Densities, Sound Speed, and IR Studies of (Methanol + 1-Acetoxybutane) and (Methanol + 1,1-Dimethylethyl Ester) at (298.15, 303.15, 308.15, and 313.15) K

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Densities and sound speeds for (methanol + 1-acetoxybutane) and (methanol + 1,1-dimethylethyl ester) have been measured over the entire range of compositions, at temperatures of (298.15, 303.15, 308.15, and 313.15) K and at atmospheric pressure of about 0.1 MPa. From the experimental values of density and ultrasonic velocity, the excess molar volumes V^E and deviations in isentropic compressibility $\Delta\kappa_s$ have been calculated. The V^E and $\Delta\kappa_s$ are negative for both the binaries studied over the whole composition. FT-IR studies of these mixtures are also carried out at $T = 298.15$ K.

Introduction

Studies on thermodynamic, transport properties, and spectroscopic studies of binary liquid mixtures provide information on the nature of interactions in the constituent binaries. The literature provides extensive data on the density and viscosity of liquid mixtures, but a combined study of density, viscosity, ultrasonic velocity, and FT-IR is quite scarce. The effects of molecular size, shape, chain length, and degree of molecular association of normal alkanols and branched alkanols, on the volumetric, viscometric, and acoustic properties of binary mixtures containing acetonitrile, dimethylsulfoxide, ethyl acetate, benzonitrile, chloroform, and methylbenzene, have been reported earlier.[1−11] 1-Acetoxybutane is widely used in the perfume industry, as solvent in the production of different synthetic products, and as a flavoring agent for foods and pharmaceuticals. IR is the powerful tool in studying inter- and intramolecular associations from the position of the O−H band, bandwidth, and the intensity of the first overtone band. We now report density, sound speed data, and FT-IR studies for the binary mixtures of (methanol + 1-acetoxybutane) and (methanol + 1,1-dimethylethyl ester) at temperatures of (298.15, 303.15, 308.15, and 313.15) K.

Experimental Section

1-Acetoxybutane (E.Merck, mass fraction purity of 0.995) and 1,1-dimethylethyl ester (s.d. fine chem, mass fraction purity of 0.99) were used after single distillation. Methanol (s.d. fine chem., mass fraction purity of 0.99) was shaken several times with distilled water to remove ethanol, and it was dried over anhydrous calcium chloride and then fractionally distilled. The purity of the solvents, after purification, was ascertained by comparing their densities and ultrasonic velocities with the corresponding literature values at $T = 298.15$ K (Table 1). Binary mixtures were prepared by mass in airtight stoppered glass bottles. The masses were recorded on an Adairdutt balance to an accuracy of $\pm 1 \cdot 10^{-4}$ g. Care was taken to avoid evaporation and contamination during mixing. The estimated uncertainty in mole fraction was $< 1 \cdot 10^{-4}$.

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Table 1. Comparison of Experimental Density ρ and Sound Speed u Velocity of Pure Liquids with Literature Values at $T = 298.15$ K

	$\rho/(g \cdot cm^{-3})$		$u/(m \cdot s^{-1})$	
pure liquid	exptl	lit.	exptl	lit.
1-acetoxybutane	0.87618	0.87636[a]	1190	1201[b]
1,1-dimethylethyl ester	0.85975	0.86057[c]	1091	1092.7[d]
methanol	0.78638	0.78637[e]	1109	1108[f]

[a] Ref 18. [b] Ref 19. [c] Ref 20. [d] Ref 21. [e] Ref 1. [f] Ref 22.

Densities were determined by using a 15 cm^3 bicapillary pycnometer as described earlier.[12,13] The pycnometer was calibrated using conductivity water with 0.99705 $g \cdot cm^{-3}$ as its density[14] at $T = 298.15$ K. The pycnometer filled with air bubble free experimental liquids was kept in a transparent-walled water bath (maintained constant to ± 0.01 K) for (600 to 900) s to attain thermal equilibrium. The positions of the liquid levels in the two arms were recorded with the help of a traveling microscope, which could read to 0.01 mm. The estimated uncertainty of density measurements of solvent and binary mixtures was 0.00005 $g \cdot cm^{-3}$. At least three to four measurements were made which had an average deviation of ± 0.00005 $g \cdot cm^{-3}$.

