

Mixing Properties for Binary Liquid Mixtures of Methyl *tert*-Butyl Ether with Propylamine and Dipropylamine at Temperatures from (288.15 to 308.15) K

Amalendu Pal,^{*,†} Harsh Kumar,^{*,‡} Sanjay Sharma,[§] Ritu Maan,^{||} and Harish Kumar Sharma^{||}

Department of Chemistry, Kurukshetra University, Kurukshetra 136119, Haryana, India, Department of Chemistry, Dr. B. R. Ambedkar National Institute of Technology, Jalandhar 144011, Punjab, India, National Institute of Technology, Kurukshetra 136119, Haryana, India, and Department of Chemistry, M. M. University, Mullana, Ambala, Haryana, India

Densities and sound velocity have been measured over the whole composition range for the binary liquid mixtures of methyl *tert*-butyl ether with propylamine and dipropylamine using an Anton Paar DSA 5000 density and sound analyzer at temperatures of (288.15, 293.15, 298.15, 303.15, and 308.15) K and atmospheric pressure. From these densities and speeds of sound, excess molar volumes and excess isentropic compressibility were calculated. All of the properties were fitted to Redlich–Kister equation. The variation of these properties with composition and temperature of the mixture is discussed in terms of molecular interactions.

Introduction

The increasing use of alkyl amines in many industrial processes has greatly stimulated the need for extensive information on the thermodynamic properties of alkyl amines and their mixtures. On the other hand, branched ethers are used as oxygenating agents and as an additive in gasoline technology, mainly, methyl *tert*-butyl ether (tertiary aliphatic ether), an effective octane booster,^{1,2} a volume extender,³ and an excellent blowing agent for production of polyurethane foams,⁴ the properties of which can be improved with the addition of suitable amines as solvent. A lot of processes and syntheses have been carried out involving methyl *tert*-butyl ether and amines together. In earlier studies, we have reported the excess molar volumes, viscosities, and speeds of sound for binary liquid mixtures of alkoxyalkanols and polyethers with amines.^{5–8} In a continuing effort, in this work, we report new experimental results on the density, ρ , and speeds of sound, u , for binary liquid mixtures of methyl *tert*-butyl ether (1) + propylamine (2) and + dipropylamine (2) at (288.15, 293.15, 298.15, 303.15, and 308.15) K over the whole composition range and atmospheric pressure. Investigations into literature have shown that excess properties of binary mixtures of amines with straight chain, branched chain, or cyclic ethers^{9–11} and with alcohols^{12,13} have previously been studied by various authors. The present study will therefore shed more light on the dissociation of hydrogen bond structure and formation of new N–H–O bonds and mixed species and their influence on the excess properties of the mixtures.

Experimental Section

Materials. Methyl *tert*-butyl ether (Fluka GC > 99 %), propylamine (Merck-Schuchardt, Germany, zur-Synthese GC > 99 %), and dipropylamine (Merck-Schuchardt, Germany, zur-

Synthese GC > 99 %) were used directly without further purification. All of the liquids were kept tightly sealed in dark bottles to minimize the absorption of atmospheric moisture. Prior to actual measurements all liquids were stored over 0.4 nm molecular sieves to reduce water content and were partially degassed under vacuum. Further, the purities of liquids were checked by comparing densities and speeds of sound of pure solvents at desired temperatures, with their corresponding literature values,^{13–30} as reported in Table 1.

Apparatus and Procedure. Densities and speeds of sound of pure liquids and mixtures were simultaneously and automatically measured using an Anton Paar DSA 5000 density and sound analyzer provided with two Pt 100 platinum thermometers. Both the densities and the speeds of sound are extremely sensitive to temperature, so the apparatus was controlled to ± 0.001 K by a built-in solid state thermostat. Before each series of measurements, the apparatus was calibrated with double-distilled and degassed water, hexane, heptane, octane, cyclohexane, and benzene. The reproducibility of density and speeds of sound measurements was $\pm 1 \cdot 10^{-6} \text{ g} \cdot \text{cm}^{-3}$ and $\pm 1 \cdot 10^{-2} \text{ m} \cdot \text{s}^{-1}$, respectively, and the uncertainties of these were assumed to be less than $5 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ and $5 \cdot 10^{-1} \text{ m} \cdot \text{s}^{-1}$.

