.76	1166.00 [33]	1.3985	1.3989 [33]
	318.15	698.36	698.12 [34]	1125.20	1126.00 [33]	1.3934	1.3938 [33]

TABLE-3
EXPERIMENTAL REFRACTIVE INDICES (n), DEVIATION IN REFRACTIVE INDICES (Δn),
EXPERIMENTAL ULTRASONIC SPEEDS (u, m s^{-1}), DEVIATION IN ULTRASONIC SPEEDS (Δu, m s^{-1}),
EXCESS ISENTROPIC COMPRESSIBILITY (K_s^E, TPa^{-1}) OF BINARY LIQUID MIXTURES

x_1	n	Δn	u	Δu	K_s^E	x_1	n	Δn	u	Δu	K_s^E
Ethanol (1) + diisopropyl ether (2)						Ethanol (1) + *n*-hexane (2)					
T = 298.15 K						T = 298.15 K					
0.0000	1.3654	0.0000	1001.24	0.00	0.00	0.0000	1.3733	0.0000	1077.01	0.00	0.00
0.0503	1.3664	0.0012	1007.69	-0.93	-1.57	0.0423	1.3729	0.0001	1072.83	-7.18	21.10
0.0967	1.3670	0.0020	1012.91	-2.51	-0.26	0.0731	1.3726	0.0002	1070.47	-11.72	34.60
0.1303	1.3673	0.0024	1016.10	-4.26	2.31	0.1349	1.3720	0.0003	1068.51	-18.07	54.10
0.2824	1.3674	0.0032	1030.02	-12.64	18.10	0.2545	1.3707	0.0005	1067.60	-27.46	82.36
0.3845	1.3672	0.0034	1039.98	-17.66	27.51	0.4113	1.3690	0.0007	1070.18	-35.99	105.80
0.4857	1.3669	0.0035	1052.39	-20.09	31.27	0.5212	1.3676	0.0006	1073.51	-40.46	115.48
0.5817	1.3665	0.0035	1065.56	-21.00	32.38	0.5884	1.3667	0.0005	1078.01	-40.72	114.38
0.6816	1.3659	0.0034	1081.74	-19.46	29.05	0.7429	1.3647	0.0004	1093.49	-36.19	96.60
0.7276	1.3654	0.0031	1089.98	-17.97	26.38	0.7735	1.3643	0.0004	1099.50	-32.35	86.06
0.8963	1.3630	0.0014	1124.69	-8.00	9.84	0.8149	1.3637	0.0003	1106.85	-27.93	73.65
0.9669	1.3617	0.0004	1140.35	-2.71	3.22	0.9620	1.3618	0.0001	1139.26	-5.95	15.81
1.0000	1.3612	0.0000	1147.91	0.00	0.00	1.0000	1.3612	0.0000	1147.91	0.00	0.00
T = 308.15 K						T = 308.15 K					
0.0000	1.3598	0.0000	956.85	0.00	0.00	0.0000	1.3679	0.0000	1032.16	0.00	0.0
0.0503	1.3606	0.0010	963.66	-1.11	-2.78	0.0423	1.3675	0.0001	1027.85	-7.78	26.6
0.0967	1.3611	0.0016	968.99	-3.07	-0.57	0.0731	1.3672	0.0001	1025.41	-12.74	42.8
0.1303	1.3613	0.0019	972.90	-4.45	0.66	0.1349	1.3666	0.0002	1023.49	-19.74	65.6
0.2824	1.3616	0.0027	987.58	-13.70	19.31	0.2545	1.3655	0.0005	1022.95	-30.09	99.2
0.3845	1.3617	0.0031	998.44	-18.91	30.61	0.4113	1.3639	0.0006	1026.57	-39.33	125.6
0.4857	1.3618	0.0036	1011.07	-22.20	36.60	0.5212	1.3626	0.0006	1031.54	-43.37	134.5
0.5817	1.3615	0.0036	1025.33	-23.04	37.35	0.5884	1.3617	0.0004	1036.30	-44.12	133.8
0.6816	1.3612	0.0036	1042.61	-21.47	33.53	0.7429	1.3598	0.0003	1053.06	-40.03	113.5
0.7276	1.3608	0.0033	1051.55	-19.77	30.19	0.7735	1.3594	0.0002	1059.78	-35.82	100.5
0.8963	1.3585	0.0016	1088.75	-9.11	11.56	0.8149	1.3589	0.0002	1066.85	-32.14	88.1
0.9669	1.3576	0.0009	1105.92	-3.06	3.68	0.9620	1.3571	0.0001	1103.05	-8.01	20.9
1.0000	1.3566	0.0000	1114.18	0.00	0.00	1.0000	1.3566	0.0000	1114.18	0.00	0.0
T = 318.15 K						T = 318.15 K					
0.0000	1.3541	0.0000	912.95	0.00	0.00	0.0000	1.3628	0.0000	987.62	0.00	0.0
0.0503	1.3548	0.0007	920.59	-0.80	-5.29	0.0423	1.3624	0.0001	983.28	-8.28	32.3
0.0967	1.3551	0.0012	925.55	-3.62	-0.50	0.0731	1.3621	0.0001	980.52	-13.90	52.7
0.1303	1.3561	0.0015	930.00	-4.82	-0.39	0.1349	1.3615	0.0002	978.62	-21.56	80.4
0.2824	1.3561	0.0025	945.65	-14.68	21.04	0.2545	1.3605	0.0004	978.42	-32.90	120.5
0.3845	1.3562	0.0031	956.59	-20.88	36.08	0.4113	1.3590	0.0006	982.97	-42.94	151.2
0.4857	1.3566	0.0034	970.93	-23.51	40.15	0.5212	1.3577	0.0005	988.56	-47.59	161.7
0.5817	1.3563	0.0036	985.60	-24.95	42.42	0.5884	1.3568	0.0004	994.65	-47.75	158.4
0.6816	1.3563	0.0036	1004.08	-23.22	37.70	0.7429	1.3550	0.0002	1013.70	-43.08	132.8
0.7276	1.3558	0.0034	1012.98	-22.04	35.48	0.7735	1.3546	0.0002	1019.81	-39.83	120.5
0.8963	1.3540	0.0019	1053.21	-10.10	13.14	0.8149	1.3541	0.0001	1028.58	-34.90	103.2
0.9669	1.3531	0.0007	1071.57	-3.60	4.55	0.9620	1.3525	0.0001	1068.99	-8.19	23.0
1.0000	1.3520	0.0000	1080.72	0.00	0.00	1.0000	1.3520	0.0000	1080.72	0.00	0.0
Ethanol (1) + cyclohexane (2)						Ethanol (1) + *n*-heptane (2)					
T = 298.15 K						T = 298.15 K					
0.0000	1.4237	0.0000	1253.00	0.00	0.00	0.0000	1.3846	0.0000	1129.74	0.00	0.00
0.0584	1.4215	0.0015	1238.01	-8.85	12.88	0.0511	1.3841	0.0007	1124.10	-6.57	18.92
0.1136	1.4189	0.0023	1230.97	-10.09	15.07	0.1461	1.3831	0.0019	1119.30	-13.09	40.49
0.2144	1.4138	0.0035	1218.03	-12.44	19.30	0.2322	1.3815	0.0023	1116.29	-17.67	55.69
0.3215	1.4080	0.0044	1205.58	-13.64	22.29	0.3469	1.3797	0.0032	1113.93	-22.11	71.18
0.4034	1.4034	0.0049	1196.58	-14.02	23.81	0.4291	1.3782	0.0036	1112.75	-24.79	79.79
0.5079	1.3975	0.0055	1185.83	-13.79	24.66	0.5270	1.3758	0.0035	1111.89	-27.43	87.09
0.6258	1.3897	0.0051	1173.01	-14.22	26.71	0.6178	1.3733	0.0032	1112.34	-28.63	89.00
0.7355	1.3817	0.0040	1163.26	-12.44	24.58	0.7247	1.3702	0.0026	1114.53	-28.38	85.16
0.8226	1.3743	0.0020	1156.90	-9.65	19.37	0.8191	1.3669	0.0015	1119.45	-25.17	72.21
0.9204	1.3668	0.0006	1152.21	-4.07	8.80	0.9086	1.3637	0.0004	1128.75	-17.50	47.84
0.9598	1.3638	0.0001	1150.26	-1.87	3.65	0.9563	1.3624	0.0002	1137.60	-9.52	24.68
1.0000	1.3612	0.0000	1147.91	0.00	0.00	1.0000	1.3612	0.0000	1147.91	0.00	0.00

