

Molecular Interactions of Ethyl Butyrate with Alkoxyalkanols

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ABSTRACT

In this work, densities and speeds of sound of binary mixtures of alkoxyalkanols with Ethyl butyrate (EtBu) have been measured at temperatures 298.15 – 323.15K at atmospheric pressure. With the help of experimental results, a discussion is carried out on the molecular interactions and the effect of temperature on interactions through excess properties such as excess molar volumes, V_m^E , excess isentropic compressibility, κ_s^E , excess speeds of sound, u^E , excess molar isentropic compressibility, $K_{s,m}^E$, excess isobaric thermal expansion, α_p^E . The excess properties are adequately fitted with the Redlich-Kister polynomial equation. The excess partial molar volumes, $\bar{V}_{m,1}^E$ and $\bar{V}_{m,2}^E$; excess partial molar isentropic compressibilities, $\bar{K}_{s,m,1}^E$ and $\bar{K}_{s,m,2}^E$; excess partial molar volumes, $\bar{V}_{m,1}^{\circ E}$ and $\bar{V}_{m,2}^{\circ E}$; excess partial molar isentropic compressibilities, $\bar{K}_{s,m,1}^{\circ E}$ and $\bar{K}_{s,m,2}^{\circ E}$ of the components at infinite dilution also been measured. The results have been discussed in terms of intermolecular interactions prevailing in these mixtures. The results indicated that the interactions in these systems follow the order: 2-methoxyethanol > 2-ethoxyethanol.

Keywords: Density, Speed of sound, Ethyl butyrate, Alkoxy alkanols, Excess Properties.

1. INTRODUCTION

In view of increasing pressure to minimize greenhouse gases and the concerns over the increasing scarcity of fossil fuels replacing transport fuels with more sustainable alternatives is a pressing scientific and engineering challenge. One of the alternatives is biofuels. The fatty acid methyl esters derived from vegetable, animal or waste oils provide alternative, renewable fuels for the motor cars [1]. They are ecologically more acceptable than

conventional fuels and also conserve significantly the fossil sources of energy. Experimental study of the key thermodynamic properties of the biofuels is a very difficult task, as they are complex, largely in volatile mixtures of methyl and ethyl esters of fatty acids. Volatile Organic Acids such as Ethyl acetate (EtAc), Ethyl propionate (EtPr), and Ethyl butyrate (EtBu) are produced from low-value biomass wastes. So, they are identified as alternative bioenergy fuels. Generally, these acids have not been used in internal combustion engines because of the resistance of materials. Ethyl acetate, ethyl propionate and ethyl butyrate have been shown to be suitable fuels for a Homogeneous Charge Compression Ignition (HCCI) engine, though they ignite slower than ethanol and these are acidogenesis products. Acidogenesis is commonly used to decrease negative ecological effects of polluting compounds. The smaller ignition delay of EtBu could help reduce the inlet temperature and make the use of these esters as transportation fuels [2]. The successful implementation of these fuels may require to mix them with other fuels or to use various compositions to control the engine.

The literature survey indicates that the systematic volumetric, acoustic, optical and spectroscopic studies of binary mixtures of EtBu with 2-methoxyethanol/2-ethoxyethanol have not been reported earlier. The 2-alkoxyethanols belongs to the group of cellosolves and amphiphilic compounds which have both alcoholic - OH and partially etheric - O - in its structure, and are well-known for their proton-donating and proton-accepting ability, which makes it possible to form inter- and intra-molecular hydrogen bond [3,4] between their molecules in pure state. 2-Alkoxyethanols in pure form and in aqueous solutions are used as a solvent for electrolytes up to some extent as an aprotic solvent [5,6]. For this reason these are often defined as “quasi-aprotic” solvents. 2-Alkoxyethanol are useful in printing and other specialized coatings applications due to fast evaporation and high solubility in water and active solvency make it ideal, for a variety of cleaning applications such as cleaning fluids, paints, coatings and inks. The knowledge of the behaviour of EtBu + alkoxyethanols is important for both industry and fundamental research. Furthermore, accurate thermophysical (volumetric properties, refractive index, expansivities and isothermal compressibilities) data are required for the optimization of the design of many industrial processes [7,8].

In the present study, we report the densities, ρ and speeds of sound, u of the binary mixtures of EtBu with 2-methoxyethanol/2-ethoxyethanol, including those of pure liquids, over whole composition range at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K and atmospheric pressure. From the experimental data, various physicochemical parameters, viz., V_m^E , κ_s^E , u^E and $K_{s,m}^E$ of the mixtures; $\bar{V}_{m,1}$ and $\bar{V}_{m,2}$, $\bar{K}_{s,m,1}$ and $\bar{K}_{s,m,2}$, $\bar{V}_{m,1}^E$ and $\bar{V}_{m,2}^E$ and $\bar{K}_{s,m,1}^E$ and $\bar{K}_{s,m,2}^E$ over whole composition range; $\bar{V}_{m,1}^\circ$ and $\bar{V}_{m,2}^\circ$; $\bar{K}_{s,m,1}^\circ$ and $\bar{K}_{s,m,2}^\circ$; $\bar{V}_{m,1}^{\circ E}$ and $\bar{K}_{s,m,1}^{\circ E}$ and $\bar{K}_{s,m,2}^{\circ E}$ of the components in the mixture at infinite dilution, have been calculated. The results have been discussed in terms of intermolecular interactions in these mixtures.

2. EXPERIMENTAL

2.1. Chemicals and preparation of samples

The Ethyl butyrate(EtBu), 2-methoxyethanol and 2-ethoxyethanol were supplied by Sigma Aldrich, India with mass fraction purity > 0.99 with less than 100 ppm water content. Water content of the chemicals was estimated by Karl Fischer titration using Karl Fisher coulometer (890 KF Titrando, Metrohm, USA) [9] and found to be within limits specified by the manufacturer. These liquids were purified by vacuum distillation over calcium oxide. To reduce water content, the liquids were stored in dark bottles over 0.4 nm molecular sieves; and were partially degassed in a nitrogen atmosphere under low pressure before use. The estimated mass fraction purities of alkoxyethanols determined by gas chromatographic analysis were better than 0.995. The final purities and other specifications of the chemicals

Chemical name (CAS number)	Source	Initial mass fraction purity (supplier purity)	Purification method	Analysis method	Final mass fraction purity	water in mass fraction (supplier)	Water analysis method
2-Methoxy Ethanol (109-86-4)	Sigma Aldrich, India	> 0.99	Vacuum distillation	GC ^a	> 0.996	< 0.006	Karl Fischer
2-Ethoxy Ethanol (110-80-5)	Sigma Aldrich, India	> 0.99	Vacuum distillation	GC ^a	> 0.996	< 0.008	Karl Fischer
Ethyl butyrate (105-54-4)	Sigma Aldrich, India	> 0.99	Vacuum distillation	GC ^a	> 0.997	< 0.001	Karl Fischer

used are given in [Table 1](#).