The mixtures were prepared by mass and were kept in special airtight stoppered glass bottles to avoid evaporation. The weighings were done with an electronic balance with a precision of ± 0.01 mg. The mole fraction of each mixture was obtained with an uncertainty of $1 \cdot 10^{-4}$ from the measured masses of the components. All molar quantities were based on the IUPAC relative atomic mass table.³¹

Results and Discussion

Experimental data on density ρ , for each of three pure liquids, methyl *tert*-butyl ether, propylamine, and dipropylamine, in the temperature range from (288.15 to 305.15) K were reported in Table 1. For dipropylamine, our experimental values of density at different temperatures are in agreement with those of literature values, but the density values for propylamine and methyl *tert*-butyl ether reported in literature are respectively lower than those of ours that may be due to the methods of measurements and

* Corresponding author. E-mail: palchem@sify.com and h.786.man@gmail.com.

[†] Kurukshetra University.

[‡] Dr. B. R. Ambedkar National Institute of Technology, Jalandhar.

[§] National Institute of Technology, Kurukshetra.

^{||} M. M. University.

Table 1. Experimental Densities (ρ), Speeds of Sound (u), and Thermal Expansion Coefficients (α) of the Pure Component Liquids Together with Literature Values

liquid	T	$\rho/(\text{kg}\cdot\text{m}^{-3})$		$u/(\text{m}\cdot\text{s}^{-1})$		$\alpha\cdot 10^3$	C_p
	K	exptl	lit.	exptl	lit.	K^{-1}	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
propylamine	288.15	725.080		1266.07		1.459 ^a	158 ^b
	293.15	719.859		1242.05		1.471 ^a	159 ^b
	298.15	714.586	712.44 ¹⁴	1217.97	1224 ¹⁴	1.481 ^a	161 ²⁹
					1215.4 ¹⁷		
					1200 ¹⁴	1.492 ^a	162 ²⁹
	303.15	709.269	707.10 ¹³	1193.96	1197 ¹⁶		
					1199 ¹⁷		
					1174 ¹⁴	1.504 ^a	164 ²⁹
					1178 ¹⁸		
	308.15	703.911	702.64 ¹⁴	1169.93			
dipropylamine	288.15	745.064		1235.06		1.230 ^a	248 ^b
	293.15	740.501		1213.41		1.238 ^a	250 ^b
	298.15	735.924	735.64 ¹⁴	1191.86	1198 ¹⁴	1.246 ^a	251 ²⁹
			733.36 ¹⁹		1195 ¹⁸		
303.15	731.333	731.21 ²⁰	1170.43	1174 ¹⁴	1.253 ^a	253 ²⁹	
				1173 ¹⁸			
methyl <i>tert</i> -butyl ether	308.15	726.732	726.76 ¹⁴	1149.03	1151 ¹⁴	1.261 ^a	254 ²⁹
	288.15	747.273	745.79 ²¹	1086.62	1082.4 ²¹	1.411 ^a	184.26 ³⁰
			745.7 ²²		1083 ²²		
	293.15	742.072	740.60 ²¹	1063.43	1059.4 ²¹	1.421 ^a	185.86 ³⁰
			740.4 ²²		1061 ²²		
	298.15	736.826	735.35 ²¹	1040.35	1036.1 ²¹	1.431 ^a	187.49 ³⁰
			735.84 ²³		1035 ²²		
			735.9 ²⁴		1037 ²⁸		
	303.15	731.532	730.06 ²¹	1017.42	1013.0 ²¹	1.441 ^a	189.15 ³⁰
			729.9 ²⁵				
724.75 ²¹			994.68	990.1 ²¹	1.452 ^a	190.84 ³⁰	
308.15	726.185	727.26 ²⁶					
		724.850 ²⁷					

^a Calculated from our measured densities. ^b From group additivity.

