Binary Mixture Properties of Methyl *tert*-Butyl Ether with Hexane or Heptane or Octane or Nonane from 288.15 K to 298.15 K

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Density, refractive index, and speed of sound of the binary mixtures methyl *tert*-butyl ether + hexane or heptane or octane or nonane from 288.15 K to 298.15 K and at atmospheric pressure have been measured over the whole composition range of mixtures. Excess molar volumes, changes of refractive index on mixing, and deviations in isentropic compressibility for the binary systems were fitted as a function of the mole fraction and temperature, and their root mean square deviations are shown. The excess molar volumes have been compared with the results from Prigogine−Flory and Prigogine−Flory−Patterson theories. Excess partial molar volumes and those corresponding to the infinite dilution condition are also calculated.

1. Introduction

The use of ethers as oxygenating agents in gasoline technology has resulted in an increased interest in the thermodynamic properties of hydrocarbon + ether systems. Ethers are useful as a gasoline additive because of their ability to prevent knocking and to improve Octane rating. We have, accordingly, undertaken a study of the thermodynamics of methyl *tert*-butyl ether (MTBE) + hexane or heptane or octane or nonane from 288.15 K to 298.15 K, knowledge of which is relevant to the design of ether production plants.

In this work, as a preliminary, the densities, refractive indices, and speeds of sound of homogeneous binary mixtures, at the aforementioned temperatures and atmospheric pressure, have been measured. The results were used to calculate excess molar volumes, changes of refractive index on mixing, and deviations in isentropic compressibility over the entire mole fraction range for the binary mixtures at several temperatures. These magnitudes were fitted as a function of the mole fraction and temperature (Romaní et al., 1994), and their root mean square deviations are shown. The Prigogine−Flory (Awwad et al., 1986) and Prigogine−Flory−Patterson (Van et al., 1982) theories have been useful in predicting the excess molar volumes of binary mixtures at 298.15 K.

A survey of the literature shows previously reported density, refractive index, and speed of sound measurements on binary mixtures of methyl *tert*-butyl ether + hexane or heptane at 298.15 K (Kumaran et al., 1993; Dománska, 1996), but data for the above binary mixtures are not available in the literature at the rest of the temperatures.

2. Experimental Section

Chemicals are supplied by Merck, except nonane is from Fluka. Quality is for analysis, for synthesis, and LiChrosolv for hexane, heptane, and octane, respectively. They were recently acquired, kept in an argon atmosphere (N-55, with the maximum water content 2 ppmv), degassed in an ultrasound bath, and stored over freshly activated Type 4 Å molecular sieves for several days before use. Chromatographic (GLC) tests of the solvents presented purities which fulfilled purchaser specifications. Their mass fraction purities were more than 99 mass % for alkanes and more than 99.8 mass % for methyl *tert*-butyl ether. The solvent purities were assessed by contrasting with recommended and published recent values. The results are listed in Table 1.

Table 1. Comparison of Data with Literature Data for Pure Liquids at 298.15 K

	ρ/(g·cm^{-3})		n_D		u/(m·s^{-1})	
component	exptl	lit.	exptl	lit.	exptl	lit.
MTBE	0.7353	0.7353[a]	1.365 97	1.366 30[c]	1035	1037[d]
		0.73528[c]				
hexane	0.6551	0.65484[a]	1.372 34	1.372 26[a]	1078	1076[e]
		0.6548[b]		1.372 26[b]		
heptane	0.6794	0.67946[a]	1.385 12	1.385 11[a]	1130	1130[f]
		0.6795[b]		1.385 11[b]		
octane	0.6985	0.69862[a]	1.395 07	1.395 05[a]	1173	1180[g]
		0.69849[b]		1.395 05[b]		
nonane	0.7139	0.71375[a]	1.403 23	1.403 11[a]	1207	1209[g]
		0.71381[b]		1.403 11[b]		

[a] *TRC Thermodynamic Tables* (1994). [b] Riddick and Bunger (1986). [c] Daubert and Danner (1989). [d] Arce et al. (1997). [e] Sastry et al. (1996). [f] Kiyohara et al. (1979). [g] Aminabhavi et al. (1995).