Table 1. Specification of the samples.

GC- Gas Chromatography

All the mixtures were prepared by mass and stored in Amber colored glass vials (8 mL) with screw caps having PFE septa, and a secure sealed with parafilm to prevent absorption of moisture from the atmosphere. All mixtures were prepared fresh prior to measurements using an electronic balance (CPA-225D, Sartorius, Germany) precisely within ± 0.01 mg. The uncertainty in the mole fraction was estimated to be within $\pm 1 \times 10^{-4}$.

2.2. Equipments and procedures

The densities and ultrasonic speeds of pure liquids and their binary mixtures were measured by using the digital vibrating tube Density and Sound Analyzer (DSA 5000M, Anton Parr, Austria) with reproducibility of $\pm 1 \times 10^{-3} \text{ kg} \cdot \text{m}^{-3}$ for density and $\pm 1 \times 10^{-2} \text{ m} \cdot \text{s}^{-1}$ for speed of sound. The densimeter was calibrated with triply-distilled freshly degassed water ($\rho = 997.075 \text{ kg} \cdot \text{m}^{-3}$) and with dry air at atmospheric pressure as described earlier [10]. The operating frequency for speed of sound measurements was 3 MHz. The standard uncertainties associated with the measurements for temperature, density and speed of sound were estimated to be within $\pm 0.01 \text{ K}$, $\pm 0.5 \text{ kg} \cdot \text{m}^{-3}$ and $\pm 0.5 \text{ m} \cdot \text{s}^{-1}$, respectively.

3. THEORY

The values of the experimental density, ρ , speed of sound, u , V_m^E , κ_s^E , u^E , $K_{s,m}^E$ and α_p^E of the binary mixtures of EtBu with 2-methoxyethanol and 2-ethoxyethanol as a function of mole fraction, x_1 of EtBu at different temperatures are given in [Tables 2 and 3](#).

Table 2. Density (ρ), Speed of sound (u), excess molar volume (V_m^E), excess isentropic compressibility (κ_s^E), excess molar isentropic compressibility ($K_{s,m}^E$), excess speed of sound (u^E) and excess isobaric expansivity (α_p^E) as a function of mole fraction, x_1 of EtBu for Ethyl butyrate + 2-Methoxyethanol at the temperatures $T = (298.15 \text{ to } 323.15) \text{ K}$ at pressure $p = 0.1 \text{ MPa}$.

T/K	ρ kg·m ⁻³	u m·s ⁻¹	V_m^E 10 ⁶ m ³ ·mol ⁻¹	κ_s^E 10 ¹⁰ m ² ·N ⁻¹	$K_{s,m}^E$ 10 ¹⁴ kg·m ⁻³	u^E 10 ⁻² m·s ⁻¹	α_p^E 10 ³ m ³ ·mol ⁻¹
T=298.15 K							
0.0000	960.32	1342.5	0.0000	0.000	0.000	0.000	0.000
0.1126	945.51	1307.0	-0.0251	-0.099	-0.086	0.101	-0.423
0.2144	933.78	1280.4	-0.0457	-0.146	-0.136	0.138	-0.657
0.3222	922.77	1257.0	-0.0627	-0.169	-0.167	0.148	-0.779
0.4394	912.16	1236.2	-0.0768	-0.174	-0.184	0.142	-0.792
0.5390	904.05	1221.5	-0.0823	-0.167	-0.187	0.131	-0.726
0.6245	897.65	1210.6	-0.0796	-0.154	-0.180	0.117	-0.627
0.7327	890.19	1198.4	-0.0680	-0.129	-0.158	0.094	-0.464
0.8248	884.35	1189.0	-0.0517	-0.097	-0.124	0.069	-0.305
0.9000	879.88	1181.6	-0.0324	-0.063	-0.083	0.044	-0.171
1.0000	874.31	1171.8	0.0000	0.000	0.000	0.000	0.000
T=303.15 K							
0.0000	955.71	1325.3	0.0000	0.000	0.000	0.000	0.000
0.1126	940.77	1289.2	-0.0284	-0.109	-0.095	0.106	-0.468
0.2144	928.93	1262.1	-0.0511	-0.160	-0.150	0.144	-0.714
0.3222	917.80	1238.2	-0.0687	-0.185	-0.185	0.154	-0.835
0.4394	907.08	1217.0	-0.0824	-0.190	-0.203	0.148	-0.842
0.5390	898.88	1202.0	-0.0876	-0.183	-0.206	0.136	-0.773
0.6245	892.42	1190.8	-0.0848	-0.169	-0.199	0.121	-0.672
0.7327	884.90	1178.4	-0.0740	-0.142	-0.175	0.098	-0.507
0.8248	879.01	1168.7	-0.0575	-0.107	-0.137	0.071	-0.342
0.9000	874.49	1161.1	-0.0357	-0.068	-0.090	0.045	-0.198
1.0000	868.85	1151.1	0.0000	0.000	0.000	0.000	0.000
T=308.15 K							
0.0000	951.08	1308.1	0.0000	0.000	0.000	0.000	0.000
0.1126	936.02	1271.5	-0.0325	-0.120	-0.105	0.111	-0.515
0.2144	924.07	1243.8	-0.0566	-0.177	-0.167	0.151	-0.773
0.3222	912.83	1219.5	-0.0755	-0.205	-0.206	0.162	-0.892
0.4394	902.00	1197.8	-0.0887	-0.211	-0.226	0.155	-0.894
0.5390	893.72	1182.5	-0.0929	-0.204	-0.230	0.143	-0.823