Table 2. Standard Deviations (σ) and Parameters A_i in Equation 1 for the Density (ρ) of Pure Liquids

liquid	A_0	A_1	A_2	σ
propylamine	740.483	-1.013	-0.909	0.002
dipropylamine	758.679	-0.904	-0.257	0.001
methyl <i>tert</i> -butyl ether	762.577	-1.006	-0.971	0.002

the purity of the samples. The data of density were fitted to following equation

$$\rho/\text{kg}\cdot\text{m}^{-3} = \sum_{i=0}^n A_i(T/\text{K} - 273.15)^i \quad (1)$$

Coefficients A_i are listed in Table 2.

Table 3. Densities (ρ) and Speeds of Sound (u) for Methyl *tert*-Butyl Ether (1) + Propylamine (2) and + Dipropylamine (2) Mixtures at $T = (288.15, 293.15, 298.15, 303.15, \text{ and } 308.15) \text{ K}$

x_1	$\rho\cdot 10^3/(\text{kg}\cdot\text{m}^{-3})$					$u/(\text{m}\cdot\text{s}^{-1})$				
	$T = 288.15 \text{ K}$	$T = 293.15 \text{ K}$	$T = 298.15 \text{ K}$	$T = 303.15 \text{ K}$	$T = 308.15 \text{ K}$	$T = 288.15 \text{ K}$	$T = 293.15 \text{ K}$	$T = 298.15 \text{ K}$	$T = 303.15 \text{ K}$	$T = 308.15 \text{ K}$
	Methyl <i>tert</i> -Butyl Ether (1) + Propylamine (2)									
0.0000	0.725080	0.719859	0.714586	0.709269	0.703911	1266.07	1242.02	1217.97	1193.96	1169.93
0.0709	0.727856	0.722621	0.717583	0.712014	0.706643	1251.37	1227.16	1203.08	1179.1	1155.28
0.0971	0.729030	0.723784	0.718729	0.713152	0.707762	1244.03	1220.00	1196.04	1172.15	1148.18
0.2112	0.733000	0.727745	0.722617	0.717065	0.711678	1214.39	1190.50	1166.55	1142.94	1119.08
0.2915	0.734914	0.729567	0.724408	0.718869	0.713452	1204.18	1180.33	1156.19	1132.57	1109.04
0.3956	0.737188	0.731938	0.726763	0.721277	0.715895	1174.40	1150.67	1126.99	1103.41	1079.77
0.5551	0.740109	0.734863	0.729642	0.724214	0.718801	1146.05	1122.47	1098.92	1075.42	1052.21
0.7171	0.742564	0.737327	0.732071	0.726691	0.721338	1120.60	1097.13	1073.70	1050.5	1027.32
0.7747	0.743456	0.738220	0.732941	0.727578	0.722269	1111.57	1087.97	1064.45	1040.96	1017.79
0.8604	0.744503	0.739270	0.733994	0.728673	0.723302	1101.25	1077.75	1054.21	1030.91	1007.55
0.9268	0.745600	0.740382	0.735117	0.729806	0.724452	1094.24	1070.72	1047.53	1024.23	1001.07
1.0000	0.747273	0.742072	0.736826	0.731532	0.726185	1086.62	1063.43	1040.35	1017.42	994.68
	Methyl <i>tert</i> -Butyl Ether (1) + Dipropylamine (2)									
0.0000	0.745064	0.740501	0.735924	0.731333	0.726732	1235.06	1213.41	1191.86	1170.43	1149.03
0.0455	0.744529	0.739961	0.735381	0.730779	0.726199	1226.46	1204.63	1182.93	1161.45	1140.10
0.0993	0.743741	0.739141	0.734529	0.729903	0.725268	1218.47	1196.61	1174.89	1153.39	1132.00
0.1886	0.743725	0.739088	0.734436	0.729765	0.725081	1206.79	1184.86	1163.04	1141.42	1119.98
0.304	0.744015	0.739319	0.734607	0.729854	0.725082	1191.22	1169.11	1147.18	1125.49	1103.88
0.3981	0.744373	0.739628	0.73496	0.730165	0.725325	1179.00	1156.83	1134.78	1112.90	1091.16
0.4954	0.744920	0.740107	0.735272	0.73041	0.725531	1164.88	1142.77	1120.84	1099.06	1076.76
0.5839	0.745360	0.740490	0.735593	0.730664	0.725713	1152.30	1130.01	1107.85	1085.90	1063.76
0.7057	0.745893	0.740912	0.735904	0.730891	0.725831	1131.88	1109.4	1087.04	1064.86	1042.54
0.7685	0.746206	0.741193	0.736153	0.731058	0.725925	1121.71	1099.07	1076.59	1054.37	1031.98
0.8876	0.746684	0.741588	0.736455	0.731289	0.726066	1103.92	1080.77	1057.92	1035.26	1012.91
0.9337	0.746947	0.741806	0.736641	0.731421	0.726159	1096.96	1073.64	1050.70	1028.00	1005.42
1.0000	0.747273	0.742072	0.736826	0.731532	0.726185	1086.92	1063.43	1040.35	1017.42	994.68