T = 308.15 K						T = 308.15 K					
0.0000	1.4180	0.0000	1204.43	0.00	0.00	0.0000	1.3793	0.0000	1086.87	0.00	0.00
0.0584	1.4169	0.0025	1189.47	-9.69	16.48	0.0511	1.3789	0.0008	1081.27	-7.00	22.44
0.1136	1.4151	0.0041	1182.87	-11.30	19.86	0.1461	1.3781	0.0021	1076.40	-14.46	48.69
0.2144	1.4099	0.0051	1170.63	-14.45	26.41	0.2322	1.3766	0.0026	1073.43	-19.78	67.24
0.3215	1.4037	0.0054	1160.28	-15.14	28.95	0.3469	1.3747	0.0033	1071.46	-24.88	85.73
0.4034	1.3985	0.0053	1151.41	-16.61	32.64	0.4291	1.3731	0.0035	1070.67	-27.92	95.92
0.5079	1.3918	0.0050	1142.03	-16.56	33.87	0.5270	1.3709	0.0036	1070.63	-30.63	103.87
0.6258	1.3841	0.0045	1131.01	-16.94	35.86	0.6178	1.3685	0.0032	1071.96	-31.78	105.55
0.7355	1.3759	0.0031	1123.69	-14.36	31.30	0.7247	1.3654	0.0026	1075.43	-31.23	100.21
0.8226	1.3690	0.0015	1119.06	-11.13	24.57	0.8191	1.3624	0.0017	1081.88	-27.36	84.12
0.9204	1.3621	0.0006	1116.61	-4.76	10.50	0.9086	1.3592	0.0005	1093.85	-17.83	53.18
0.9598	1.3595	0.0004	1115.26	-2.54	5.60	0.9563	1.3578	0.0002	1102.95	-10.04	28.07
1.0000	1.3566	0.0000	1114.18	0.00	0.00	1.0000	1.3566	0.0000	1114.18	0.00	0.00
T = 318.15 K						T = 318.15 K					
0.0000	1.4123	0.0000	1156.74	0.00	0.00	0.0000	1.3740	0.0000	1044.49	0.00	0.00
0.0584	1.4110	0.0022	1142.89	-9.41	18.89	0.0511	1.3739	0.0010	1038.90	-7.44	26.74
0.1136	1.4092	0.0038	1134.45	-13.65	27.78	0.1461	1.3730	0.0022	1033.84	-15.94	58.92
0.2144	1.4041	0.0047	1123.96	-16.48	35.14	0.2322	1.3716	0.0027	1031.00	-21.90	81.25
0.3215	1.3981	0.0052	1114.28	-18.02	39.96	0.3469	1.3696	0.0032	1029.21	-27.85	103.80
0.4034	1.3928	0.0048	1106.74	-19.33	43.97	0.4291	1.3679	0.0033	1028.91	-31.13	115.51
0.5079	1.3864	0.0047	1098.75	-19.38	45.57	0.5270	1.3658	0.0034	1029.57	-34.01	124.40
0.6258	1.3788	0.0042	1089.01	-20.15	48.53	0.6178	1.3635	0.0031	1031.69	-35.18	125.88
0.7355	1.3709	0.0030	1084.30	-16.53	40.80	0.7247	1.3605	0.0024	1036.47	-34.28	118.50
0.8226	1.3639	0.0012	1081.46	-12.75	31.74	0.8191	1.3577	0.0017	1044.44	-29.73	98.53
0.9204	1.3571	0.0003	1081.51	-5.26	13.25	0.9086	1.3547	0.0007	1058.07	-19.34	61.92
0.9598	1.3546	0.0002	1081.26	-2.51	6.33	0.9563	1.3534	0.0004	1068.40	-10.74	32.37
1.0000	1.3520	0.0000	1080.72	0.00	0.00	1.0000	1.3520	0.0000	1080.72	0.00	0.00
Ethanol (1) + *n*-octane (2)						Ethanol (1) + *n*-nonane (2)					
T = 298.15 K						T = 298.15 K					
0.0000	1.3953	0.0000	1171.72	0.00	0.00	0.0000	1.4032	0.0000	1205.98	0.00	0.00
0.0568	1.3945	0.0011	1165.57	-4.80	13.90	0.0528	1.4024	0.0014	1200.52	-2.39	7.72
0.1097	1.3934	0.0018	1162.09	-7.02	22.23	0.1125	1.4008	0.0023	1195.73	-3.71	14.19
0.1951	1.3919	0.0033	1157.43	-9.64	33.29	0.1835	1.4002	0.0047	1190.56	-4.76	20.40
0.3033	1.3892	0.0042	1152.64	-11.86	44.12	0.3158	1.3965	0.0066	1181.98	-5.66	29.33
0.3855	1.3873	0.0051	1149.29	-13.25	50.83	0.4069	1.3944	0.0083	1176.17	-6.18	34.43