The mixtures were prepared by weighing amounts of the pure liquids by syringing into stoppered bottles to prevent evaporation and reduce possible errors in mole fraction calculations. A Mettler AT-261 Delta Range balance was used with a precision of $\pm 10^{-5}$ g, covering the whole composition range of the mixture. The density and the speed of sound of the pure liquids and mixtures were measured with an Anton Paar DSA-48 densimeter and sound analyzer with precisions of $\pm 10^{-4}$ g·cm^{-3} and ± 1 m·s.$^{-1}$ The refractive index was measured with the automatic refractometer ABBEMAT-HP Dr Kernchen with a

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Table 2. Density ρ, Refractive Index n_D, Speed of Sound u, Excess Molar Volumes V_m^E, Changes of Refractive Index on Mixing Δn_D, Isentropic Compressibility κ_S and Deviation in Isentropic Compressibility $\Delta\kappa_S$ for Binary Mixtures from 298.15 K to 288.15 K

x_1	ρ/ (g·cm^{-3})	V_m^E/ (cm^3·mol^{-1})	n_D	$\Delta_{mix}n_D$	u/ (m·s^{-1})	κ_S/ (TPa^{-1})	$\Delta\kappa_S$/ (TPa^{-1})	x_1	ρ/ (g·cm^{-3})	V_m^E/ (cm^3·mol^{-1})	n_D	$\Delta_{mix}n_D$	u/ (m·s^{-1})	κ_S/ (TPa^{-1})	$\Delta\kappa_S$/ (TPa^{-1})
						T = 298.15 K									
		MTBE (1) + Hexane (2)								MTBE (1) + Heptane (2)					
0	0.6551	0	1.37234	0	1078	1314.0	0	0	0.6794	0	1.38512	0	1130	1151.7	0
0.0624	0.6592	0.096	1.37177	−0.0002	1073	1318.2	7.1	0.0509	0.6814	0.072	1.38426	0.0001	1125	1160.0.	2.3
0.1106	0.6624	0.170	1.37135	−0.0003	1069	1320.9	11.9	0.1112	0.6839	0.139	1.38315	0.0002	1118	1169.8	5.2
0.1864	0.6676	0.262	1.37064	−0.0005	1064	1323.5	18.0	0.1886	0.6872	0.224	1.38167	0.0002	1109	1182.2	8.4
0.2978	0.6755	0.371	1.36973	−0.0007	1057	1325.0	24.5	0.3088	0.6926	0.339	1.37939	0.0002	1097	1200.4	12.6
0.4007	0.6832	0.421	1.36888	−0.0009	1051	1324.0	28.1	0.3954	0.6968	0.392	1.37764	0.0001	1088	1212.8	14.9
0.4974	0.6907	0.443	1.36815	−0.0010	1047	1320.7	29.3	0.5034	0.7024	0.428	1.37555	0.0001	1077	1227.1	16.6
0.5939	0.6985	0.432	1.36751	−0.0011	1043	1315.4	28.4	0.6023	0.7079	0.433	1.37356	−0.0000	1068	1239.0	16.9
0.6940	0.7070	0.375	1.36695	−0.0010	1040	1307.4	24.9	0.6976	0.7137	0.388	1.37167	−0.0001	1059	1248.6	15.4
0.8078	0.7171	0.272	1.36645	−0.0007	1037	1295.5	18.2	0.7969	0.7202	0.306	1.36979	−0.0001	1051	1257.3	12.5
0.9067	0.7262	0.160	1.36616	−0.0004	1036	1282.6	9.8	0.8974	0.7273	0.187	1.36789	−0.0000	1043	1264.0	7.4
1	0.7353	0	1.36597	0	1035	1268.6	0	0.9486	0.7312	0.101	1.36694	−0.0000	1039	1266.3	3.7
								1	0.7353	0	1.36597	0	1035	1268.6	0