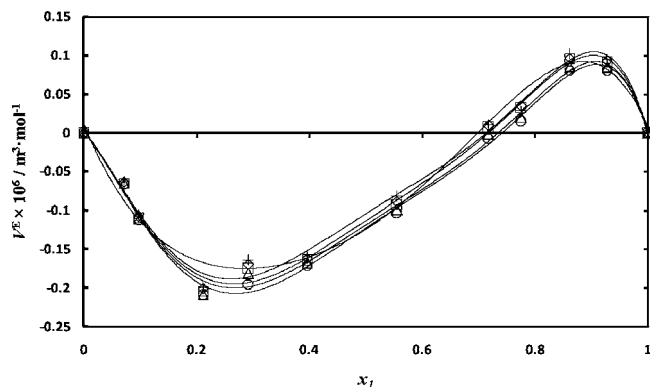


Figure 1. Excess molar volumes, V^E , for methyl *tert*-butyl ether (1) + propylamine (2): ○, 288.15 K; △, 293.15 K; □, 298.15 K; ◇, 303.15 K; +, 308.15 K. Smooth curves have been drawn from polynomial curve fitting.

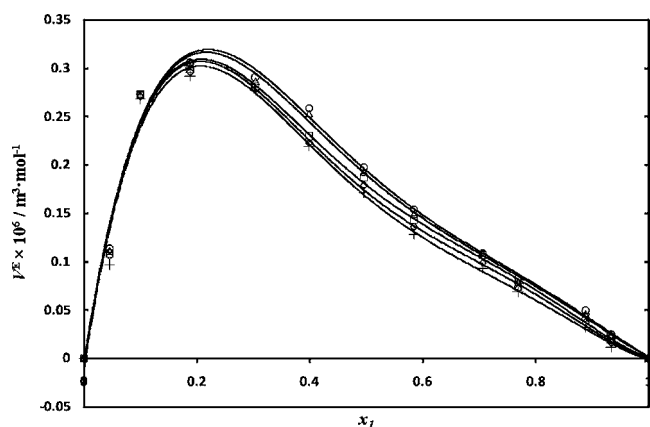


Figure 2. Excess molar volumes, V^E , for methyl *tert*-butyl ether (1) + dipropylamine (2): ○, 288.15 K; △, 293.15 K; □, 298.15 K; ◇, 303.15 K; +, 308.15 K. Smooth curves have been drawn from polynomial curve fitting.