0.4825	1.3845	0.0057	1145.61	-14.62	57.01	0.5128	1.3911	0.0094	1169.59	-6.61	38.87
0.5882	1.3813	0.0061	1141.53	-16.19	61.93	0.6268	1.3855	0.0086	1162.76	-6.82	41.02
0.6833	1.3776	0.0056	1138.43	-17.02	63.20	0.7219	1.3801	0.0072	1157.06	-7.00	40.38
0.8047	1.3723	0.0044	1135.84	-16.72	56.92	0.8029	1.3763	0.0068	1153.02	-6.33	35.99
0.9025	1.3672	0.0027	1137.40	-12.83	40.21	0.8992	1.3691	0.0037	1149.24	-4.52	24.77
0.9655	1.3635	0.0011	1142.49	-6.24	18.08	0.9700	1.3654	0.0029	1148.11	-1.54	8.06
1.0000	1.3612	0.0000	1147.91	0.00	0.00	1.0000	1.3612	0.0000	1147.91	0.00	0.00
T = 308.15 K						T = 308.15 K					
0.0000	1.3902	0.0000	1130.67	0.00	0.00	0.0000	1.3985	0.0000	1165.76	0.00	0.00
0.0568	1.3887	0.0004	1124.24	-5.49	17.12	0.0528	1.3986	0.0023	1160.24	-2.79	9.37
0.1097	1.3886	0.0021	1120.66	-8.20	27.41	0.1125	1.3988	0.0050	1155.33	-4.63	17.27
0.1951	1.3875	0.0039	1116.01	-11.44	40.93	0.1835	1.3996	0.0088	1150.66	-5.64	24.10
0.3033	1.3846	0.0046	1111.31	-14.36	54.31	0.3158	1.4001	0.0148	1141.85	-7.62	36.46
0.3855	1.3823	0.0051	1108.25	-16.06	62.33	0.4069	1.3971	0.0156	1136.43	-8.34	42.65
0.4825	1.3794	0.0054	1104.96	-17.75	69.70	0.5128	1.3920	0.0150	1130.59	-8.72	46.84
0.5882	1.3764	0.0060	1101.71	-19.26	74.94	0.6268	1.3863	0.0141	1124.51	-8.92	48.91
0.6833	1.3728	0.0056	1099.42	-19.98	75.91	0.7219	1.3820	0.0137	1120.06	-8.46	46.18
0.8047	1.3674	0.0042	1098.42	-18.98	67.33	0.8029	1.3763	0.0114	1116.70	-7.64	41.25
0.9025	1.3625	0.0026	1101.61	-14.18	46.89	0.8992	1.3691	0.0083	1113.43	-5.95	28.75
0.9655	1.3583	0.0005	1108.08	-6.67	20.69	0.9700	1.3614	0.0035	1113.86	-1.87	9.52
1.0000	1.3566	0.0000	1114.18	0.00	0.00	1.0000	1.3566	0.0000	1114.18	0.00	0.00
T = 318.15 K						T = 318.15 K					
0.0000	1.3853	0.0000	1089.97	0.00	0.00	0.0000	1.3934	0.0000	1125.20	0.00	0.00
0.0568	1.3837	0.0003	1083.26	-6.18	21.01	0.0528	1.3918	0.0006	1120.38	-2.47	10.03
0.1097	1.3839	0.0023	1079.52	-9.43	33.79	0.1125	1.3918	0.0031	1115.33	-4.86	20.12
0.1951	1.3826	0.0038	1074.85	-13.31	50.34	0.1835	1.3927	0.0069	1110.51	-6.53	29.09
0.3033	1.3797	0.0045	1070.19	-16.97	66.89	0.3158	1.3940	0.0137	1103.15	-8.00	41.59
0.3855	1.3774	0.0049	1067.37	-19.03	76.54	0.4069	1.3906	0.0140	1098.47	-8.63	48.07
0.4825	1.3746	0.0054	1064.49	-21.02	85.26	0.5128	1.3860	0.0138	1093.19	-9.20	53.18
0.5882	1.3716	0.0059	1062.91	-21.62	88.64	0.6268	1.3782	0.0107	1087.56	-9.76	55.67
0.6833	1.3680	0.0055	1060.59	-23.06	91.30	0.7219	1.3723	0.0088	1083.06	-10.03	54.53
0.8047	1.3627	0.0042	1061.09	-21.44	80.08	0.8029	1.3679	0.0077	1079.52	-9.97	50.62
0.9025	1.3578	0.0026	1065.95	-15.67	55.06	0.8992	1.3615	0.0053	1077.76	-7.44	34.92
0.9655	1.3535	0.0004	1073.75	-7.29	24.12	0.9700	1.3555	0.0023	1078.94	-3.11	12.99
1.0000	1.3520	0.0000	1080.72	0.00	0.00	1.0000	1.3520	0.0000	1080.72	0.00	0.00