The sound speeds u were measured at a frequency of 2 MHz in these solutions through the interferometric method (using Mittal's F-81 model) at temperatures of (298.15, 303.15, 308.15, and 313.15) K (where the temperatures was determined with an uncertainty of ± 0.05 K). The uncertainty in sound speed measurements is ± 0.1 %. The other experimental details are the same as reported earlier.[2−4]

FTIR spectra of the above sample were recorded on a FTIR spectrometer model-SHIMADZU 8400S PC by using KBr pellet in the region (400 to 4000) cm^{-1} with 4.0 cm^{-1} resolution. The transmission values were read in steps of 5 %. The spectrometer possesses out to aligned energy optimization and a dynamically aligned interferometer. It is fitted with a KBr beam splitter and a DLATGS detector. A baseline correction was made for the spectra recorded.

Results and Discussion

Experimental values of densities, ρ, and ultrasonic velocities, u, of mixtures at temperatures (298.15, 303.15, 308.15, and

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Table 2. Density ρ, Sound Speed u, Isentropic Compressibility κ_s, Excess Molar Volume V^E, and Deviation in Isentropic Compressibility $\Delta\kappa_s$ for 1-Acetoxybutane and 1,1-Dimethylethyl Ester (1) + Methanol (2) at Temperatures of (298.15,303.15, 308.15, and 313.15) K