Experimental results of density, ρ , and speeds of sound, u , for the binary liquid mixtures methyl *tert*-butyl ether (1) + propylamine (2) and + dipropylamine (2) at temperatures of (288.15, 293.15, 298.15, 303.15, and 308.15) K are listed in Table 3. Excess molar volumes, V^E , were calculated from our density measurements with the well-known equation available in literature.

Isentropic compressibility, κ_S , is a property that can be calculated from the experimental values of density and speed of sound through the equation

$$\kappa_S = (\rho u^2)^{-1} = V_m (M u^2)^{-1} \quad (2)$$

where ρ is the density, M is the molar mass, and V_m is the molar volume of the binary mixture.

The excess isentropic compressibility, κ_S^E , was calculated by

$$\kappa_S^E = \kappa_S - \kappa_S^{\text{id}} \quad (3)$$

where^{32–34}

$$\kappa_S^{\text{id}} = \sum \phi_i \{ \kappa_{S,i}^* + T V_i^* (\alpha_{P,i}^*)^2 / C_{P,i}^* \} - T \left(\sum x_i V_i^* \right) \sum (\phi_i \alpha_{P,i}^*)^2 / \sum x_i C_{P,i}^* \quad (4)$$

where ϕ_i , $\alpha_{P,i}^*$, and $C_{P,i}^*$ are the volume fraction, isobaric expansivity, and isobaric molar heat capacity of the i th component, respectively. Excess molar volumes V^E are plotted in Figures 1 and 2 and excess isentropic compressibilities κ_S^E in

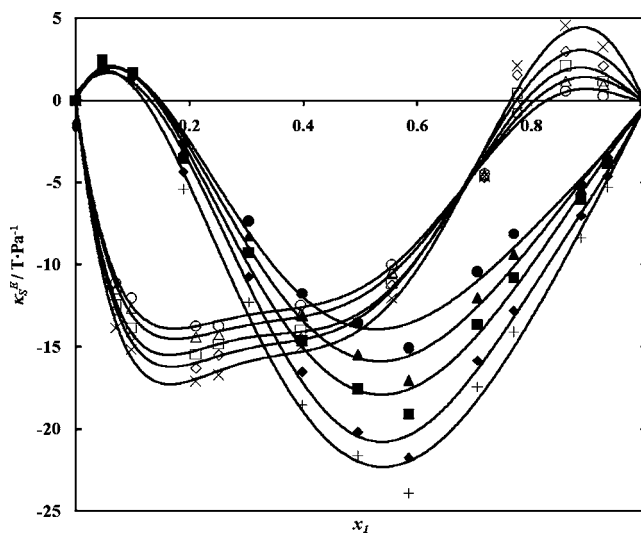


Figure 3. Excess isentropic compressibility, κ_S^E , for methyl *tert*-butyl ether (1) + propylamine (2): ○, 288.15 K; △, 293.15 K; □, 298.15 K; ◇, 303.15 K; ×, 308.15 K. + dipropylamine (2): ●, 288.15 K; ▲, 293.15 K; ■, 298.15 K; ◆, 303.15 K; +, 308.15 K. Smooth curves have been drawn from polynomial curve fitting.

Figure 3; the corresponding numerical values are reported in Table 4.

For compact and smooth representation of results, the measured speeds of sound were fitted to a polynomial of the type

$$u/\text{m}\cdot\text{s}^{-1} = \sum_{i=0}^n A_i x_1^i \quad (5)$$

The coefficients A_i for the correlation of u composition data, evaluated using the least-squares method, are given in Table 5a along with the resulting standard deviations.