0.6245	887.20	1171.2	-0.0907	-0.189	-0.223	0.128	-0.722
0.7327	879.62	1158.5	-0.0802	-0.160	-0.198	0.104	-0.554
0.8248	873.67	1148.5	-0.0626	-0.121	-0.157	0.077	-0.384
0.9000	869.10	1140.6	-0.0399	-0.078	-0.104	0.048	-0.228
1.0000	863.40	1130.2	0.0000	0.000	0.000	0.000	0.000
T=313.15 K							
0.0000	946.42	1290.9	0.0000	0.000	0.000	0.000	0.000
0.1126	931.24	1253.7	-0.0369	-0.134	-0.118	0.118	-0.566
0.2144	919.17	1225.6	-0.0619	-0.198	-0.187	0.160	-0.833
0.3222	907.84	1200.8	-0.0821	-0.230	-0.232	0.172	-0.947
0.4394	896.89	1178.8	-0.0941	-0.238	-0.256	0.166	-0.941
0.5390	888.53	1163.2	-0.0980	-0.231	-0.263	0.153	-0.867
0.6245	881.96	1151.7	-0.0961	-0.217	-0.257	0.139	-0.766
0.7327	874.32	1138.7	-0.0860	-0.186	-0.232	0.114	-0.600
0.8248	868.33	1128.5	-0.0690	-0.143	-0.187	0.085	-0.425
0.9000	863.71	1120.3	-0.0440	-0.094	-0.126	0.055	-0.260
1.0000	857.94	1109.0	0.0000	0.000	0.000	0.000	0.000
T=318.15 K							
0.0000	941.72	1273.7	0.0000	0.000	0.000	0.000	0.000
0.1126	926.44	1236.0	-0.0417	-0.148	-0.132	0.125	-0.621
0.2144	914.27	1207.4	-0.0687	-0.220	-0.209	0.169	-0.896
0.3222	902.82	1182.2	-0.0879	-0.256	-0.259	0.181	-1.004
0.4394	891.77	1159.8	-0.0998	-0.266	-0.288	0.176	-0.991
0.5390	883.35	1144.0	-0.1041	-0.260	-0.297	0.163	-0.913
0.6245	876.72	1132.2	-0.1022	-0.246	-0.293	0.148	-0.814
0.7327	869.02	1119.0	-0.0921	-0.213	-0.267	0.123	-0.649
0.8248	862.98	1108.5	-0.0746	-0.166	-0.218	0.093	-0.471
0.9000	858.33	1099.9	-0.0492	-0.110	-0.149	0.060	-0.294
1.0000	852.49	1088.0	0.0000	0.000	0.000	0.000	0.000
T=323.15 K							
0.0000	936.89	1256.5	0.0000	0.000	0.000	0.000	0.000
0.1126	921.54	1218.1	-0.0471	-0.162	-0.145	0.130	-0.679
0.2144	909.28	1189.1	-0.0760	-0.242	-0.232	0.176	-0.961
0.3222	897.73	1163.6	-0.0942	-0.283	-0.289	0.190	-1.058
0.4394	886.59	1140.9	-0.1056	-0.296	-0.323	0.185	-1.033
0.5390	878.10	1124.8	-0.1090	-0.291	-0.334	0.172	-0.955
0.6245	871.43	1112.9	-0.1073	-0.276	-0.330	0.157	-0.859
0.7327	863.69	1099.3	-0.0981	-0.240	-0.303	0.131	-0.700
0.8248	857.62	1088.6	-0.0816	-0.190	-0.250	0.100	-0.522
0.9000	852.93	1080.0	-0.0541	-0.131	-0.177	0.067	-0.334
1.0000	847.03	1067.1	0.0000	0.000	0.000	0.000	0.000

Table 3. Density (ρ), Speed of sound (u), excess molar volume (V_m^E), excess isentropic compressibility (κ_s^E), excess molar isentropic compressibility ($K_{s,m}^E$), excess speed of sound (u^E) and excess isobaric expansivity (α_p^E) as a function of mole fraction, x_1 of EtBufor Ethyl butyrate + 2-Ethoxyethanol at the temperatures $T = (298.15 \text{ to } 323.15) \text{ K}$ at pressure $p = 0.1 \text{ MPa}$

T/K	ρ kg·m ⁻³	u m.s ⁻¹	V_m^E 10 ⁶ m ³ .mol ⁻¹	κ_s^E 10 ¹⁰ m ² . N ⁻¹	$K_{s,m}^E$ 10 ¹⁴ kg·m ⁻³	u^E 10 ⁻² m.s ⁻¹	α_p^E 10 ³ m ³ .mol ⁻¹
T=298.15 K							
0.0000	925.17	1302.6	0.000	0.000	0.0000	0.0000	0.0000
0.1155	917.58	1280.5	-0.122	-0.154	-0.1437	0.1370	-0.4914
0.2144	911.49	1263.5	-0.192	-0.236	-0.2330	0.1988	-0.9569
0.3296	904.72	1245.9	-0.226	-0.286	-0.2993	0.2292	-1.4548
0.4291	899.22	1232.3	-0.224	-0.299	-0.3269	0.2308	-1.7830
0.5291	894.00	1219.9	-0.198	-0.288	-0.3287	0.2162	-1.9712
0.6292	889.15	1208.6	-0.160	-0.258	-0.3066	0.1892	-1.9802
0.7310	884.59	1198.1	-0.114	-0.211	-0.2605	0.1517	-1.7739
0.8133	881.19	1190.0	-0.077	-0.162	-0.2062	0.1148	-1.4304
0.9150	877.30	1180.6	-0.033	-0.089	-0.1166	0.0619	-0.7684
1.0000	874.31	1171.8	0.000	0.000	0.0000	0.0000	0.0000
T=303.15 K							
0.0000	920.61	1285.0	0.000	0.000	0.0000	0.0000	0.0000
0.1155	912.92	1262.4	-0.129	-0.165	-0.1552	0.1399	-0.5446
0.2144	906.67	1245.0	-0.197	-0.253	-0.2507	0.2026	-1.0356
0.3296	899.79	1227.0	-0.233	-0.307	-0.3225	0.2332	-1.5456
0.4291	894.20	1213.1	-0.233	-0.320	-0.3525	0.2346	-1.8728
0.5291	888.91	1200.4	-0.209	-0.309	-0.3552	0.2196	-2.0525
0.6292	883.98	1188.9	-0.170	-0.277	-0.3318	0.1921	-2.0476
0.7310	879.35	1178.0	-0.124	-0.227	-0.2825	0.1539	-1.8240
0.8133	875.88	1169.8	-0.085	-0.175	-0.2238	0.1165	-1.4651
0.9150	871.91	1160.1	-0.037	-0.096	-0.1268	0.0629	-0.7839
1.0000	868.85	1151.1	0.000	0.000	0.0000	0.0000	0.0000
T=308.15 K							
0.0000	916.03	1267.4	0.000	0.000	0.0000	0.0000	0.0000
0.1155	908.22	1244.2	-0.135	-0.177	-0.1674	0.1430	-0.6055
0.2144	901.86	1226.5	-0.205	-0.272	-0.2708	0.2069	-1.1249
0.3296	894.86	1208.2	-0.242	-0.331	-0.3491	0.2383	-1.6474
0.4291	889.18	1194.0	-0.242	-0.346	-0.3828	0.2400	-1.9725
0.5291	883.82	1181.0	-0.219	-0.335	-0.3874	0.2251	-2.1416
0.6292	878.82	1169.2	-0.181	-0.302	-0.3637	0.1975	-2.1205
0.7310	874.12	1158.1	-0.135	-0.249	-0.3116	0.1588	-1.8771
0.8133	870.58	1149.6	-0.093	-0.192	-0.2480	0.1207	-1.5012
0.9150	866.54	1139.6	-0.043	-0.106	-0.1420	0.0656	-0.7995
1.0000	863.40	1130.2	0.000	0.000	0.0000	0.0000	0.0000
T=313.15 K							
0.0000	911.42	1249.7	0.000	0.000	0.0000	0.0000	0.0000
0.1155	903.50	1226.1	-0.141	-0.192	-0.1821	0.1472	-0.6791
0.2144	897.03	1208.1	-0.212	-0.295	-0.2950	0.2131	-1.2304