x_1	ϕ_1	$\rho\cdot10^{-3}$ / kg·m^{-3}	$V^E\cdot10^6$ / m^3·mol^{-1}	u / m·s^{-1}	κ_s / TPa^{-1}	$\Delta\kappa_s$ / TPa^{-1}	x_1	ϕ_1	$\rho\cdot10^{-3}$ / kg·m^{-3}	$V^E\cdot10^6$ / m^3·mol^{-1}	u / m·s^{-1}	κ_s / TPa^{-1}	$\Delta\kappa_s$ / TPa^{-1}
1-Acetoxybutane (1) + Methanol (2)							1-Acetoxybutane (1) + Methanol (2)						
298.15 K							298.15 K						
0.0000	0.0000	0.78638	0.000	1109	1034	0	0.5988	0.8292	0.86130	−0.051	1185	827	−18
0.1004	0.2664	0.81058	−0.017	1130	966	−7	0.6994	0.8833	0.86605	−0.042	1189	817	−16
0.2329	0.4970	0.83149	−0.036	1151	908	−13	0.7912	0.9270	0.86971	−0.035	1191	811	−12
0.2996	0.5819	0.83918	−0.044	1160	886	−16	0.8992	0.9667	0.87330	−0.016	1191	807	−6
0.4008	0.6852	0.84846	−0.050	1171	860	−18	1.0000	1.0000	0.87618	0.000	1190	806	0
0.4980	0.7651	0.85546	−0.053	1179	841	−19							
303.15 K													
0.0000	0.0000	0.78165	0.000	1092	1073	0	0.5988	0.8292	0.85634	−0.043	1165	860	−15
0.1004	0.2663	0.80575	−0.015	1112	1004	−6	0.6994	0.8833	0.86110	−0.036	1170	848	−14
0.2329	0.4969	0.82661	−0.033	1132	944	−10	0.7912	0.927	0.86474	−0.026	1172	842	−10
0.2996	0.5818	0.83429	−0.041	1140	922	−12	0.8992	0.9667	0.86838	−0.014	1173	837	−5
0.4008	0.6851	0.84352	−0.044	1151	895	−14	1.0000	1.0000	0.87127	0.000	1173	834	0
0.4980	0.7651	0.85052	−0.046	1159	875	−15							
1-Acetoxybutane (1) + Methanol (2)							1-Acetoxybutane (1) + Methanol (2)						
308.15 K							308.15 K						
0.0000	0.0000	0.77652	0.000	1074	1116	0	0.5988	0.8292	0.85055	−0.037	1141	903	−12
0.1004	0.2664	0.80039	−0.012	1092	1048	−4	0.6994	0.8833	0.85528	−0.030	1145	892	−10
0.2329	0.4969	0.82109	−0.031	1111	987	−9	0.7912	0.9270	0.85891	−0.023	1148	883	−9
0.2996	0.5819	0.82866	−0.035	1118	965	−10	0.8992	0.9667	0.86252	−0.010	1149	878	−4
0.4008	0.6851	0.83784	−0.039	1128	938	−12	1.0000	1.0000	0.86541	0.000	1150	874	0
0.4980	0.7651	0.84477	−0.040	1136	917	−14							
313.15 K													
0.0000	0.0000	0.77215	0.000	1060	1153	0	0.5988	0.8292	0.84566	−0.033	1122	939	−11
0.1004	0.2664	0.79584	−0.011	1076	1085	−2	0.6994	0.8833	0.85036	−0.026	1126	928	−10
0.2329	0.4969	0.81638	−0.027	1093	1025	−6	0.7912	0.9270	0.85398	−0.020	1128	920	−7
0.2996	0.5819	0.82389	−0.030	1100	1003	−8	0.8992	0.9667	0.85758	−0.009	1130	913	−3
0.4008	0.6852	0.83302	−0.035	1109	976	−9	1.0000	1.0000	0.86046	0.000	1131	909	0
0.4980	0.7651	0.83991	−0.036	1116	956	−10							
1,1-Dimethylethyl Ester (1) + Methanol (2)							1,1-Dimethylethyl Ester (1) + Methanol (2)						
298.15 K							298.15 K						
0.0000	0.0000	0.78638	0.000	1109	1034	0	0.5988	0.8319	0.84772	−0.035	1102	971	−20
0.1004	0.2701	0.80642	−0.014	1107	1012	−6	0.6994	0.8853	0.85157	−0.030	1100	970	−18
0.1997	0.4528	0.81995	−0.025	1105	999	−15	0.7985	0.9283	0.85472	−0.021	1097	972	−13
0.2996	0.5865	0.82979	−0.031	1105	987	−19	0.8992	0.9673	0.85743	−0.012	1094	974	−7
0.3916	0.6810	0.83673	−0.036	1104	981	−20	1.0000	1.0000	0.85975	0.000	1091	977	0
0.5003	0.7685	0.84312	−0.037	1103	975	−20							
303.15 K													
0.0000	0.0000	0.78165	0.000	1092	1073	0	0.5988	0.8320	0.84205	−0.030	1086	1007	−18
0.1004	0.2703	0.80136	−0.011	1090	1050	−6	0.6994	0.8853	0.84585	−0.025	1085	1004	−15
0.1997	0.4530	0.81466	−0.019	1089	1035	−13	0.7985	0.9284	0.84896	−0.018	1083	1004	−12
0.2996	0.5867	0.82437	−0.026	1089	1023	−15	0.8992	0.9673	0.85165	−0.011	1080	1007	−7
0.3916	0.6811	0.83121	−0.030	1088	1016	−17	1.0000	1.0000	0.85394	0.000	1078	1008	0
0.5003	0.7687	0.83752	−0.032	1087	1011	−19							
1,1-Dimethylethyl Esters (1) + Methanol (2)							1,1-Dimethylethyl Esters (1) + Methanol (2)						
308.15 K							308.15 K						
0.0000	0.0000	0.77652	0.000	1074	1116	0	0.5988	0.8320	0.83648	−0.024	1057	1070	−14
0.1004	0.2703	0.79606	−0.008	1069	1099	−6	0.6994	0.8853	0.84026	−0.020	1055	1069	−12
0.1997	0.4530	0.80927	−0.016	1065	1089	−10	0.7985	0.9284	0.84336	−0.013	1053	1069	−10
0.2996	0.5867	0.81891	−0.022	1063	1081	−13	0.8992	0.9673	0.84604	−0.007	1051	1070	−5
0.3916	0.6811	0.82570	−0.025	1061	1076	−13	1.0000	1.0000	0.84834	0.000	1049	1071	0
0.5003	0.7687	0.83198	−0.027	1059	1072	−15							
313.15 K													
0.0000	0.0000	0.77215	0.000	1060	1153	0	0.5988	0.8322	0.83100	−0.020	1046	1100	−11
0.1004	0.2705	0.79134	−0.008	1055	1135	−5	0.6994	0.8854	0.83472	−0.017	1045	1097	−9
0.1997	0.4532	0.80429	−0.013	1052	1123	−8	0.7985	0.9284	0.83777	−0.011	1043	1097	−7
0.2996	0.5870	0.81375	−0.018	1051	1113	−10	0.8992	0.9674	0.84040	−0.005	1041	1098	−4
0.3916	0.6814	0.82041	−0.020	1049	1108	−11	1.0000	1.0000	0.84267	0.000	1040	1097	0
0.5003	0.7688	0.82657	−0.022	1048	1102	−12							

