Density, Viscosity, Refractive Index, and Speed of Sound for Binary Mixtures of 1,4-Dioxane with Different Organic Liquids at (298.15, 303.15, and 308.15) K

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The density, viscosity, and refractive index at (298.15, 303.15, and 308.15) K and the speed of sound at 298.15 K in binary mixtures of 1,4-dioxane with 1,2-dichlorobenzene, ethyl acetate, trichloroethylene, 2-chloroethanol, dimethyl acetamide, diethylmalonate, and 1-butanol were measured over the entire mole fraction range of the binary mixtures. Using these data, the excess molar volume, deviations in viscosity, molar refraction, speed of sound, and isentropic compressibility were calculated. The computed quantities were fitted to the Redlich−Kister equation to derive the coefficients and estimate the standard error values.

Introduction

The present paper is part of our ongoing research on the thermodynamic properties of binary mixtures containing dioxane studied earlier in our laboratory.[1−5] Therefore, their binary mixture properties are needed as a useful database in a variety of industrial applications. Therefore, their interactions with different types of liquids such as 1,2-dichlorobenzene, ethyl acetate, trichloroethylene, 2-chloroethanol, dimethyl acetamide, diethylmalonate and 1-butanol are important from a fundamental viewpoint. A wide range of important binary mixtures containing the above liquids have been studied by different authors.[6−18] Moreover, to the best of our knowledge, no physical property data on the mixtures in the present study are available. This prompted us to undertake a study on the measurement of physical properties such as the density, ρ, viscosity, η, and refractive index, n_D, at 298.15 K, 303.15 K, and 308.15 K as well as the speed of sound, u, at 298.15 K. Using these data, the excess molar volume, V^E, deviations in viscosity, $\Delta\eta$, molar refraction, ΔR, speed of sound, Δu, and isentropic compressibility, Δk_S, were calculated. These results were further fitted to the Redlich−Kister polynomial equation[23] to derive the binary coefficients and to estimate the standard errors.

Experimental Section

Materials. HPLC-grade samples of ethyl acetate and dimethylacetamide were procured from E. Merck (India) Mumbai and S. D. Fine Chemicals (Mumbai, India), respectively. 2-Chloroethanol was a pure sample obtained from Sisco Research Laboratory Pvt. Ltd. (Mumbai, India). 1,4-Dioxane and 1,2-dichlorobenzene were pure samples, whereas trichloroethylene and diethylmalonate were L. R.-grade samples procured from S. D. Fine Chemicals (Mumbai, India). 1-Butanol was an A. R.-grade sample procured from Qualigens Fine Chemicals Pvt. Ltd. (Mumbai, India). The purities of all of the liquids as determined by GC (HP 6890) using an FID detector were >99 mol % and are reported in Table 1. Density and refractive index data at 298.15 K for the pure liquids are compared with the literature values in Table 1.

Table 1. Comparison of Experimental Densities (ρ) and Refractive Indices (n_D) of Pure Liquids with Literature Values at 298.15 K

liquid	mol % purity	ρ/kg·m^{-3} exptl	ρ/kg·m^{-3} lit	n_D exptl	n_D lit
1,4-dioxane	>99.0	1028.6	1028.6[25]	1.4203	1.4203[26]
1,2-dichlorobenzene	>99.0	1300.9	1300.3[26]	1.5498	1.5491[26]
ethyl acetate	>99.0	894.2	894.5[26]	1.3713	1.3714[25]
1-butanol	>99.0	805.8	805.8[26]	1.3983	1.3974[27]
trichloroethylene	>98.0	1455.4	1455.5[28]	1.4760	1.4745[28]
2-chloroethanol	>99.0	1200.9	1198.0[29]	1.4411	1.4416[29]
dimethylacetamide	>99.7	946.7	946.3[26]	1.4364	1.4356[26]
diethylmalonate	>99.0	1044.2	1044.6[26]	1.4132	1.4140[26]

Binary mixtures were prepared by mass in specially designed glass-stoppered bottles.[19−21] The mass measurements accurate to ±0.01 mg were made on a digital electronic balance (Mettler, AE 240, Switzerland). A set of nine compositions were prepared for each system, and their physical properties were measured at the respective composition starting from 0.1 to 0.9 mole fraction in steps of 0.1. The possible uncertainty in the mole fraction is less than 10^{-4} in all cases.

Methods. The Densities of liquids and liquid mixtures were measured with an uncertainty of ±0.0005 using a capillary pycnometer of about 10 cm^3 volume and a capillary bore with an internal diameter of 1 mm. Doubly distilled, deionized, and degassed water with a specific conductance of $1 \times 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ was used for calibration as per the experimental details given earlier.[19−21]

In addition to a pycnometer, we have also used density meter DMA 4500 (Anton Paar) for some mixtures. The DMA 4500 is the oscillating U-tube density meter that measures density to the highest accuracy in wide viscosity and temperature ranges. A unique reference oscillator, in addition to the U-tube oscillator, provides extraordinary long-term stability and makes adjustments at tempera-