0.3296	889.91	1189.4	-0.250	-0.360	-0.3819	0.2461	-1.7643
0.4291	884.15	1174.9	-0.251	-0.379	-0.4211	0.2488	-2.0835
0.5291	878.72	1161.8	-0.231	-0.369	-0.4290	0.2345	-2.2371
0.6292	873.66	1149.7	-0.194	-0.335	-0.4061	0.2069	-2.1952
0.7310	868.89	1138.3	-0.147	-0.278	-0.3511	0.1675	-1.9284
0.8133	865.30	1129.5	-0.105	-0.217	-0.2820	0.1282	-1.5341
0.9150	861.17	1119.1	-0.049	-0.122	-0.1637	0.0705	-0.8124
1.0000	857.95	1109.0	0.000	0.000	0.0000	0.0000	0.0000
T=318.15 K							
0.0000	906.76	1232.1	0.000	0.000	0.0000	0.0000	0.0000
0.1155	898.72	1208.0	-0.145	-0.207	-0.1969	0.1507	-0.7324
0.2144	892.15	1189.6	-0.219	-0.318	-0.3199	0.2184	-1.3058
0.3296	884.91	1170.6	-0.257	-0.390	-0.4157	0.2528	-1.8460
0.4291	879.06	1156.0	-0.257	-0.412	-0.4603	0.2563	-2.1593
0.5291	873.56	1142.6	-0.237	-0.404	-0.4716	0.2425	-2.3006
0.6292	868.44	1130.3	-0.202	-0.369	-0.4494	0.2150	-2.2429
0.7310	863.62	1118.6	-0.156	-0.309	-0.3918	0.1751	-1.9594
0.8133	859.99	1109.5	-0.115	-0.242	-0.3174	0.1347	-1.5528
0.9150	855.79	1098.6	-0.056	-0.138	-0.1867	0.0749	-0.8188
1.0000	852.49	1088.0	0.000	0.000	0.0000	0.0000	0.0000
T=323.15 K							
0.0000	902.07	1214.5	0.000	0.000	0.0000	0.0000	0.0000
0.1155	893.92	1189.9	-0.150	-0.222	-0.2128	0.1541	-0.7949
0.2144	887.24	1171.2	-0.225	-0.343	-0.3463	0.2233	-1.3930
0.3296	879.89	1151.9	-0.263	-0.422	-0.4516	0.2589	-1.9387
0.4291	873.96	1137.0	-0.264	-0.448	-0.5022	0.2632	-2.2435
0.5291	868.39	1123.4	-0.245	-0.441	-0.5171	0.2499	-2.3688
0.6292	863.23	1110.9	-0.212	-0.405	-0.4962	0.2225	-2.2921
0.7310	858.35	1099.0	-0.167	-0.341	-0.4357	0.1821	-1.9892
0.8133	854.68	1089.7	-0.125	-0.270	-0.3556	0.1408	-1.5691
0.9150	850.41	1078.4	-0.063	-0.155	-0.2116	0.0790	-0.8232
1.0000	847.03	1067.1	0.000	0.000	0.0000	0.0000	0.0000

3.1. Excess properties

The excess molar volume, V_m^E , deviations in isentropic compressibility, κ_s^E , excess speeds of sound, u^E , excess molar isentropic compressibility, $K_{s,m}^E$ have been calculated using the following equation [11–14]

$$V_m^E = V_m - (x_1 V_{m,1} + x_2 V_{m,2}) \quad (1)$$

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

$$u^E = u - (\rho^{\text{id}} k_s^{\text{id}})^{-1/2} \quad (3)$$

$$K_{s,m}^E = K_{s,m} - K_{s,m}^{\text{id}} \quad (4)$$

where V_m is the molar volume, subscript 1 and 2 refer to EtBu and 2-methoxyethanol/2-ethoxyethanol, respectively; κ_s is the isentropic compressibility, $K_{s,m}$ is the molar isentropic compressibility, the superscript 'id' represents ideal mixture. The values of V_m , κ_s , $K_{s,m}$, ρ^{id} , κ_s^{id} and $K_{s,m}^{\text{id}}$ are calculated using the relations [15,16]