313.15) K are listed as a function of mole fraction in Table 2. The density values have been used to calculate excess molar volumes V^E using the following equation

$$V^E/\mathrm{cm}^3\cdot\mathrm{mol}^{-1} = (x_1M_1 + x_2M_2)/\rho_{mix} - (x_1M_1/\rho_1) - (x_2M_2/\rho_2) \quad (1)$$

where ρ_{mix} is the density of the mixture and x_1, M_1, ρ_1, and x_2, M_2, ρ_2 are the mole fraction, the molecular weight, and the density of pure components 1 and 2, respectively.

The deviation from isentropic compressibility ($\Delta\kappa_s$) was obtained using the relation

$$\Delta\kappa_s/\mathrm{TPa}^{-1} = \kappa_{s,mix} - \phi_1\kappa_{s1} - \phi_2\kappa_{s2} \quad (2)$$

where $\kappa_{s,mix}$ is the experimental isentropic compressibility of the mixture; ϕ_1, ϕ_2 and κ_{s1}, κ_{s2} are the volume fraction and isentropic compressibility of pure components.

The variation of V^E with the mole fraction x_1 of 1-acetoxybutane and 1,1-dimethylethyl ester with methanol at all tem-

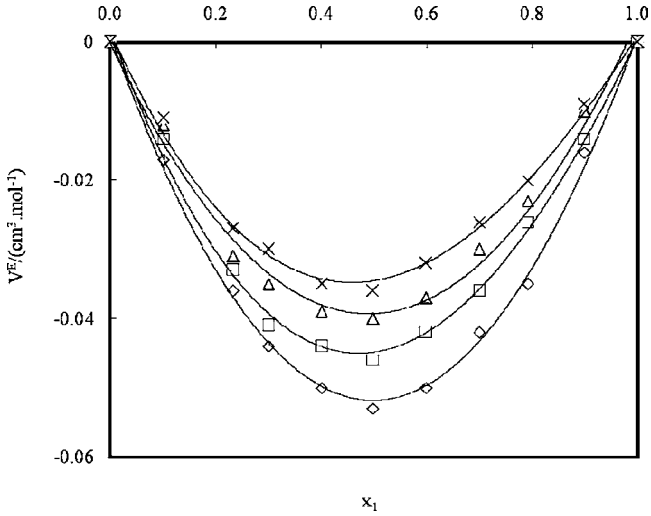

Figure 1. Excess molar volumes V^E for x_1 1-acetoxybutane + (1 − x_1) methanol: ◇, 298.15 K; □, 303.15 K; Δ, 308.15 K; ×, 313.15 K.