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Table 2. Experimental Density (ρ/kg·m^{-3}), Viscosity (η/mPa·s), Refractive Index (n_D), and Speed of Sound (u/m·s^{-1}) of the Binary Mixtures at Different Temperatures

x_1	ρ/kg·m^{-3}	η/mPa·s	n_D	u/m·s^{-1}	x_1	ρ/kg·m^{-3}	η/mPa·s	n_D	u/m·s^{-1}	x_1	ρ/kg·m^{-3}	η/mPa·s	n_D	u/m·s^{-1}
1,4-Dioxane (1) + 1,2-Dichlorobenzene (2)														
T = 298.15 K														
0.0000	1300.9	1.324	1.5499	1280	0.3965	1208.5	1.273	1.5048	1305	0.7992	1094.7	1.221	1.4513	1332
0.1025	1278.5	1.311	1.5374	1287	0.4955	1182.5	1.260	1.4924	1312	0.8971	1063.3	1.209	1.4365	1338
0.2030	1255.8	1.298	1.5269	1293	0.5960	1154.9	1.247	1.4799	1319	1.0000	1028.6	1.196	1.4203	1345
0.2983	1232.9	1.285	1.5171	1299	0.6976	1125.6	1.234	1.4652	1325					
T = 303.15 K														
0.0000	1295.4	1.214	1.5476		0.3965	1202.8	1.169	1.5023		0.7992	1089.1	1.124	1.4484	
0.1025	1272.9	1.203	1.5333		0.4955	1176.9	1.158	1.4902		0.8971	1057.7	1.113	1.4337	
0.2030	1250.1	1.191	1.5246		0.5960	1149.3	1.147	1.4768		1.0000	1022.9	1.102	1.4164	
0.2983	1227.3	1.181	1.5148		0.6976	1120.0	1.135	1.4628						
T = 308.15 K														
0.0000	1289.7	1.105	1.5450		0.3965	1197.1	1.066	1.4998		0.7992	1083.4	1.027	1.4455	
0.1025	1267.3	1.095	1.5325		0.4955	1171.2	1.056	1.4879		0.8971	1051.9	1.018	1.4308	
0.2030	1244.5	1.085	1.5224		0.5960	1143.6	1.047	1.4738		1.0000	1017.2	1.008	1.4145	
0.2983	1221.6	1.076	1.5125		0.6976	1114.3	1.037	1.4604						
1,4-Dioxane (1) + Ethyl Acetate (2)														
T = 298.15 K														
0.0000	894.2	0.438	1.3713	1155	0.4002	944.7	0.595	1.3890	1231	0.7990	998.7	0.908	1.4094	1307
0.1004	906.2	0.467	1.3753	1174	0.5071	958.7	0.646	1.3942	1250	0.8991	1013.3	1.029	1.4148	1327
0.2001	918.8	0.505	1.3798	1193	0.6001	971.1	0.707	1.3991	1269	1.0000	1028.6	1.195	1.4203	1345
0.3021	931.9	0.543	1.3843	1212	0.6972	984.4	0.791	1.4041	1288					
T = 303.15 K														
0.0000	887.9	0.414	1.3673		0.4002	938.7	0.560	1.3862		0.7990	993.0	0.843	1.4069	
0.1004	900.0	0.442	1.3716		0.5071	952.8	0.607	1.3915		0.8991	1007.7	0.951	1.4122	
0.2001	912.7	0.478	1.3764		0.6001	965.2	0.671	1.3964		1.0000	1022.9	1.095	1.4164	
0.3021	925.8	0.513	1.3813		0.6972	978.6	0.735	1.4015						
T = 308.15 K														
0.0000	881.6	0.392	1.3631		0.4002	932.7	0.525	1.3834		0.7990	987.2	0.778	1.4044	
0.1004	893.9	0.417	1.3680		0.5071	946.9	0.568	1.3889		0.8991	1001.9	0.873	1.4097	
0.2001	906.6	0.450	1.3730		0.6001	959.5	0.616	1.3938		1.0000	1017.2	1.008	1.4145	
0.3021	919.8	0.482	1.3782		0.6972	972.8	0.684	1.3989						
1,4-Dioxane (1) + 1-Butanol (2)														
T = 298.15 K														
0.0000	805.8	2.564	1.3983	1237	0.3995	888.7	1.327	1.4052	1281	0.8020	981.1	1.162	1.4145	1320
0.1014	826.1	2.150	1.3999	1249	0.4945	909.6	1.241	1.4071	1291	0.9017	1004.9	1.170	1.4172	1332
0.2015	846.7	1.757	1.4016	1260	0.5993	933.5	1.177	1.4095	1301	1.0000	1028.6	1.196	1.4203	1345
0.2982	866.9	1.489	1.4032	1270	0.7023	957.5	1.153	1.4119	1310					
T = 303.15 K														
0.0000	802.0	2.245	1.3955		0.3995	884.0	1.196	1.4028		0.8020	975.8	1.070	1.4118	
0.1014	822.1	1.926	1.3976		0.4945	904.8	1.130	1.4046		0.9017	999.5	1.078	1.4145	
0.2015	842.4	1.602	1.3992		0.5993	928.4	1.081	1.4069		1.0000	1022.9	1.095	1.4164	
0.2982	862.4	1.347	1.4008		0.7023	952.3	1.063	1.4094						
T = 308.15 K														
0.0000	798.0	1.981	1.3937		0.3995	879.5	1.066	1.4003		0.8020	970.4	0.979	1.4093	
0.1014	818.1	1.703	1.3952		0.4945	900.1	1.030	1.4022		0.9017	994.0	0.986	1.4118	
0.2015	838.1	1.447	1.3968		0.5993	923.4	0.985	1.4044		1.0000	1017.2	1.008	1.4145	
0.2982	858.0	1.204	1.3984		0.7023	947.1	0.972	1.4068						
1,4-Dioxane (1) + Trichloroethylene (2)														
T = 298.15 K														
0.0000	1455.4	0.573	1.4760	1027	0.3995	1284.4	0.821	1.4536	1152	0.8020	1114.0	1.072	1.4314	1276
0.1006	1412.7	0.635	1.4704	1059	0.5070	1238.6	0.888	1.4476	1187	0.9003	1072.1	1.133	1.4260	1307
0.2010	1370.1	0.697	1.4648	1091	0.5993	1199.3	0.945	1.4426	1215	1.0000	1028.6	1.196	1.4203	1345
0.2983	1327.9	0.758	1.4592	1122	0.6969	1158.5	1.006	1.4373	1246					
T = 303.15 K														
0.0000	1447.0	0.547	1.4729		0.3995	1277.2	0.768	1.4507		0.8020	1107.7	0.991	1.4285	
0.1006	1404.6	0.602	1.4673		0.5070	1231.5	0.827	1.4446		0.9003	1066.2	1.046	1.4231	
0.2010	1362.2	0.658	1.4618		0.5993	1192.5	0.878	1.4396		1.0000	1022.9	1.102	1.4164	
0.2983	1320.3	0.712	1.4562		0.6969	1152.1	0.933	1.4344						
T = 308.15 K														
0.0000	1438.5	0.521	1.4698		0.3995	1270.0	0.714	1.4477		0.8020	1101.5	0.911	1.4256	
0.1006	1396.4	0.569	1.4643		0.5070	1224.5	0.767	1.4417		0.9003	1060.0	0.959	1.4202	
0.2010	1354.2	0.618	1.4587		0.5993	1185.7	0.812	1.4366		1.0000	1017.2	1.008	1.4145	
0.2983	1312.8	0.665	1.4532		0.6969	1145.6	0.859	1.4315						