$$V_m = (x_1 M_1 + x_2 M_2) / \rho \quad (5)$$

$$\kappa_s = 1 / u^2 \rho \quad (6)$$

$$K_{s,m} = \kappa_s V \quad (7)$$

$$\rho^{\text{id}} = x_1 \rho_1 + x_2 \rho_2 \quad (8)$$

$$\phi_i = x_i V_{m,i} / \sum_{i=1}^2 x_i V_{m,i} \quad (9)$$

$$\kappa_s^{\text{id}} = \phi_1 \kappa_{s,1} + \phi_2 \kappa_{s,2} + T \left[\frac{\phi_1 V_{m,1} (\alpha_{p,1})^2}{C_{p,1}} + \frac{\phi_2 V_{m,2} (\alpha_{p,2})^2}{C_{p,2}} - \frac{V_m^{\text{id}} (\alpha_p^{\text{id}})^2}{C_p^{\text{id}}} \right] \quad (10)$$

$$K_{s,m}^{\text{id}} = x_1 K_{s,m,1} + x_2 K_{s,m,2} + T \left[\frac{x_1 (V_{m,1} \alpha_{p,1})^2}{C_{p,1}} + \frac{x_2 (V_{m,2} \alpha_{p,2})^2}{C_{p,2}} - \frac{(V_m^{\text{id}} \alpha_p^{\text{id}})^2}{C_p^{\text{id}}} \right] \quad (11)$$

where α_p is the isobaric expansivity, C_p is the molar isobaric heat capacity. The values of V_m^{id} , α_p^{id} and C_p^{id} are calculated using the following relations

$$V_m^{\text{id}} = x_1 V_{m,1} + x_2 V_{m,2} \quad (12)$$

$$\alpha_p^{\text{id}} = \phi_1 \alpha_{p,1} + \phi_2 \alpha_{p,2} \quad (13)$$

$$C_p^{\text{id}} = x_1 C_{p,1} + x_2 C_{p,2} \quad (14)$$

The values of α_p are calculated the temperature dependence of the density data of pure liquids by using the relation, $(-1/\rho)(\partial\rho/\partial T)_p$.

The values of V_m^E , κ_s^E , u^E , $K_{s,m}^E$ and α_p^E have been fitted to a Redlich-Kister type [17] polynomial equation:

$$Y^E = x_1 (1 - x_1) \sum_{i=0}^j A_i (2x_1 - 1)^i \quad (15)$$

where Y^E is V_m^E or κ_s^E or u^E or $K_{s,m}^E$ or α_p^E . The volume fraction, ϕ is used in place of x in equation (15) for fitting of κ_s^E . The values of coefficients, A_i were evaluated by using the method of least squares, with all points weighted equally. The standard deviations, σ of fit have been calculated by using the relation

$$\sigma = \left[\sum (Y_{m, \text{Calc.}}^E - Y_{m, \text{Expt.}}^E)^2 / (n - j) \right]^{1/2} \quad (16)$$

where n is the number of experimental data points and j is the number of A_i coefficients considered ($j+1$ in the present study). The coefficients, A_i and corresponding standard deviations, σ of fit for the mixtures are listed in Table 4. The variation of V_m^E , κ_s^E , u^E , $K_{s,m}^E$

and α_p^E with composition and temperature, along with smoothed values from equation (15) are presented graphically in Figures 1–5, respectively.

Table 4. Coefficients A_i of equation (13) along with standard deviations σ of binary mixture properties.

T/K	A_0	A_1	A_2	σ
EtBu + 2-Methoxyethanol				
$V_m^E \text{ } 10^6 \text{ m}^3 \cdot \text{mol}^{-1}$				
298.15	-0.322	-0.074	0.031	0.0006
303.15	-0.344	-0.076	0.001	0.0005
308.15	-0.368	-0.075	-0.030	0.0003
313.15	-0.389	-0.076	-0.072	0.0007
318.15	-0.412	-0.075	-0.117	0.0005
323.15	-0.432	-0.072	-0.177	0.0008
$\kappa_s^E \text{ } 10^{10} \text{ m}^2 \cdot \text{N}^{-1}$				
298.15	-0.682	0.177	-0.260	0.001
303.15	-0.748	0.196	-0.283	0.001
308.15	-0.832	0.199	-0.329	0.001
313.15	-0.941	0.180	-0.404	0.001
318.15	-1.056	0.162	-0.480	0.001
323.15	-1.176	0.140	-0.562	0.001
$K_{s,m}^E \text{ } 10^{14} \text{ m}^5 \cdot \text{N}^{-1} \cdot \text{mol}^{-1}$				
298.15	-0.746	-0.028	-0.227	0.0003
303.15	-0.824	-0.029	-0.248	0.0002
308.15	-0.921	-0.055	-0.300	0.0003
313.15	-1.047	-0.114	-0.394	0.0008
318.15	-1.181	-0.176	-0.489	0.0012
323.15	-1.321	-0.244	-0.599	0.0033
$u^E \text{ } 10^{-2} \text{ m} \cdot \text{s}^{-1}$				
298.15	0.542	-0.299	0.329	0.002
303.15	0.563	-0.317	0.343	0.003
308.15	0.592	-0.325	0.372	0.003
313.15	0.634	-0.323	0.415	0.003
318.15	0.673	-0.324	0.454	0.003
323.15	0.708	-0.321	0.488	0.002
$\alpha_p^E \text{ } 10^3 \text{ K}^{-1}$				
298.15	-3.047	1.487		0.003
303.15	-3.273	1.535		0.013
308.15	-3.517	1.608		0.022
313.15	-3.776	1.678		0.036
318.15	-4.013	1.768		0.051
323.15	-4.266	1.809		0.068
EtBu + 2-Ethoxyethanol				
$V_m^E \text{ } 10^6 \text{ m}^3 \cdot \text{mol}^{-1}$				
298.15	-0.831	0.529		0.002