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

where $X^{(n)}$ represents adjustable parameters and mentioned in Table-4 with their standard deviations $\sigma(X_m^E)$.

$$\sigma(X_m^E) = \left\{\left[\sum\left(X_m^E - X_{calcd.(eqn.1)}^E\right)^2\right] \Big/ (m-n)\right\}^{1/2} \quad (3)$$

where m and n represents the number of measured data points and number of adjustable parameters in eqn. 1, respectively.

TABLE-4
VALUES OF ADJUSTABLE PARAMETERS OF REDLICH–KISTER EQUATION AND STANDARD DEVIATION (σ_m) FOR VARIOUS PROPERTIES AT DIFFERENT TEMPERATURES

Property	Temp. (K)	A0	A1	A2	A3	σ_m
Ethanol (1) + diisopropyl ether (2)						
Δn	298.15	0.0143	0.0018	0.0069	-0.0110	0.0001
	308.15	0.0140	0.0049	0.0066	-0.0071	0.0001
	318.15	0.0134	0.0046	0.0086	-0.0036	0.0003
Δu (m s^{-1})	298.15	-82.6917	-30.2102	36.4656	-8.1066	0.2004
	308.15	-90.1806	-35.8291	37.0454	-6.3621	0.1083
	318.15	-97.3134	-39.2086	35.5880	-11.0728	0.4067
K_s^E (TPa^{-1})	298.15	130.4210	42.0154	-114.7160	40.2842	0.6021
	308.15	149.5694	56.7376	-142.9091	46.2142	0.4726
	318.15	169.6902	63.8526	-165.5434	70.2398	1.5456
Ethanol (1) + *n*-hexane (2)						
Δn	298.15	0.0024	-0.0011	-0.0004	0.0017	0.0001
	308.15	0.0023	-0.0017	-0.0011	0.0023	0.0001
	318.15	0.0021	-0.0025	-0.0016	0.0036	0.0001
Δu (m s^{-1})	298.15	-158.9556	-62.5422	-21.2661	81.6809	0.4431
	308.15	-171.3140	-61.7736	-42.6460	56.8345	0.4649
	318.15	-187.0463	-66.8036	-45.1634	62.2079	0.4182
K_s^E (TPa^{-1})	298.15	456.0876	113.7438	32.6086	-197.2046	0.9140
	308.15	533.6074	108.6779	79.1801	-192.3949	1.2848
	318.15	639.3855	113.9528	91.5714	-242.9114	1.1079
Ethanol (1) + cyclohexane (2)						
Δn	298.15	0.0219	0.0050	-0.0084	-0.0235	0.0001
	308.15	0.0202	-0.0080	0.0066	-0.0193	0.0002
	318.15	0.0192	-0.0068	0.0033	-0.0215	0.0002
Δu (m s^{-1})	298.15	-56.1808	-12.8834	-46.8110	74.0860	0.7802
	308.15	-66.4607	-16.1385	-48.0636	82.3230	0.8117
	318.15	-78.8046	-17.2119	-46.6095	90.6265	0.4714
K_s^E (TPa^{-1})	298.15	100.9506	46.1668	71.3185	-117.5217	1.1435
	308.15	136.6520	54.6562	79.1405	-152.1680	1.2858
	318.15	185.7458	63.908	86.1832	-193.172	0.9457
Ethanol (1) + *n*-heptane (2)						
Δn	298.15	0.0144	-0.0002	-0.0062	-0.0081	0.0002
	308.15	0.0143	-0.0004	-0.0031	-0.0081	0.0001
	318.15	0.0135	-0.0012	0.0011	-0.0072	0.0001
Δu (m s^{-1})	298.15	-105.5777	-47.5709	-79.4478	-12.9735	0.4819
	308.15	-118.8608	-51.3951	-75.8313	-6.1332	0.3660
	318.15	-132.4496	-53.9962	-76.7537	-8.2758	0.3278
K_s^E (TPa^{-1})	298.15	338.5556	128.0426	167.1657	7.9418	1.0722
	308.15	405.9269	144.1718	175.3598	-11.6293	0.8967
	318.15	487.6231	159.0874	193.5349	-16.2428	0.9646
Ethanol (1) + *n*-octane (2)						
Δn	298.15	0.0231	0.0077	0.0031	-0.0018	0.0001
	308.15	0.0230	0.0047	0.0028	0.0002	0.0004
	318.15	0.0227	0.0052	0.0026	-0.0021	0.0005
Δu (m s^{-1})	298.15	-58.2019	-28.4023	-76.3789	-23.4125	0.4764
	308.15	-70.6445	-31.1751	-78.0102	-21.7415	0.4749
	318.15	-82.6103	-30.9236	-82.9949	-27.7174	0.5205
K_s^E (TPa^{-1})	298.15	229.6628	106.7669	169.2594	47.0123	0.8748
	308.15	280.4142	121.7591	189.6023	43.8643	0.9823
	318.15	340.058	131.2125	220.9297	57.5215	1.2453
Ethanol (1) + *n*-nonane (2)						
Δn	298.15	0.0353	0.0042	0.0010	0.0149	0.0007
	308.15	0.0622	-0.0135	0.0154	0.0642	0.0005
	318.15	0.0551	-0.0341	-0.0177	0.0866	0.0003
Δu (m s^{-1})	298.15	-25.7885	-8.6754	-27.8822	3.9144	0.1397
	308.15	-34.1852	-6.4601	-29.2183	-4.8991	0.3340
	318.15	-35.9522	-9.3769	-45.8898	-18.9989	0.1378
K_s^E (TPa^{-1})	298.15	152.5738	72.3760	82.0102	8.3113	0.4060
	308.15	184.8424	67.9914	82.5335	28.3303	0.7830
	318.15	208.9524	79.1796	129.3039	58.9335	0.4038