Table 2 (Continued)

x_1	ρ/kg·m^{-3}	η/mPa·s	n_D	u/m·s^{-1}	x_1	ρ/kg·m^{-3}	η/mPa·s	n_D	u/m·s^{-1}	x_1	ρ/kg·m^{-3}	η/mPa·s	n_D	u/m·s^{-1}
1,4-Dioxane (1) + 2-Chloroethanol (2)														
T = 298.15 K														
0.0000	1200.9	3.104	1.4411	1358	0.4041	1118.2	1.858	1.4314	1353	0.8009	1054.9	1.304	1.4235	1347
0.1024	1177.7	2.755	1.4389	1357	0.5047	1100.8	1.649	1.4290	1352	0.9003	1041.6	1.233	1.4214	1346
0.2001	1157.0	2.431	1.4363	1356	0.6031	1084.8	1.505	1.4273	1350	1.0000	1028.6	1.196	1.4203	1345
0.3035	1136.7	2.088	1.4337	1354	0.7015	1069.5	1.377	1.4256	1349					
T = 303.15 K														
0.0000	1192.5	2.669	1.4380		0.4041	1112.7	1.682	1.4291		0.8009	1049.5	1.199	1.4211	
0.1024	1171.1	2.457	1.4356		0.5047	1095.4	1.496	1.4269		0.9003	1030.9	1.136	1.4191	
0.2001	1151.1	2.170	1.4337		0.6031	1079.4	1.376	1.4249		1.0000	1022.9	1.095	1.4164	
0.3035	1131.1	1.877	1.4314		0.7015	1064.1	1.265	1.4231						
T = 308.15 K														
0.0000	1187.1	2.347	1.4326		0.4041	1107.2	1.505	1.4268		0.8009	1044.1	1.095	1.4187	
0.1024	1165.1	2.160	1.4324		0.5047	1090.0	1.344	1.4247		0.9003	1030.2	1.038	1.4168	
0.2001	1145.2	1.909	1.4310		0.6031	1073.9	1.248	1.4225		1.0000	1017.2	1.008	1.4145	
0.3035	1125.5	1.666	1.4292		0.7015	1058.7	1.152	1.4205						
1,4-Dioxane (1) + *N*,*N*-Dimethylacetamide (2)														
T = 298.15 K														
0.0000	946.8	1.261	1.4363	1458	0.4222	977.9	1.235	1.4293	1413	0.8157	1010.5	1.209	1.4226	1367
0.1121	954.8	1.255	1.4346	1447	0.5242	985.9	1.228	1.4275	1401	0.9116	1019.2	1.202	1.4210	1356
0.2162	962.4	1.248	1.4328	1436	0.6219	993.9	1.222	1.4259	1390	1.0000	1028.6	1.196	1.4203	1345
0.3203	970.0	1.242	1.4310	1424	0.7198	1002.1	1.215	1.4242	1379					
T = 303.15 K														
0.0000	942.1	1.154	1.4342		0.4222	972.9	1.133	1.4269		0.8157	1005.3	1.105	1.4210	
0.1121	950.1	1.149	1.4324		0.5242	980.9	1.128	1.4252		0.9116	1013.7	1.099	1.4195	
0.2162	957.6	1.144	1.4306		0.6219	988.8	1.123	1.4234		1.0000	1022.9	1.095	1.4164	
0.3203	965.2	1.138	1.4287		0.7198	996.8	1.117	1.4226						
T = 308.15 K														
0.0000	937.5	1.047	1.4320		0.4222	968.0	1.031	1.4246		0.8157	999.8	1.016	1.4174	
0.1121	945.4	1.043	1.4302		0.5242	975.9	1.027	1.4228		0.9116	1008.2	1.012	1.4157	
0.2162	952.9	1.039	1.4284		0.6219	983.6	1.023	1.4210		1.0000	1017.2	1.008	1.4145	
0.3203	960.3	1.035	1.4264		0.7198	991.6	1.019	1.4191						
1,4-Dioxane (1) + Diethylmalonate (2)														
T = 298.15 K														
0.0000	1049.6	1.941	1.4132	1304	0.3959	1043.0	1.619	1.4147	1320	0.7960	1033.7	1.316	1.4181	1337
0.1005	1048.1	1.858	1.4135	1308	0.4959	1041.0	1.542	1.4150	1324	0.8977	1030.9	1.249	1.4192	1341
0.1982	1046.6	1.777	1.4139	1312	0.5951	1038.8	1.465	1.4161	1328	1.0000	1028.6	1.196	1.4203	1345
0.2959	1044.9	1.700	1.4143	1316	0.6944	1036.4	1.391	1.4171	1332					
T = 303.15 K														
0.0000	1044.2	1.755	1.4108		0.3959	1037.7	1.484	1.4127		0.7960	1028.2	1.214	1.4167	
0.1005	1042.8	1.698	1.4113		0.4959	1035.6	1.415	1.4137		0.8977	1025.4	1.153	1.4231	
0.1982	1041.2	1.626	1.4120		0.5951	1033.4	1.346	1.4147		1.0000	1022.9	1.095	1.4164	
0.2959	1039.6	1.556	1.4123		0.6944	1030.9	1.280	1.4157						
T = 308.15 K														
0.0000	1038.8	1.602	1.4085		0.3959	1032.3	1.349	1.4099		0.7960	1022.8	1.111	1.4132	
0.1005	1037.4	1.537	1.4090		0.4959	1030.2	1.287	1.4103		0.8977	1019.9	1.057	1.4141	
0.1982	1035.8	1.476	1.4093		0.5951	1028.0	1.227	1.4113		1.0000	1017.2	1.008	1.4145	
0.2959	1034.2	1.413	1.4095		0.6944	1025.5	1.170	1.4122						