303.15	-0.872	0.520		0.002
308.15	-0.918	0.506		0.002
313.15	-0.967	0.483		0.003
318.15	-1.002	0.464		0.005
323.15	-1.041	0.438		0.007
$\kappa_s^E 10^{10} \text{m}^2 \cdot \text{N}^{-1}$				
298.15	-1.169	0.287	-0.219	0.002
303.15	-1.254	0.303	-0.238	0.002
308.15	-1.358	0.300	-0.269	0.002
313.15	-1.493	0.280	-0.313	0.003
318.15	-1.630	0.256	-0.360	0.003
323.15	-1.775	0.230	-0.413	0.004
$K_{s,m}^E 10^{14} \text{m}^5 \cdot \text{N}^{-1} \cdot \text{mol}^{-1}$				
298.15	-1.318	0.026	-0.163	0.003
303.15	-1.423	0.018	-0.183	0.003
308.15	-1.550	-0.015	-0.220	0.004
313.15	-1.712	-0.080	-0.280	0.005
318.15	-1.878	-0.148	-0.348	0.006
323.15	-2.055	-0.224	-0.422	0.007
$u^E 10^{-2} \text{m} \cdot \text{s}^{-1}$				
298.15	0.884	-0.365	0.279	0.001
303.15	0.898	-0.375	0.289	0.001
308.15	0.920	-0.374	0.304	0.001
313.15	0.957	-0.364	0.323	0.001
318.15	0.988	-0.355	0.341	0.001
323.15	1.016	-0.347	0.359	0.002
$\alpha_p^E 10^3 \text{K}^{-1}$				
298.15	-7.617	-3.144		0.024
303.15	-7.969	-2.936		0.023
308.15	-8.346	-2.701		0.021
313.15	-8.761	-2.361		0.019
318.15	-9.043	-2.062		0.017
323.15	-9.341	-1.748		0.015

3.2. Partial molar properties

The partial molar properties (partial molar volume and partial molar compressibility), $\bar{Y}_{m,1}$ of component 1 (EtBu) and $\bar{Y}_{m,2}$ of component 2 (2-methoxyethanol/2-ethoxyethanol) in these mixtures over entire composition range were calculated by using the following relations [18,19]

$$\bar{Y}_{m,1} = Y^E + Y_{m,1}^* + x_2 \left(\partial Y^E / \partial x_1 \right)_{T,p} \quad (17)$$

$$\bar{Y}_{m,2} = Y^E + Y_{m,2}^* - x_1 \left(\partial Y^E / \partial x_1 \right)_{T,p} \quad (18)$$

where Y is V or K_s ; $Y_{m,1}^*$ and $Y_{m,2}^*$ are the molar properties for pure components, EtBu and 2-methoxyethanol/2-ethoxyethanol, respectively. The derivative, $(\partial Y^E / \partial x_1)_{T,p}$ in equations

(17) and (18) was obtained by differentiation of the equation (16), which leads to the following equations for $\bar{Y}_{m,1}$ and $\bar{Y}_{m,2}$

$$\bar{Y}_{m,1} = Y_{m,1}^* + x_2^2 \sum_{i=0}^n A_i (2x_1 - 1)^i - 2x_1 x_2^2 \sum_{i=1}^n A_i (2x_1 - 1)^{i-1} \quad (19)$$

$$\bar{Y}_{m,2} = Y_{m,2}^* - x_1^2 \sum_{i=0}^n A_i (2x_1 - 1)^i + 2x_1^2 x_2 \sum_{i=1}^n A_i (2x_1 - 1)^{i-1} \quad (20)$$

The excess partial molar properties, $\bar{Y}_{m,1}^E$ and $\bar{Y}_{m,2}^E$ over the whole composition range were calculated by using the following relations

$$\bar{Y}_{m,1}^E = \bar{Y}_{m,1} - Y_{m,1}^* \quad (21)$$

$$\bar{Y}_{m,2}^E = \bar{Y}_{m,2} - Y_{m,2}^* \quad (22)$$

4. RESULTS AND DISCUSSION

The V_m^E data for all the binary systems of EtBu with 2-alkoxyethanols were reported in Tables 2 and 3 and are graphically represented in Fig. 1. An examination of V_m^E data in Fig. 1 suggests that excess volume (V_m^E) data for the chosen mixtures are negative over the entire composition range at all temperatures. Negative V_m^E values are stemming from interactions between unlike molecules [20] or due to structural effects arising from changes in free volume and also due to variation in interstitial accommodation of one of the components with respect to the other. In case of 2-methoxyethanol, the maximum values (negative) are found associated with $x_1 = 0.5390$, nearly at equimolar region. For 2-ethoxyethanol, the maximum values (negative) are found associated with $x_1 = 0.3296$, similar behavior can be observed for all mixtures at all the temperatures studied.

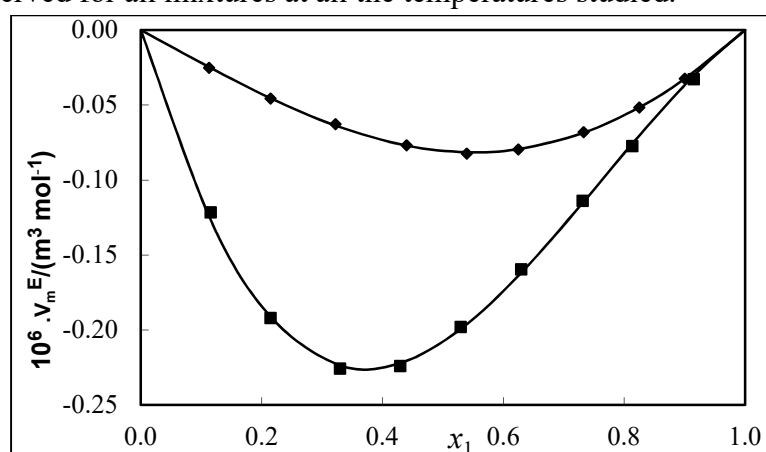


Figure1. Variation of excess molar volume (V_m^E) with mole fraction x_1 of Ethyl butyrate in the binary mixtures of Ethyl butyrate(1) with 2-alkoxyalkanols (2); (\diamond), 2 - ME; (\blacksquare), 2 - EE; at T=298.15 K. The points represent experimental values and solid lines have been drawn from equation (15) using the coefficients given in Table 4.

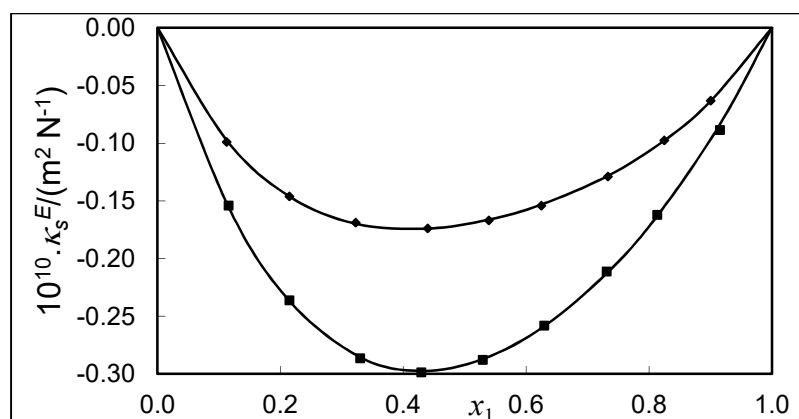


Figure2. Excess isentropic compressibilities (κ_s^E) with mole fraction x_1 of Ethyl butyrate in the binary mixtures of Ethyl butyrate (1) with 2-alkoxyalkanols (2); (♦), 2-ME; (■), 2-EE; (▲) at T=298.15 K. The points represent experimental values and solid lines have been drawn from equation (15) using the coefficients given in Table 4.