The Δu and Δn values are shown graphically in Figs. 1 and 2, respectively.

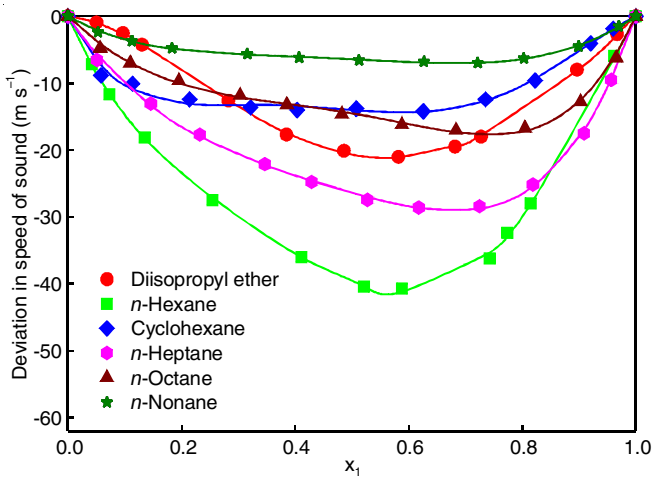


Fig. 1. Deviation in ultrasonic speed of binary mixtures of ethanol (1) + diisopropyl ether or cyclohexane or *n*-alkanes (2) as functions of mole fraction of ethanol at 298.15 K; symbols represent experimental values and lines represent values calculated from Redlich-Kister equation

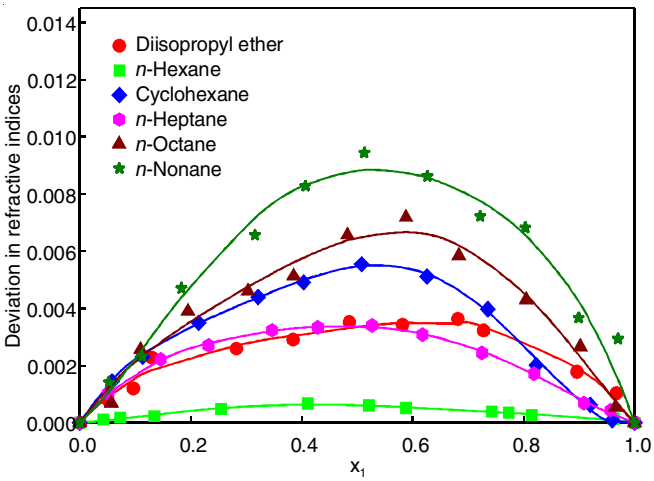


Fig. 2. Deviation in refractive indices of binary mixtures of ethanol (1) + diisopropyl ether or cyclohexane or *n*-alkanes (2) as functions of mole fraction of ethanol at 298.15 K; symbols represent experimental values and lines represent values calculated from Redlich-Kister equation

The u values for all binary liquid solutions were also correlated using different empirical correlations [36] such as Nomoto, impedence dependence relation and Van Dael ideal mixing relation. The percentage standard deviations of the measured data using different correlations with experimental measured values are specified in Table-5. The u for binary liquid mixtures were also computed theoretically using eqn. 4 as per Schaaff's collision factor theory (CFT).

$$u_{mix} = \frac{u_\infty (x_1S_1 + x_2S_2)(x_1b_1 + x_2b_2)}{V_{mix}} \quad (4)$$

where the value of u_∞ is 1600 m s^{-1}, S and b are collision factor and geometric volume of two components, respectively which were calculated using eqns. 5 and 6.

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

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

Free length theory (FLT) [36] was used to compute intermolecular free length (L_f^E) of mixtures by using following equations:

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

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

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

Every term in above mentioned equations has its standard meaning [36] and L_f of binary liquid mixtures was computed using eqn. 10.