tures other than 293.15 K. By measuring the damping of the U-tube's oscillation caused by the viscosity of the filled-in sample, the DMA 4500 automatically corrects viscosity-related errors. Two integrated (Pt 100) platinum thermometers provide the highest accuracy of temperature control as given in the manufacturer's manual and are traceable to national standards.

To perform the measurement, we select 1 out of a total of 10 individual measuring methods and fill the measuring cell with the sample. An acoustic signal will inform us when the measurement is completed. The results are automatically converted (including temperature compensation wherever necessary) into concentration, specific gravity, or other density-related units using the built-in conversion tables and functions. The density results, including sample number or name, shown on the programmable LC display are transferred to the data memory.

Viscosities were measured using a Cannon Fenske viscometer (size 75, ASTM D 445 supplied by Industrial Research Glassware Ltd., Roselle, NJ). An electronic digital stopwatch with a readability of ±0.01 s was used for the flow time measurements. The uncertainty in the measured viscosity values is ±0.001 mPa·s. Calibrations of the pycnometer and viscometer and the measurements of density and viscosity are the same as described earlier.[20,22]

Refractive indices for the sodium D line were measured using a thermostatically controlled Abbe refractometer (Atago 3T, Japan). A minimum of three independent readings were taken for each composition, and their average value was used in all of the calculations. The uncertainty in the results of refractive indices is ±0.0001 units.

Speed of sound values were measured by using a variable-path single-crystal interferometer (Mittal Enter-

Table 3. Estimated Parameters of Equation 3 for Various Functions of the Binary Mixtures at Different Temperatures