The calculated values of V^E and κ_S^E of the binary mixtures were fitted to a Redlich–Kister³⁵ type polynomial equation.

$$Y(x) = x_1 x_2 \sum_{i=0}^n A_i (x_1 - x_2)^i \quad (6)$$

where $Y(x)$ stands for $V^E/\text{cm}^3\cdot\text{mol}^{-1}$ and $\kappa_S^E/\text{T}\cdot\text{Pa}^{-1}$. The coefficients A_i for the correlation of $Y(x)$ composition data, evaluated using the least-squares method, are given in Table 5b along with the resulting standard deviations σ . The standard deviation was calculated by

$$\sigma = \left[\sum_{i=1}^n (Y(x) - Y(x)_{\text{calcd}})^2 / (n - m) \right]^{1/2} \quad (7)$$

where n and m are the number of experimental points and parameters, respectively.

From the Table 4 and Figures 1 and 2, it is observed that excess molar volumes for methyl *tert*-butyl ether (1) + propylamine (2) shows negative and positive deviations. On the other hand, excess molar volume values are positive for methyl *tert*-butyl ether (1) + dipropylamine (2) mixtures at all temperatures. The magnitude of excess molar volumes decreases with an increase in temperature for all of the mixtures studied.

From Table 4 and Figure 3, it is observed that excess isentropic compressibilities for methyl *tert*-butyl ether (1) + propylamine (2) and + dipropylamine (2) show negative deviations, but they change sign at high mole fractions and low mole fractions of ether with propylamine and dipropylamine,

Table 4. Excess Molar Volumes (V^E) and Isentropic Compressibilities (κ_s) for Methyl *tert*-Butyl Ether (1) + Propylamine (2) and + Dipropylamine (2) Mixtures at $T = (288.15, 293.15, 298.15, 303.15, \text{ and } 308.15) \text{ K}$