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

where K represents Jacobson constant and its value varies from 618 to 642 as temperature varies from 298.15 to 318.15 K. The L_f^E values calculated using eqn. 1 are shown in Fig. 3.

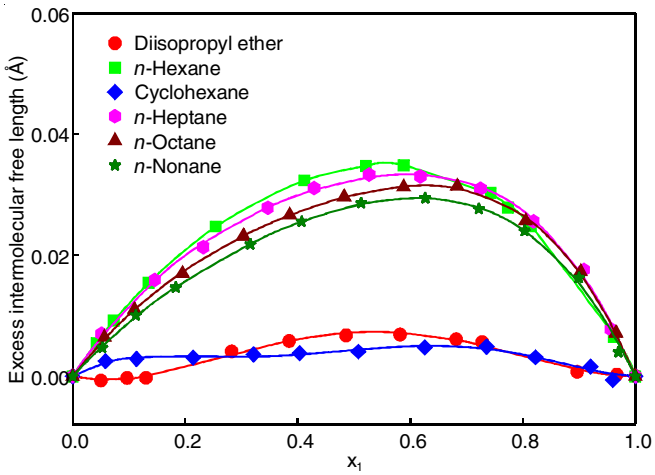


Fig. 3. Excess intermolecular free length of ethanol (1) + diisopropyl ether or cyclohexane or *n*-alkanes (2) as functions of mole fraction of ethanol at 298.15 K; symbols represent experimental values and lines represent values calculated from Redlich-Kister equation

TABLE-5
STANDARD DEVIATION OF CALCULATED VALUES OF ULTRASONIC SPEED USING VARIOUS CORRELATIONS FOR THE BINARY MIXTURE AT 298.15 K

Binary mixture	Nomoto	Van Dael	Impedance	CFT
Ethanol (1) + diisopropyl ether (2)	0.9517	2.9150	1.5893	2.0482
Ethanol (1) + *n*-hexane (2)	1.7957	0.2571	2.9919	2.4889
Ethanol (1) + cyclohexane (2)a	1.9121	3.3930	0.9580	0.5283
Ethanol (1) + *n*-heptane (2)	1.8297	3.5309	2.1664	1.7210
Ethanol (1) + *n*-octane (2)	1.6056	6.8013	1.1664	0.8316
Ethanol (1) + *n*-nonane (2)	1.4536	9.2635	0.3944	2.6436

The K_s^E values were calculated using following equations.

$$K_s^E = K_s - K_s^{id} \quad (11)$$

$$K_s = (u^2\rho)^{-1} \quad (12)$$

K_s^{id} was calculated from general equation [36]. The K_s^E values are presented in Table-3 and Fig. 4.

The value of u depend on extent of intermolecular interaction. The stronger interaction due to some specific strong interactions in between unlike species of binary systems is responsible for more denser medium, which in turn provides better medium for propagation of ultrasonic sound. The values of u is more for more denser medium. The Δu values are negative for all binary mixture and magnitude of negative deviation for mixture of ethanol with *n*-alkane decreases as chain length increases. Negative Δu values point towards the presence of weak relations between unlike molecules.

As K_s^E is depended on interactional strength in between unlike molecules of binary system. More is the available volume more will be the compressibility. At equimolar composition ($x_i = 0.5$), K_s^E follows order: *n*-hexane > *n*-heptane > *n*-octane > *n*-nonane > diisopropyl ether > cyclohexane as shown in Fig. 4. Weak interaction between unlike molecules is responsible for positive deviation in isentropic compressibility. With increase in chain length, available volume decreases resulting in decrease in compressibility.

L_f^E is the distance between two adjacent molecules which is depended on extent of association and type of packing in given liquids. The L_f^E value is positive for all systems as shown in Fig. 3. L_f^E follows the same order as followed by K_s^E. High compressibility in between components means high available volume in mixture, which in turns leads to high intermolecular free length.

The Δn values computed using eqn. 1 are presented in Table-3 and Fig. 2. Arago-Biot (A-B); Gladstone-Dale (G-D); Heller (H); Lorentz-Lorentz (L-L); Eyring-John (E-J); Newton (Nw); Weiner (W) correlations discussed in detail earlier [37] were used for calculating refractive indices of selected systems theoretically and their standard deviation are given in Table-6. All mixing rules are well correlated with experimental data.

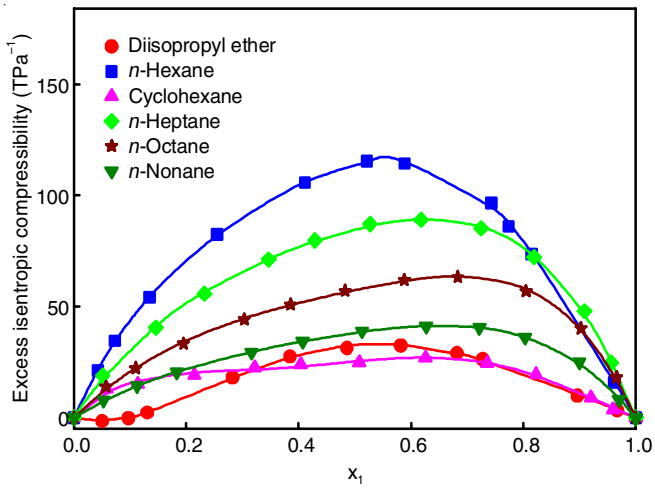


Fig. 4. Excess isentropic compressibility of ethanol (1) + diisopropyl ether or cyclohexane or *n*-alkanes (2) as functions of mole fraction of ethanol at 298.15 K; symbols represent experimental values and lines represent values calculated from Redlich-Kister equation

The n values depend on speed of light, which in turn decrease with increase in density of solution. The Δn is positive for all binary mixtures which indicate the presence of weak intermolecular interactions between unlike molecules which supports our results obtained from ultrasonic studies. Order for Δn value is *n*-nonane > *n*-octane > cyclohexane > diisopropyl ether > *n*-heptane > *n*-hexane as shown in Fig. 2. Magnitude of positive deviation increases with increase in chain length due to decrease in intermolecular interaction with increase in chain length. Temperature also affects refractive index value. With increase in temperature positive Δn value become more positive as molecular interaction decreases with increase in temperature. The calculated n values using various mixing rules are able to predict values close to the experimental data as indicated by their standard deviation specified in Table-6.