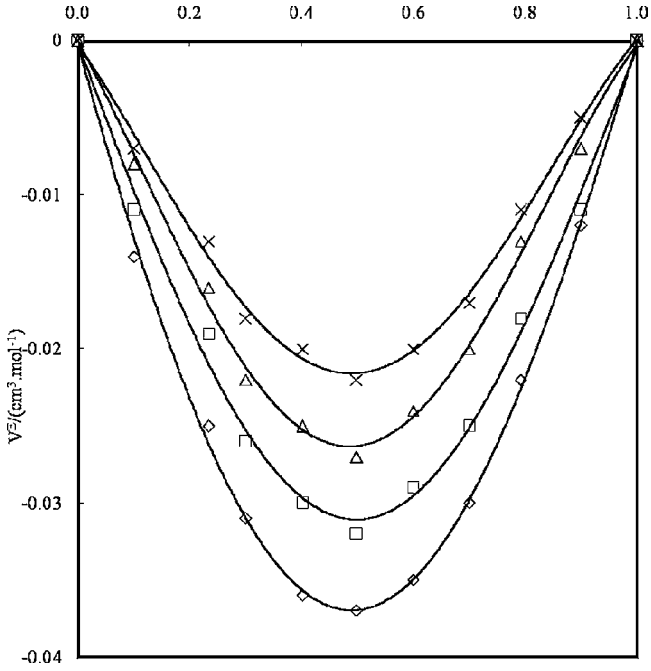

Figure 2. Excess molar volumes V^E for x_1 1,1-dimethylethyl ester + (1 − x_1) methanol: ◇ 298.15 K; □, 303.15 K; Δ, 308.15 K; ×, 313.15 K.

peratures is represented in Figures 1 and 2. V^E values are negative for both the binary mixtures at all four temperatures reported here. Our value of V^E at $T = 298.15$ K for 1-acetoxybutane with methanol at $x_1 \approx 0.5$ mol fraction (−0.053 $cm^3 \cdot mol^{-1}$) is in good agreement with that reported by Iloukhani and Nojini[15](−0.044 $cm^3 \cdot mol^{-1}$). The V^E for 1,1-dimethylethyl ester is slightly less as compared with 1-acetoxybutane.

The variation of $\Delta\kappa_s$ with volume fraction of 1-acetoxybutane and 1,1-dimethylethyl ester ϕ_1, is represented in Figures 3 and 4. Kiyohara and Benson[16] have suggested that $\Delta\kappa_s$ is the result of several opposing effects. A strong molecular interaction through hydrogen bond[17] interaction lead to a more compact structure making $\Delta\kappa_s$ being negative, and breakup of the methanol structure tends to make $\Delta\kappa_s$ positive. The magnitude of $\Delta\kappa_s$ for mixtures of methanol with 1-acetoxybutane and 1,1-dimethylethyl ester increases with temperature. It is to be noted that our $\Delta\kappa_s$ values do not go through an inversion in sign as reported by Iloukhani and Nojini.[16]