x_1	$V^E \cdot 10^6$	κ_s	x_1	$V^E \cdot 10^6$	κ_s
	$\text{m}^3 \cdot \text{mol}^{-1}$	$\text{T} \cdot \text{Pa}^{-1}$		$\text{m}^3 \cdot \text{mol}^{-1}$	$\text{T} \cdot \text{Pa}^{-1}$
Methyl <i>tert</i> -Butyl Ether (1) + Propylamine (2)			Methyl <i>tert</i> -Butyl Ether (1) + Dipropylamine (2)		
T = 288.15 K			T = 288.15 K		
0.0000	0.000	860.39	0.0000	0.0000	879.89
0.0709	-0.066	877.37	0.0455	0.113	892.92
0.0971	-0.112	886.33	0.0993	0.273	905.63
0.2112	-0.209	925.08	0.1886	0.305	923.26
0.2915	-0.195	938.38	0.304	0.290	947.18
0.3956	-0.171	983.54	0.3981	0.259	966.46
0.5551	-0.103	1028.72	0.4954	0.198	989.29
0.7171	-0.007	1072.42	0.5839	0.154	1010.42
0.7747	0.015	1088.61	0.7057	0.109	1046.46
0.8604	0.081	1107.55	0.7685	0.082	1065.08
0.9268	0.081	1120.13	0.8876	0.049	1098.98
1.0000	0.000	1133.35	0.9337	0.025	1112.57
			1.0000	0.000	1132.73
T = 293.15 K			T = 293.15 K		
0.0000	0.000	900.52	0.0000	0.000	917.19
0.0709	-0.065	918.94	0.0455	0.111	931.29
0.0971	-0.111	928.26	0.0993	0.273	944.86
0.2112	-0.208	969.53	0.1886	0.302	963.76
0.2915	-0.181	983.85	0.304	0.287	989.59
0.3956	-0.168	1031.87	0.3981	0.253	1010.29
0.5551	-0.099	1080.05	0.4954	0.193	1034.64
0.7171	-0.002	1126.74	0.5839	0.149	1057.59
0.7747	0.020	1144.41	0.7057	0.109	1096.62
0.8604	0.086	1164.56	0.7685	0.079	1116.91
0.9268	0.085	1178.13	0.8876	0.046	1154.44
1.0000	0.000	1191.62	0.9337	0.024	1169.48
			1.0000	0.000	1191.62
T = 298.15 K			T = 298.15 K		
0.0000	0.000	943.35	0.0000	0.000	956.57
0.0709	-0.065	962.81	0.0455	0.108	971.78
0.0971	-0.109	972.62	0.0993	0.272	986.27
0.2112	-0.204	1016.92	0.1886	0.299	1006.59
0.2915	-0.175	1032.66	0.304	0.281	1034.38
0.3956	-0.164	1083.35	0.3981	0.229	1056.61
0.5551	-0.092	1134.90	0.4954	0.187	1082.59
0.7171	0.007	1184.89	0.5839	0.143	1107.65
0.7747	0.032	1204.15	0.7057	0.107	1149.97
0.8604	0.096	1225.89	0.7685	0.074	1172.01
0.9268	0.091	1239.68	0.8876	0.042	1213.24
1.0000	0.000	1253.94	0.9337	0.019	1229.67
			1.0000	0.000	1253.94
T = 303.15 K			T = 303.15 K		
0.0000	0.0000	989.03	0.0000	0.000	998.15
0.0709	-0.064	1010.21	0.0455	0.106	1014.41
0.0971	-0.108	1020.59	0.0993	0.271	1029.87
0.2112	-0.201	1067.57	0.1886	0.296	1051.78
0.2915	-0.169	1084.48	0.304	0.279	1081.64
0.3956	-0.161	1138.74	0.3981	0.223	1105.78
0.5551	-0.089	1193.93	0.4954	0.179	1133.42
0.7171	0.010	1246.98	0.5839	0.136	1160.65
0.7747	0.035	1268.39	0.7057	0.099	1206.59
0.8604	0.097	1291.29	0.7685	0.072	1230.45
0.9268	0.093	1306.16	0.8876	0.037	1275.89
1.0000	0.000	1320.58	0.9337	0.016	1293.74
			1.0000	0.000	1320.58
T = 308.15 K			T = 308.15 K		
0.0000	0.000	1037.92	0.0000	0.000	1042.23
0.0709	-0.064	1060.29	0.0455	0.097	1059.39
0.0971	-0.106	1071.75	0.0993	0.268	1075.99
0.2112	-0.200	1122.00	0.1886	0.292	1099.49
0.2915	-0.164	1139.57	0.304	0.277	1131.79
0.3956	-0.159	1198.09	0.3981	0.219	1157.95
0.5551	-0.082	1256.57	0.4954	0.171	1188.79
0.7171	0.011	1313.56	0.5839	0.128	1217.72
0.7747	0.029	1336.55	0.7057	0.093	1267.59
0.8604	0.102	1361.91	0.7685	0.069	1293.49
0.9268	0.095	1377.40	0.8876	0.032	1342.41
1.0000	0.000	1391.83	0.9337	0.011	1362.30
			1.0000	0.000	1391.83