Conclusion

The ultrasonic speeds (u) and refractive index (n) for the binary systems of ethanol with diisopropyl ether or cyclohexane

TABLE-6
STANDARD DEVIATION OF CALCULATED VALUES OF REFRACTIVE INDEX USING VARIOUS CORRELATIONS

System	Temp. (K)	AB	GD	LL	Wernier	Heller	Newton	Eyring
Ethanol (1) + diisopropyl ether (2)	298.15	0.0022	0.0022	0.0022	0.0022	0.0022	0.0022	0.0022
	308.15K	0.0023	0.0023	0.0023	0.0023	0.0023	0.0023	0.0023
	318.15	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024
Ethanol (1) + *n*-hexane (2)	298.15	0.0014	0.0014	0.0014	0.0015	0.0014	0.0014	0.0014
	308.15K	0.0013	0.0013	0.0013	0.0014	0.0013	0.0013	0.0013
	318.15	0.0013	0.0013	0.0013	0.0014	0.0013	0.0013	0.0013
Ethanol (1) + cyclohexane (2)	298.15	0.0034	0.0034	0.0032	0.0056	0.0032	0.0037	0.0033
	308.15K	0.0035	0.0035	0.0033	0.0053	0.0034	0.0037	0.0034
	318.15	0.0036	0.0036	0.0034	0.0054	0.0035	0.0039	0.0035
Ethanol (1) + *n*-heptane (2)	298.15	0.0018	0.0018	0.0018	0.0021	0.0018	0.0019	0.0018
	308.15K	0.0016	0.0016	0.0016	0.0018	0.0016	0.0016	0.0016
	318.15	0.0015	0.0015	0.0015	0.0017	0.0015	0.0016	0.0015
Ethanol (1) + *n*-octane (2)	298.15	0.0022	0.0022	0.0021	0.0029	0.0021	0.0022	0.0021
	308.15K	0.0018	0.0018	0.0017	0.0025	0.0017	0.0019	0.0018
	318.15	0.0017	0.0017	0.0016	0.0023	0.0016	0.0017	0.0016
Ethanol (1) + *n*-nonane (2)	298.15	0.0021	0.0021	0.0020	0.0031	0.0020	0.0022	0.0021
	308.15	0.0039	0.0039	0.0039	0.0029	0.0040	0.0038	0.0039
	318.15	0.0030	0.0030	0.0030	0.0028	0.0031	0.0030	0.0030

or alkane (C_6-C_9) were measured from 298.15 to 318.15 K. From u and n data, the Δu, K_s^E, L_f^E and Δn values were calculated. Further, calculated u and n using various empirical relation were compared with experimentally measured values and estimation capability of various correlation were given in terms of their percentage standard deviation. The Δu values are negative for all binary mixture and magnitude of negative deviation for mixture of ethanol with *n*-alkane decreases as chain length increases. Order for K_s^E and L_f^E value is *n*-hexane > *n*-heptane > *n*-otcane > *n*-nonane > diisopropyl ether > cyclohexane, which is positive for all the systems. L_f^E and K_s^E follow the same order because high compressibility in between components means high available volume in mixture which in turns leads to high intermolecular free length. The Δn is positive for all binary mixtures, which indicate the presence of weak intermolecular interactions between unlike molecules. The Δn value become more positive as molecular interaction decreases with increase in temperature. The various mixing rules are able to predict n values well.