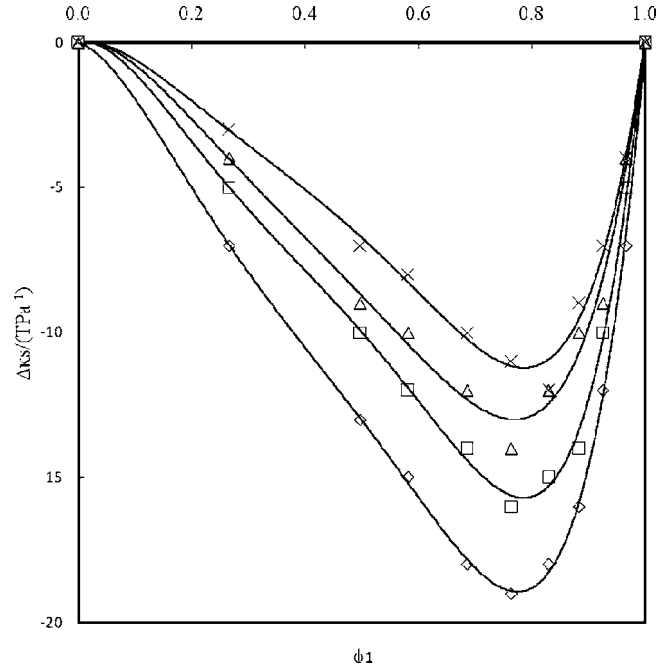

Figure 3. Deviations in isentropic compressibility ($\Delta\kappa_s$) for ϕ_1 1-acetoxybutane + (1 − ϕ_1) methanol: ◇, 298.15 K; □, 303.15 K; Δ, 308.15 K; ×, 313.15 K.

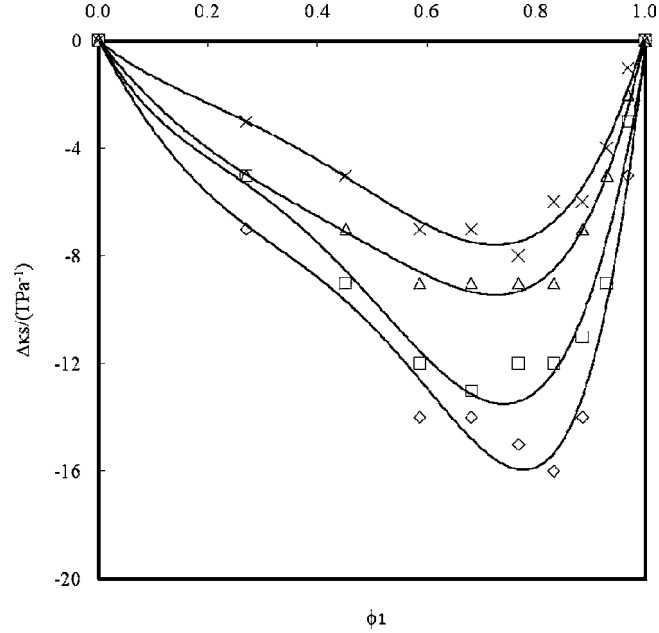

Figure 4. Deviations in isentropic compressibility ($\Delta\kappa_s$) for ϕ_1 1,1-dimethylethyl ester + (1 − ϕ_1) methanol: ◇, 298.15 K; □, 303.15 K; Δ, 308.15 K; ×, 313.15 K.

The spectrum of primary alcohols shows two absorption bands. The sharp band around 3650 cm^{-1} is due to free −OH, while the weak band observed at 3350 cm^{-1} is due to hydrogen bonded −OH.

Hydrogen bonding alters the force constant of groups involved in hydrogen bonding, hence both stretching and bending vibrations of the group change. Intermolecular hydrogen bonding causes association of two or more molecules of the same or different compounds, i.e., dimerization/polymerization of molecules. The bands that result from intermolecular hydrogen bonding appear at a lower value.

It can be seen from Table 3 that systems studied in this investigation confirm the presence of intermolecular interactions.

Table 3. Neat FT-IR Frequencies of ν-OH (cm^{-1}) in the 1-Acetoxybutane and 1,1-Dimethylethyl Ester (1) + Methanol (2) System

x_1	1-acetoxybutane + methanol	1,1-dimethylethyl ester + methanol
0.1	3427.3	3358.2
0.2	3456.2	3377.5
0.3	3460.1	−
0.4	3460.1	3439.2
0.5	3462.0	3443.1
0.6	3348.2	3454.6
0.7	3373.3	−
0.8	3429.2	3358.2
0.9	3462.0	−

Change in the ν-OH for methanol + acetate mixtures is observed after $x_1 \cong 0.5$, and the magnitude is more for the 1,1-dimethylethyl ester + methanol system compared to the 1-acetoxybutane + methanol system.

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