Table 5

a. Standard Deviations (σ) and Parameters A_i in Equation 5 for Speeds of Sound ($u/m \cdot s^{-1}$)							
T/K	A_0	A_1	A_2	A_3	A_4	$\sigma/m \cdot s^{-1}$	
Methyl <i>tert</i> -Butyl Ether (1) + Propylamine (2)							
288.15	1267.08	-243.89	29.65	33.98			2.74
293.15	1242.87	-241.07	23.54	38.59			2.68
298.15	1218.79	-240.58	23.94	38.62			2.58
303.15	1194.72	-237.92	19.45	41.49			2.57
308.15	1170.67	-235.95	17.31	42.79			2.65
Methyl <i>tert</i> -Butyl Ether (1) + Dipropylamine (2)							
288.15	1234.56	-173.77	182.40	-306.22	150.46		0.68
293.15	1212.89	-176.68	190.81	-317.34	154.21		0.65
298.15	1191.35	-179.72	200.78	-332.14	160.53		0.63
303.15	1169.94	-181.53	205.11	-338.14	162.48		0.62
308.15	1148.50	-178.69	185.88	-309.62	149.06		0.66
b. Standard Deviations (σ) and Parameters A_i in Equation 6							
$Y(x)$	T/K	A_0	A_1	A_2	A_3	A_4	σ
Methyl <i>tert</i> -Butyl Ether (1) + Propylamine (2)							
$V^E \cdot 10^6/(m^3 \cdot mol^{-1})$	288.15	-0.489	0.971	-0.658	0.633	1.918	0.015
	293.15	-0.473	0.937	-0.572	0.726	1.818	0.018
	298.15	-0.452	0.959	-0.464	0.761	1.727	0.018
	303.15	-0.439	0.945	-0.426	0.786	1.675	0.019
	308.15	-0.416	0.915	-0.567	0.848	1.889	0.020
$\kappa_S^E/(T \cdot Pa^{-1})$	288.15	-45.74	37.76	43.57	84.967	-117.787	0.72
	293.15	-47.79	39.99	47.78	95.19	-116.91	0.81
	298.15	-51.58	43.06	63.21	106.79	-136.94	0.98
	303.15	-52.76	46.23	64.68	120.69	-131.82	1.33
	308.15	-55.90	46.47	70.41	146.30	-128.35	1.41
Methyl <i>tert</i> -Butyl Ether (1) + Dipropylamine (2)							
$V^E \cdot 10^6/(m^3 \cdot mol^{-1})$	288.15	0.778	-1.033	1.249	-0.613		0.019
	293.15	0.759	-1.016	1.255	-0.650		0.019
	298.15	0.719	-0.939	1.278	-0.819		0.021
	303.15	0.693	-0.954	1.282	-0.815		0.021
	308.15	0.672	-0.983	1.246	-0.756		0.023
$\kappa_S^E/(T \cdot Pa^{-1})$	288.15	-55.34	-12.21	-63.112	-45.21		1.01
	293.15	-62.84	-17.72	73.19	-38.04		1.02
	298.15	-70.76	-21.49	80.61	-38.49		1.08
	303.15	-80.62	-27.01	85.89	-37.50		1.16
	308.15	-87.99	-26.02	84.01	-45.66		1.29

respectively. With an increase in temperature, the magnitude of excess isentropic compressibility values increases for the mixtures studied.

The negative values of excess molar volumes for methyl *tert*-butyl ether (1) + amine (2) can be compared with negative V^E values of methyl *tert*-butyl ether + 1-alkanol mixtures,³⁶ which is due to different effects like specific interactions due to the formation of multimers of alkanol and ether molecules, possible breaking of hydrogen bonded alkanol structure, and geometrical fitting of ether into the remaining alkanol structure. The mixing of ether with amine would induce mutual dissociation of hydrogen bonded structures; that is, O–H–O and N–H–N present in pure liquids with subsequent formation of new N–H–O bonds between the hydrogen atoms of the –NH group of amine and oxygen atoms of the ether molecule lead to a contraction in volume which should result in negative excess molar volumes.

In the case of positive excess molar volumes for methyl *tert*-butyl ether (1) + dipropylamine (2) mixtures, the breaking up of associated structures present in pure liquids leads to an expansion in volume. The excess molar volume values change from negative to positive as we move from propylamine to dipropylamine. This change is due to an increase in steric hindrance with an increase in one propyl group which leads to a decrease in hydrogen bonding.

The behavior of excess molar volumes is found to be consistent with the excess isentropic compressibility values for

methyl *tert*-butyl ether (1) + propylamine (2) mixtures. Negative excess isentropic compressibility values mean that the mixture is less compressible than the corresponding ideal mixture suggesting strong intermolecular hydrogen bonding with the amine molecule.

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