function	T/K	A_1	A_2	A_3	σ
1,4-Dioxane (1) + 1,2-Dichlorobenzene (2)					
$V^E/10^{-6}$ m^3·mol^{-1}	298.15	0.719	−0.226	0.087	0.0106
	303.15	0.659	−0.223	0.201	0.0143
	308.15	0.711	−0.197	0.034	0.0059
$\Delta\eta$/mPa·s	298.15	−0.002	0.000	0.002	0.0001
	303.15	−0.001	0.000	0.001	0.0000
	308.15	−0.001	0.000	0.001	0.0000
$\Delta R \times 10^6$/m^3·mol^{-1}	298.15	−3.713	0.817	−1.037	0.1341
	303.15	−3.639	0.882	−0.759	0.1211
	308.15	−3.687	0.615	−0.739	0.1103
Δu/m·s^{-1}	298.15	0.320	0.730	0.320	0.1780
Δk_S/TPa^{-1}	298.15	−29.66	0.660	−0.370	0.2170
1,4-Dioxane (1) + Ethyl Acetate (2)					
$V^E/10^{-6}$(m^3·mol^{-1})	298.15	−0.429	−0.209	0.480	0.0096
	303.15	−0.461	−0.185	0.376	0.0145
	308.15	−0.542	−0.231	0.324	0.0070
$\Delta\eta$/mPa·s	298.15	−0.693	0.299	−0.048	0.0048
	303.15	−0.591	0.247	−0.039	0.0067
	308.15	−0.540	0.243	−0.049	0.0042
$\Delta R \times 10^6$/m^3·mol^{-1}	298.15	−0.169	0.210	0.062	0.0044
	303.15	0.076	0.346	0.239	0.0065
	308.15	0.158	0.171	0.130	0.0026
Δu/m·s^{-1}	298.15	−1.240	−6.450	9.440	0.6610
Δk_S/TPa^{-1}	298.15	−118.3	16.77	−7.720	0.5770
1,4-Dioxane (1) + 1-Butanol(2)					
$V^E/10^{-6}$ m^3·mol^{-1}	298.15	0.909	0.460	−0.445	0.0042
	303.15	1.192	2.865	−6.278	0.4120
	308.15	1.005	0.470	−0.511	0.0078
$\Delta\eta$/mPa·s	298.15	−2.632	−1.117	0.134	0.0263
	303.15	−2.215	−1.461	−0.871	0.0191
	308.15	−1.953	−0.712	0.452	0.0328
$\Delta R \times 10^6$/m^3·mol^{-1}	298.15	−0.120	−0.160	−0.099	0.0016
	303.15	0.135	−0.783	−1.290	0.0924
	308.15	−0.068	−0.120	−0.079	0.0003
Δu/m·s^{-1}	298.15	−1.180	24.34	−11.77	0.4970
Δk_S/TPa^{-1}	298.15	−79.12	31.68	−0.580	0.4560
1,4-Dioxane (1) + Trichloroethylene (2)					
$V^E/10^{-6}$ m^3·mol^{-1}	298.15	1.700	−0.000	−1.069	0.0130
	303.15	1.707	0.013	−1.119	0.0118
	308.15	1.694	−0.039	−0.981	0.0206
$\Delta\eta$/mPa·s	298.15	−0.004	−0.001	0.001	0.0000
	303.15	−0.004	−0.001	0.001	0.0000
	308.15	−0.004	−0.000	0.002	0.000
$\Delta R \times 10^6$/m^3·mol^{-1}	298.15	0.161	0.003	−0.171	0.0022
	303.15	0.159	−0.001	−0.222	0.0029
	308.15	0.161	0.011	−0.174	0.0028
Δu/m·s^{-1}	298.15	−4.720	25.94	−40.80	1.408
Δk_S/TPa^{-1}	298.15	−87.30	32.37	21.95	1.3078
1,4-Dioxane (1) + 2-Chloroethanol (2)					
$V^E/10^{-6}$ m^3·mol^{-1}	298.15	0.734	0.003	0.172	0.0145
	303.15	0.175	−0.923	1.901	0.1391
	308.15	0.306	−0.116	0.124	0.0054
$\Delta\eta$/mPa·s	298.15	−1.971	−0.133	0.463	0.0239
	303.15	−1.519	0.136	0.719	0.0310
	308.15	−1.299	0.073	0.603	0.0257
$\Delta R \times 10^6$/m^3·mol^{-1}	298.15	−0.785	−0.170	−0.091	0.0222
	303.15	−0.735	0.219	0.670	0.0277
	308.15	−0.512	−0.293	0.324	0.0062
Δu/m·s^{-1}	298.15	0.230	1.480	−2.290	0.1040
Δk_S/TPa^{-1}	298.15	−11.45	0.210	3.210	0.1316
1,4-Dioxane (1) + Dimethylacetamide (2)					
$V^E/10^{-6}$ m^3·mol^{-1}	298.15	0.790	−0.501	0.361	0.0112
	303.15	0.757	−0.444	0.267	0.0120
	308.15	0.727	0.727	0.300	0.0106
$\Delta\eta$/mPa·s	298.15	0.006	−0.000	0.002	0.0000
	303.15	0.040	0.032	0.012	0.0030
	308.15	0.004	−0.000	0.001	0.0000
$\Delta R \times 10^6$/m^3·mol^{-1}	298.15	−0.081	−0.026	−0.017	0.0024
	303.15	0.003	0.375	0.642	0.0165
	308.15	−0.049	−0.008	0.006	0.0007
Δu/m·s^{-1}	298.15	10.24	−0.960	3.500	0.0810
Δk_S/TPa^{-1}	298.15	−3.670	2.120	−0.500	0.0440
1,4-Dioxane (1) + Diethylmalonate (2)					
$V^E/10^{-6}$ m^3·mol^{-1}	298.15	0.492	−0.435	0.387	0.0057
	303.15	0.458	−0.399	0.328	0.0058
	308.15	0.429	−0.360	0.276	0.0054
$\Delta\eta$/mPa·s	298.15	−0.119	0.077	−0.079	0.0016
	303.15	−0.057	0.090	0.061	0.0013
	308.15	−0.080	0.039	−0.008	0.0007
$\Delta R \times 10^6$/m^3·mol^{-1}	298.15	−9.125	2.860	−0.613	0.0136
	303.15	−9.012	3.026	−0.439	0.0113
	308.15	−9.068	2.916	−0.523	0.0107
Δu/m·s^{-1}	298.15	0.880	−0.150	0.110	0.0110
Δk_S/TPa^{-1}	298.15	−17.86	8.190	−0.990	0.0390

prises, New Delhi, model M-84). A crystal-controlled high-frequency generator was used to excite the transducer at a frequency of 1 MHz. The frequency was measured within an accuracy of 1 in 10^4 using a digital frequency meter. The interferometer cell was filled with the test liquid, and water was circulated around the measuring cell from a thermostat maintained at 298.15 ± 0.01 K. To increase the accuracy of the measurement, several such maxima were counted by changing the distance between the transducer and reflector. The total distance, d, moved by the reflector was used to calculate the wavelength, λ by using $d = {}^{n\lambda}/_{2}$. By knowing the frequency, ν, of the crystal (1 MHz), the speed of sound, u, in m·s^{-1} was calculated as $u = \nu\lambda$. The uncertainty in the speed of sound values thus calculated is ±2 in 1000 m·s^{-1}. The isentropic compressibilities were calculated using $k_S = 1/u^2\rho$, where u is in m·s^{-1} and ρ is in kg·m^{-3}).