The values of excess isentropic compressibilities, κ_s^E , for the two systems over the entire concentration range are seen to be negative (Fig.2) with all of them exhibiting an increase in the values (negative) with the increase in the temperature. The excess isentropic compressibilities, κ_s^E , have been regularly investigated to study the nature and extent of intermolecular interactions [21]. In general, the values of κ_s^E can be considered as arising from two types of interaction between the component molecules:

- (i) a physical interaction, consisting of dispersion forces or weak dipole-dipole interaction making a positive contribution,
- (ii) a chemical or specific interaction, which include charge-transfer forces, forming H-bonds and other complex forming interactions, resulting in a negative contribution to κ_s^E value.

Apart from this the negative values of κ_s^E may be due to a geometric effect, another physical contribution, that allows for the fitting of molecules of different sizes into each other's structure. In case of both EtBu + alkoxyalkanols, the excess values show an increase in the values (more negative) with increase in temperature. Furthermore, κ_s^E values for the EtBu + 2-methoxyethanol system are seen to be the least (negative) among the two systems under investigation. The observed negative κ_s^E values suggest the presence of significant donor–acceptor interactions between EtBu and alkoxyalkanol molecules in these mixtures. The isentropic compressibility value shows an increasing trend with the increase in EtBu concentration and similar trend at any given mole fraction with the rise in temperature. The trends in the values of isentropic compressibility are governed by the corresponding values of speed of sound and density.

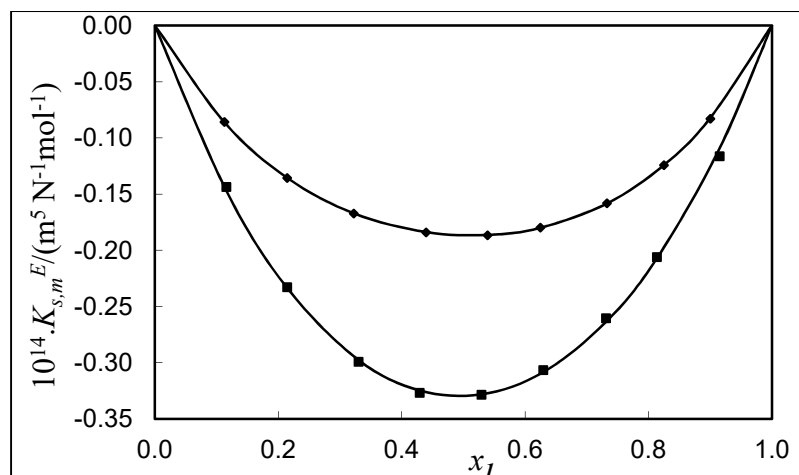


Figure 3. Excess molar isentropic compressibilities ($K_{s,m}^E$) with mole fraction x_1 of Ethylbutyrate in the binary mixtures of Ethyl butyrate (1) with 2-alkoxyalkanols (2); (◆), 2-ME; (■), 2-EE; (▲) at T=298.15 K. The points represent experimental values and solid lines have been drawn from equation (15) using the coefficients given in Table 4.

The behavior of $\kappa_{s,m}^E$, with EtBu concentration and temperature is shown in Fig.3. The $\kappa_{s,m}^E$, were negative for the studied binary systems and decreases with increasing temperature. The possible accommodation of small solvent molecules in free volumes of EtBu and specific interaction within binary mixtures support negative behavior of $\kappa_{s,m}^E$. As concentration of EtBu in binary mixtures increases, specific interaction increases leading to decrease in compressibility. Excess molar volumes V_m^E , excess isentropic compressibilities κ_s^E and excess molar isentropic compressibilities $\kappa_{s,m}^E$ reflects packing, interaction and compressibility effects [22].

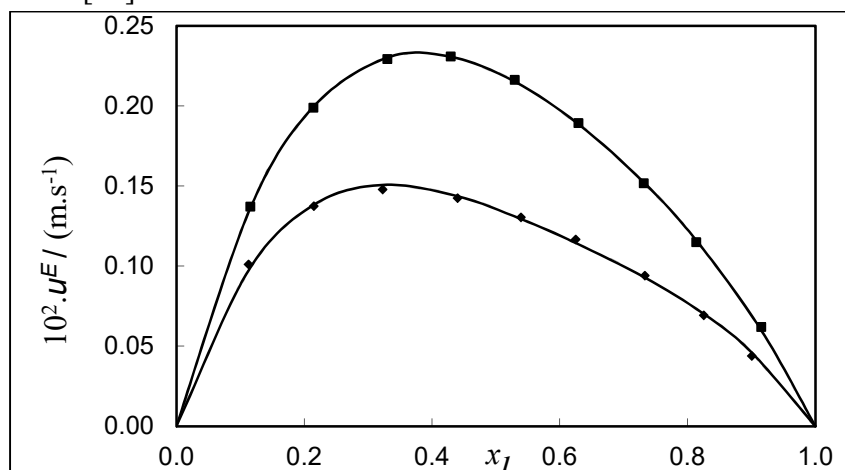


Figure 4. Excess speed of sound (u^E) with mole fraction x_1 of Ethyl butyrate in the binary mixtures of Ethyl butyrate (1) with 2-alkoxyalkanols (2); (◆), 2-ME; (■), 2-EE; (▲) at T=298.15 K. The points represent experimental values and solid lines have been drawn from equation (15) using the coefficients given in Table 4.