ACKNOWLEDGEMENTS

One of the authors, Pinki Kashyap acknowledges the UGC, New Delhi for the award of Senior Research Fellowship.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. J. Canosa, A. Rodríguez and J. Tojo, *Fluid Phase Equilib.*, **156**, 57 (1999); https://doi.org/10.1016/S0378-3812(99)00032-1.
2. S. Gahlyan, M. Rani and S. Maken, *J. Mol. Liq.*, **199**, 42 (2014); https://doi.org/10.1016/j.molliq.2014.08.011.
3. X. Zhou, Y. Chen, C. Wang, J. Guo and C. Wen, *J. Chem. Thermodyn.*, **87**, 13 (2015); https://doi.org/10.1016/j.jct.2015.03.003.
4. E. Catizzone, G. Bonura, M. Migliori, F. Frusteri and G. Giordano, *Molecules*, **23**, 31 (2018); https://doi.org/10.3390/molecules23010031.
5. S. Gahlyan, M. Rani, S. Maken, H. Kwon, K. Tak and I. Moon, *J. Ind. Eng. Chem.*, **23**, 299 (2015); https://doi.org/10.1016/j.jiec.2014.08.032.
6. R. Sharma, R.C. Thakur and B. Saini, *Asian J. Chem.*, **28**, 2331 (2016); https://doi.org/10.14233/ajchem.2016.20010.
7. R. Mehra, *J. Chem. Sci.*, **115**, 147 (2003); https://doi.org/10.1007/BF02716982.
8. J.C. Reis, I.M. Lampreia, A.F. Santos, M.L. Moita and G. Douhéret, *Chemphyschem.*, **11**, 3722 (2010); https://doi.org/10.1002/cphc.201000566.
9. A. Riddick, W. Bunger and T. Sakano Organic Solvents: Physical Properties and Methods of Purification, Wiley, New York, edn 4 (1986).
10. Z. Atik and K. Lourddani, *J. Solution Chem.*, **35**, 1453 (2006); https://doi.org/10.1007/s10953-006-9072-7.
11. H.-W. Chen and C.-H. Tu, *J. Chem. Eng. Data*, **51**, 261 (2006); https://doi.org/10.1021/je050367p.
12. A. Estrada-Baltazar, G.A. Iglesias-Silva and C. Caballero-Cerón, *J. Chem. Eng. Data*, **58**, 3351 (2013); https://doi.org/10.1021/je4004806.
13. S. Gahlyan, S. Verma, M. Rani and S. Maken, *J. Mol. Liq.*, **244**, 233 (2017); https://doi.org/10.1016/j.molliq.2017.09.015.
14. E. Jiménez, H. Casas, L. Segade and C. Franjo, *J. Chem. Eng. Data*, **45**, 862 (2000); https://doi.org/10.1021/je000060k.
15. R. Tôrres, M.I. Ortolan and P. Volpe, *J. Chem. Thermodyn.*, **40**, 442 (2008); https://doi.org/10.1016/j.jct.2007.09.007.
16. J. Ortega, *J. Chem. Eng. Data*, **27**, 312 (1982); https://doi.org/10.1021/je00029a024.
17. E.B. Freyer, J. Hubbard and D.H. Andrews, *J. Am. Chem. Soc.*, **51**, 759 (1929); https://doi.org/10.1021/ja01378a014.
18. I.H. Peng and C.-H. Tu, *J. Chem. Eng. Data*, **47**, 1457 (2002); https://doi.org/10.1021/je020077y.
19. S. Dash, S. Pradhan, B. Dalai, L. Moharana and B. Swain, *Phys. Chem. Liq.*, **50**, 735 (2012); https://doi.org/10.1080/00319104.2012.713554.
20. E. Aicart, G. Tardajos and M. Diaz Pena, *J. Chem. Eng. Data*, **25**, 140 (1980); https://doi.org/10.1021/je60085a007.
21. H. Shekaari, M.T. Zafarani-Moattar and N.J. Behrooz, *J. Chem. Thermodyn.*, **86**, 188 (2015); https://doi.org/10.1016/j.jct.2015.03.004.
22. A. Aucejo, M.C. Burguet, R. Munoz and J.L. Marques, *J. Chem. Eng. Data*, **40**, 141 (1995); https://doi.org/10.1021/je00017a032.
23. E. Alonso, H. Guerrero, D. Montaño, C. Lafuente and H. Artigas, *Thermochim. Acta*, **525**, 71 (2011); https://doi.org/10.1016/j.tca.2011.07.023.
24. T.M. Aminabhavi and V.B. Patil, *J. Chem. Eng. Data*, **42**, 641 (1997); https://doi.org/10.1021/je960382h.
25. M. (Ali) Basu, T. Samanta and D. Das, *J. Chem. Thermodyn.*, **57**, 335 (2013); https://doi.org/10.1016/j.jct.2012.09.015.
26. T.M. Aminabhavi, V.B. Patil, M.I. Aralaguppi and H.T.S. Phayde, *J. Chem. Eng. Data*, **41**, 521 (1996); https://doi.org/10.1021/je950279c.
27. S. Kouris and C. Panayiotou, *J. Chem. Eng. Data*, **34**, 200 (1989); https://doi.org/10.1021/je00056a016.
28. G.P. Dubey and M. Sharma, *J. Mol. Liq.*, **142**, 124 (2008); https://doi.org/10.1016/j.molliq.2008.05.013.
29. G.P. Dubey and M. Sharma, *J. Chem. Thermodyn.*, **40**, 991 (2008); https://doi.org/10.1016/j.jct.2008.02.005.
30. B. Orge, A. Rodríguez, J.M. Canosa, G. Marino, M. Iglesias and J. Tojo, *J. Chem. Eng. Data*, **44**, 1041 (1999); https://doi.org/10.1021/je9900676.
31. F.X. Feitosa, A.C.R. Caetano, T.B. Cidade and H.B. de Sant'Ana, *J. Chem. Eng. Data*, **54**, 2957 (2009); https://doi.org/10.1021/je800925v.
32. A. Gayol, M. Iglesias, J.M. Goenaga, R.G. Concha and J.M. Resa, *J. Mol. Liq.*, **135**, 105 (2007); https://doi.org/10.1016/j.molliq.2006.11.012.
33. T.M. Aminabhavi and G. Bindu, *J. Chem. Eng. Data*, **39**, 529 (1994); https://doi.org/10.1021/je00015a029.
34. D.C. Landaverde-Cortes, G.A. Iglesias-Silva, M. Ramos-Estrada and K.R. Hall, *J. Chem. Eng. Data*, **53**, 288 (2008); https://doi.org/10.1021/je700428f.
35. O. Redlich and A.T. Kister, *Ind. Eng. Chem.*, **40**, 345 (1948); https://doi.org/10.1021/ie50458a036.
36. S. Gahlyan, M. Rani and S. Maken, *J. Mol. Liq.*, **219**, 1107 (2016); https://doi.org/10.1016/j.molliq.2016.04.011.