In all of the above measurements, the temperature was controlled within an uncertainty of ±0.01 K using a constant-temperature bath. A Julabo immersion cooler (FT 200, Julabo Labortechnik Gmbh, Germany) was used to cool the water bath. This unit was installed at the intake of a heating circulator to draw the heat away from the circulating bath liquid. The immersion probe was connected to the instrument with a flexible, insulated tube. To prevent the immersion probe from icing, it was completely immersed in the bath liquid. At least three independent readings of the physical properties were taken for each composition, and the average of these results is given in Table 2. All of the properties were measured at ambient pressure.

Results and Discussion

The results of V^E, $\Delta\eta$, ΔR, Δu, and Δk_S of the mixtures were respectively calculated using the data of ρ, η, n_D, and u given in Table 2, following the equations used earlier:[20,22]

$$V^E = V_m - V_1x_1 - V_2x_2 \tag{1}$$

$$\Delta Y = Y_m - Y_1x_1 - Y_2x_2 \tag{2}$$

Here, V_m is the molar volume of the mixture; V_1 and V_2 are the molar volumes of the pure components; x_i represents the mole fraction of the ith component of the mixture; and ΔY represents $\Delta\eta$, ΔR, Δu, and Δk_S, respectively. Y_m is the respective mixture property, viz., the molar refractivity, R (calculated from the Lorentz−Lorenz relation), viscosity, η, speed of sound, u, and isentropic compressibility, k_S for the binary mixtures; Y_i refers to pure component properties. While calculating the ΔR and Δk_S values, the volume fraction

$$\phi_i = \frac{x_iv_i}{\sum_{i=1}^{2} x_iv_i}$$

was used.[20,22] However, for the calculation of $\Delta\eta$ and Δu, the mole fraction was used.

All quantities (V^E, $\Delta\eta$, ΔR, Δu, and Δk_S) have been fitted to the Redlich−Kister[23] equation by the method of least squares using the Marquardt algorithm[24] to derive the binary coefficients, A_j, and the standard deviation, σ, as follows:

$$V^E(\Delta Y) = x_1x_2\sum_{j=1}^{k} A_j(x_2 - x_1)^{j-1} \tag{3}$$

In each case, the optimum number of coefficients, A_j, was determined from an examination of the variation of the standard deviation, σ, as calculated by

$$\sigma = \left(\frac{\sum(Y^E_{calcd} - Y^E_{obsd})^2}{(n - m)}\right)^{1/2} \tag{4}$$

Here, n represents the number of measurements, and m is the number of coefficients used in fitting the data. The estimated values of A_j and σ for V^E, $\Delta\eta$, ΔR, Δu, and Δk_S are presented in Table 3. In all cases, the best fit was found by using only three adjustable fitting coefficients in eq 3. In all the Figures, the points represent the data calculated from eq 1 or eq 2, whereas smooth curves are drawn from the best-fit data calculated from eq 3.

The results of excess molar volume, V^E, as a function of mole fraction, x_1, of 1,4-dioxane at 298.15 K presented in Figure 1 display widely varying trends. For instance, a large positive V^E is observed for mixtures of 1,4-dioxane (1) + trichloroethylene (2), whereas a negative V^E is observed for the 1,4-dioxane (1) + ethyl acetate (2) mixture. However, for mixtures of 1,4-dioxane + 1,2-dichlorobenzene, + 1-butanol, + 2-chloroethanol, + dimethylacetamide, or + diethylmalonate, V^E plots exhibit positive trends. For mixtures of 1,4-dioxane with ethyl acetate, we expect strong attractive forces between the liquid components leading to

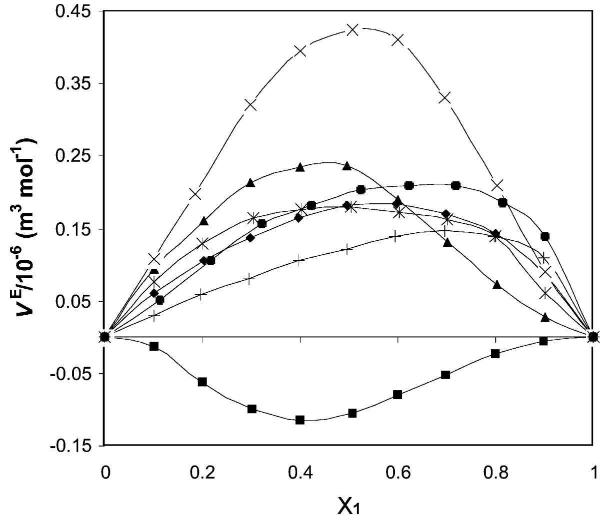

Figure 1. Excess molar volume vs mole fraction for mixtures of 1,4-dioxane with (♦), 1,2-dichlorobenzene; (■), ethyl acetate; (▲), 1-butanol; (×), trichloroethylene; (*), 2-chloroethanol; (●), dimethylacetamide; and (+), diethylmalonate at 298.15 K.