The plot of u^E vs. mole fraction (Fig.4) of the first component, shows that the values are positive over the entire range of composition, with the highest deviation being exhibited at $x_1 = 0.4$. It is further seen that the deviations increase with the increase in the temperature with the highest deviations being seen at temperature 323.15 K. Furthermore it is also observed that the speed of sound values show a rising trend with the increase in the mole fraction of the first component and this trend are replicated across the entire temperature range. It has been suggested by Eyring[23] that a lowering in speed of sound occurs during mixing thereby causing an increase in the intermolecular free length [24] and may cause a lowering of the excess isentropic compressibility. All excess speed of sound values shows a similar trend when plotted against the mole fraction of EtBu.

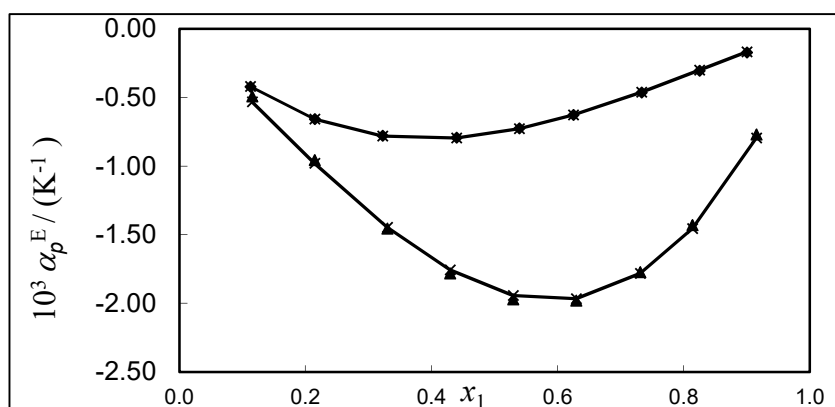


Figure 5. Excess isobaric thermal expansivity (α_p^E) with mole fraction x_1 of Ethyl butyrate in the binary mixtures of Ethyl butyrate (1) with 2-alkoxyalkanols (2); (\diamond), 2-ME; (\blacksquare), 2-EE; (\blacktriangle) at $T=298.15$ K. The points represent experimental values and solid lines have been drawn from equation (15) using the coefficients given in Table 4.

The isobaric thermal expansion coefficients for binary mixtures of EtBu with alkoxyalkanols are listed in Tables 2 and 3 along with the data for pure EtBu. For further understanding the change in the structure of the solution during mixing, isobaric thermal expansions are calculated for every composition. Negative values of α_p^E were observed for all binary systems. The comparison of excess isobaric thermal expansivity is shown for all binary systems in Fig 5. The negative values of α_p^E for the investigated mixtures suggest strong dipole–dipole interactions (between EtBu with alkoxyalkanols) and more closed packing of the constituent of mixtures in mixed state as compared to pure state. Further, temperature coefficient ($\partial V^E / \partial T$) is negative. This suggest that there may be a formation of associated species in {EtBu+alkoxyalkanols} mixture with increase in temperature which results in contraction in volume of the mixture and hence negative α_p^E values [25].

The variations of $\bar{V}_{m,1}^E$, and $\bar{V}_{m,2}^E$ with composition at 298.15 K are presented in Fig. 6. By close look at Fig. 6 the values of $\bar{V}_{m,1}^E$, and $\bar{V}_{m,2}^E$ shows negative for the two binary mixtures over the whole composition range. It means, the molar volumes of each component in the binary mixture are less than their respective molar volume in the pure state, i.e., there is a

decrease in the volume on mixing EtBu with alkoxyalkanols. In general, the negative $\bar{V}_{m,1}^E$, and $\bar{V}_{m,2}^E$ values shows the presence of significant solute–solvent interactions between unlike molecules [26] in the mixture.

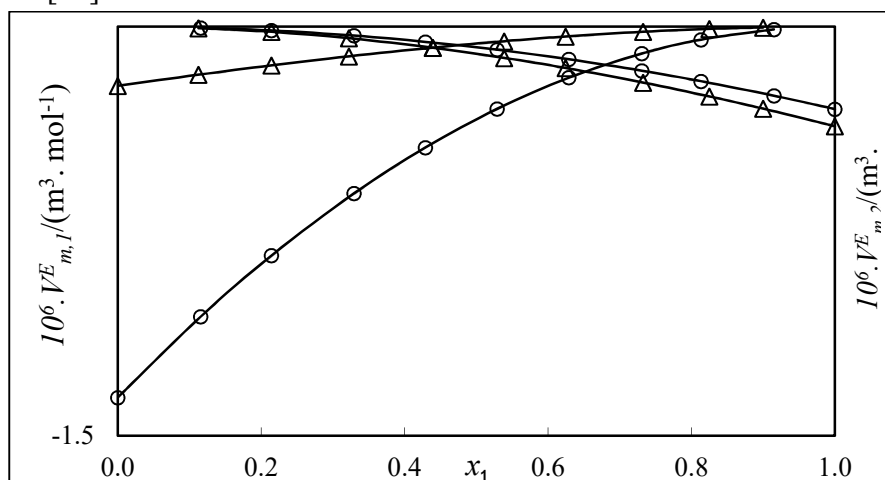


Figure6. Excess partial molar volume ($\bar{V}_{m,1}^E$ and $\bar{V}_{m,2}^E$) with mole fraction x_1 of Ethyl butyrate in the binary mixtures of Ethyl butyrate (1) with 2-alkoxyalkanols (2); (\blacklozenge), 2-ME; (\blacksquare), 2-EE; (\blacktriangle) at T=298.15 K.

CONCLUSIONS

In this paper, densities, and speeds of sound of binary mixtures of EtBu with alkoxy alkanols along with those of pure liquids at temperatures T = (298.15 to 323.15) K at the atmospheric pressure 0.1MPa, have been reported. Values of the excess molar volume V_m^E , excess isentropic compressibility κ_s^E , excess molar isentropic compressibility $\kappa_{s,m}^E$, excess speed of sound, u^E , and excess isobaric thermal expansivity α_p^E were obtained from experimentally measured densities and speeds of sound. Values of V_m^E , κ_s^E , $\kappa_{s,m}^E$, and α_p^E were negative and becomes more negative with increase in temperature. The overall negative behaviour of V_m^E , κ_s^E , $\kappa_{s,m}^E$, α_p^E and positive values of u^E may be attributed to strong ion–ion/dipole-dipole interaction and easy accommodation of alkoxy alkanols in the voids of EtBu molecule.

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