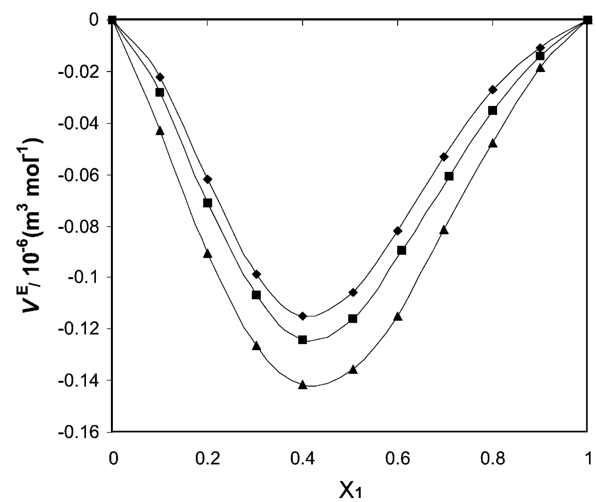

Figure 2. Effect of temperature on V^E for 1,4-dioxane (1) + ethyl acetate (2) mixtures at (♦), 298.15 K; (■), 303.15 K; and (▲), 308.15 K.

negative V^E values over the entire range of mixture composition, whereas with 1,4-dioxane + trichloroethylene the V^E values are positive. This may be due to repulsive forces caused by electronic charges on both component liquids. Such widely differing trends are attributed to varying interactions depending upon the nature of the second mixing component of the mixture. The positive deviation for dioxane + 1,2-dichlorobenzene may be due to dominant steric hindrance, in addition to the repulsive forces due to the electronic charges of both components. The same enhanced effect is observed for the dioxane + trichloroethylene system, also giving a large positive deviation. In the binary mixtures of 1,4-dioxane with butanol or 2-chloroethanol, breaking up the intermolecular hydrogen bonding between butanol molecules with possible new hydrogen bonding with 1,4-dioxane molecules leads to positive V^E values. In mixtures of 1,4-dioxane with *N,N*-dimethylacetamide or diethylmalonate, the V^E values are positive because of the repulsive forces between electronic charges on amide carbonyl oxygen and dioxane oxygen atoms. The effect of temperature on excess molar volume for dioxane + ethyl acetate is typically displayed in Figure

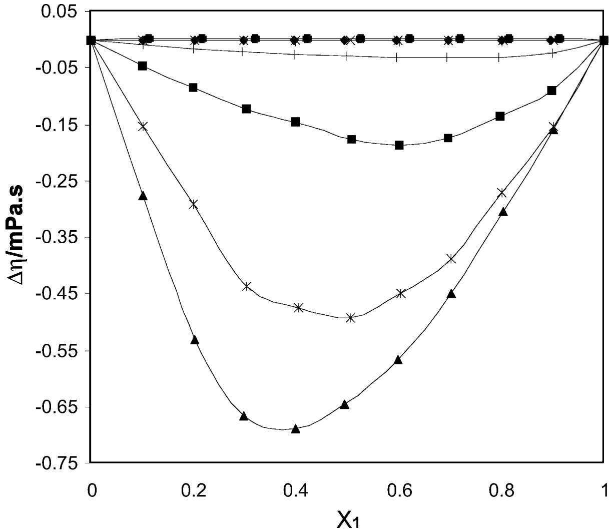

Figure 3. Deviations in viscosity vs mole fraction at 298.15 K for the binary mixtures of 1,4-dioxane. Symbols are the same as in Figure 1.

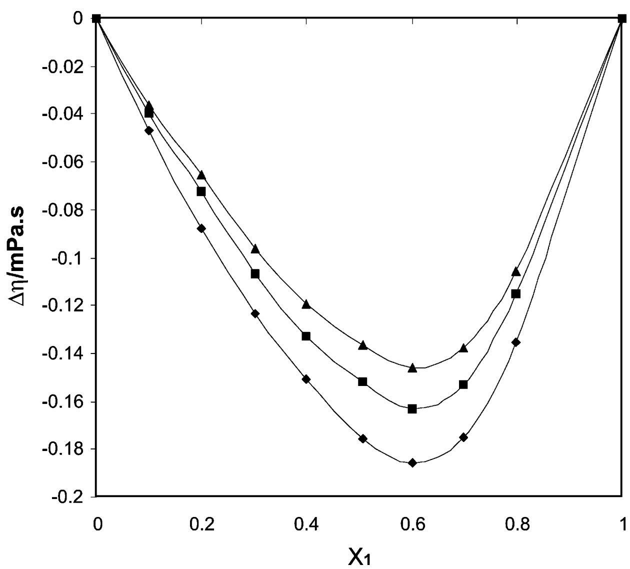

Figure 4. Effect of temperature on $\Delta\eta$ for 1,4-dioxane (1) + ethyl acetate (2) mixture at (♦), 298.15 K; (■), 303.15 K; and (▲), 308.15 K.

2. It is observed that V^E values decrease systematically with increasing temperature, whereas for mixtures with 2-chloroethanol and dimethylacetamide the effect is very small. For other mixtures, no systematic trend is observed with increasing temperature.

The variation of the deviation in viscosity, $\Delta\eta$ versus x_1 at 298.15 K displayed in Figure 3**,** shows a negative deviation in viscosity for mixtures of 1,4-dioxane + diethylmalonate, or + ethyl acetate, or + 2-chloroethanol, or + 1-butanol, or + 1,2-dichlorobenzene, or + trichloroethylene, whereas $\Delta\eta$ values for the mixtures with 1,4-dioxane + dimethylacetamide are positive. The $\Delta\eta$ values increase in the order 1-butanol < 2-chloroethanol < ethyl acetate < diethylmalonate < trichloroethylene < 1,2-dichlorobenzene < *N*,*N*-dimethylacetamide. The effect of temperature on $\Delta\eta$ for dioxane + ethyl acetate is displayed in Figure 4. The $\Delta\eta$ values increase systematically with increasing temperature. The similar temperature effect on $\Delta\eta$ values is also observed for dioxane + 1-butanol, or + 2-chloroethanol mixtures, whereas for other mixtures the effect of temperature is not observed for $\Delta\eta$ values.

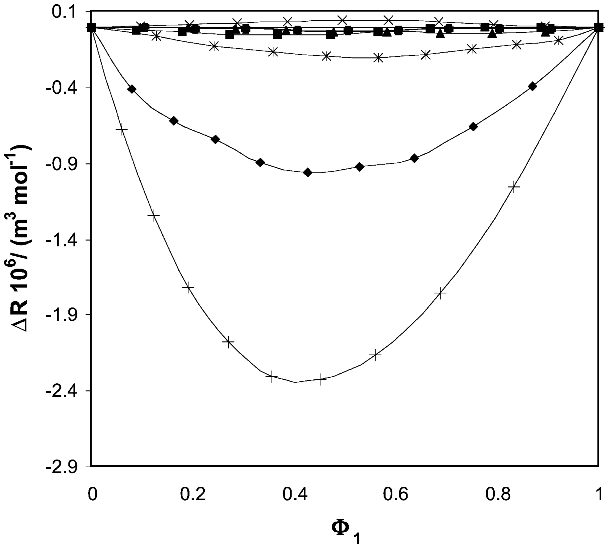

Figure 5. Deviations in molar refraction (ΔR) vs volume fraction for mixtures of 1,4-dioxane at 298.15 K. Symbols are the same as in Figure 1.

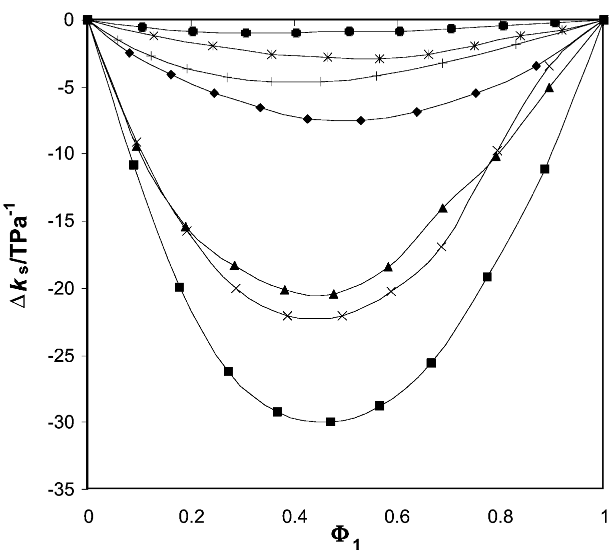

Figure 6. Deviations in isentropic compressibility (Δk_S) vs volume fraction at 298.15 K for mixtures of 1,4-dioxane. Symbols are the same as in Figure 1.

The dependence of deviation in molar refraction, ΔR, with volume fraction, ϕ_1, is shown in Figure 5. Positive deviation is observed for the 1,4-dioxane + trichloroethylene mixture, and negative ΔR is observed for mixtures of 1,4-dioxane + *N*,*N*-dimethylacetamide, or + ethyl acetate, or + 1-butanol. A large negative deviation is observed for the 1,4-dioxane + diethylmalonate mixture, and a very small negative deviation is observed for the 1,4-dioxane + 2-chloroethanol mixture. The ΔR values for 1,4-dioxane + 1,2-dichlorobenzene are between the curves for 1,4-dioxane + 2-chloroethanol or + diethylmalonate systems.

The ΔR values increase with increasing temperature for the dioxane + 2-chloroethanol system, whereas for others no systematic change is observed.

The results of the deviation in isentropic compressibility, Δk_S versus ϕ_1 at 298.15 K, are displayed in Figure 6. For all of the systems, negative Δk_S is observed. The Δk_S values vary in the sequence dimethylacetamide > 2-chloroethanol > diethylmalonate > 1,2-dichlorobenzene > 1-butanol > trichloroethylene > ethyl acetate by mixing with 1,4-dioxane.

Conclusions

In this paper, an attempt is made to measure densities, viscosities, and refractive indices at (298.15, 303.15, and 308.15) K, whereas speed of sound values are measured at 298.15 K over the entire range of mixture composition of 1,4-dioxane with 1,2-dichlorobenzene, ethyl acetate, 1-butanol, trichloroethylene, 2-chloroethanol, *N*,*N*-dimethylacetamide, and diethylmalonate. Out of these measured data, the excess molar volume, deviations in viscosity, molar refraction, speed of sound, and isentropic compressibility have been calculated and correlated by a Redlich−Kister-type polynomial equation to derive the coefficients and standard errors.

Both negative and positive deviations are observed in the case of excess molar volume, V^E, deviations in viscosity, $\Delta\eta$, and molar refraction, ΔR, and only negative Δk_S values are observed for all binary mixtures of 1,4-dioxane with 1,2-dichlorobenzene, ethyl acetate, 1-butanol, trichloroethylene, 2-chloroethanol, dimethylacetamide, and diethylmalonate.

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