		MTBE (1) + Octane (2)								MTBE (1) + Nonane (2)					
0	0.6985	0	1.39507	0	1172	1041.4	0	0	0.7139	0	1.40323	0	1207	961.2	0
0.0637	0.6999	0.080	1.39359	0.0004	1164	1054.2	−1.6	0.0611	0.7145	0.072	1.40162	0.0007	1196	974.6	−5.4
0.1089	0.7009	0.142	1.39251	0.0006	1158	1063.9	−2.2	0.1122	0.7150	0.136	1.40018	0.0011	1191	985.9	−9.7
0.2069	0.7033	0.243	1.39012	0.0011	1145	1084.5	−3.8	0.1985	0.7160	0.219	1.39774	0.0019	1178	1006.0	−16.2
0.3224	0.7064	0.342	1.38704	0.0013	1129	1109.9	−4.7	0.3084	0.7174	0.316	1.39440	0.0027	1161	1033.8	−22.2
0.3947	0.7086	0.372	1.38505	0.0015	1119	1126.3	−4.7	0.4101	0.7190	0.363	1.39101	0.0031	1144	1062.1	−25.2
0.5043	0.7122	0.401	1.38139	0.0015	1104	1151.7	−4.2	0.5059	0.7207	0.391	1.38761	0.0032	1128	1090.5	−26.2
0.6045	0.7159	0.392	1.37889	0.0014	1090	1175.2	−3.6	0.6045	0.7228	0.378	1.38387	0.0032	1111	1121.6	−25.4
0.7055	0.7200	0.359	1.37574	0.0012	1076	1198.9	−2.8	0.7053	0.7252	0.353	1.37976	0.0028	1092	1155.5	−22.5
0.8057	0.7246	0.282	1.37250	0.0009	1062	1222.6	−1.8	0.8041	0.7281	0.267	1.37550	0.0022	1074	1190.9	−17.5
0.9038	0.7297	0.159	1.36924	0.0005	1049	1245.7	−1.0	0.9047	0.7381	0.151	1.37078	0.0013	1055	1229.2	−10.1
0.8502	0.7323	0.091	1.36769	0.0003	1042	1256.7	−0.5	0.9532	0.7333	0.089	1.36840	0.0007	1045	1248.8	−5.4
1	0.7353	0	1.36597	0	1035	1268.6	0	1	0.7353	0	1.36597	0	1035	1268.6	0
						T = 293.15 K									
		MTBE (1) + Hexane (2)								MTBE (1) + Heptane (2)					
0	0.6602	0	1.37541	0	1100	1250.8	0	0	0.6837	0	1.38776	0	1152	1102.2	0
0.0832	0.6654	0.181	1.37436	−0.0005	1094	1256.6	9.8	0.0609	0.6861	0.092	1.38665	0.0000	1145	1111.5	3.2
0.1104	0.6672	0.224	1.37407	−0.0006	1092	1257.8	12.4	0.1111	0.6882	0.151	1.38580	0.0001	1140	1119.0	5.6
0.2375	0.6759	0.386	1.37298	−0.0009	1083	1261.1	21.8	0.1906	0.6916	0.246	1.38430	0.0001	1131	1130.5	9.2
0.3037	0.6807	0.434	1.37250	−0.0009	1079	1261.3	25.2	0.3130	0.6972	0.359	1.38198	0.0001	1118	1147.4	13.8
0.3912	0.6873	0.465	1.37193	−0.0010	1075	1260.0	28.1	0.4010	0.7016	0.400	1.38035	0.0001	1109	1158.4	16.1
0.4963	0.6955	0.478	1.37128	−0.0009	1070	1256.6	29.8	0.5075	0.7073	0.419	1.37828	0.0001	1099	1170.8	17.8
0.6077	0.7046	0.449	1.37063	−0.0009	1065	1250.2	28.8	0.6047	0.7129	0.404	1.37636	−0.0000	1090	1181.0	18.2
0.7081	0.7132	0.384	1.37011	−0.0007	1062	1242.0	25.5	0.6928	0.7183	0.369	1.37463	−0.0001	1082	1189.0	17.4
0.8311	0.7243	0.248	1.36953	−0.0005	1060	1228.6	18.0	0.7990	0.7254	0.274	1.37257	−0.0002	1073	1196.5	14.3
0.8892	0.7297	0.175	1.36925	−0.0004	1059	1221.1	13.3	0.8972	0.7324	0.165	1.37073	−0.0002	1066	1201.8	9.7
0.9464	0.7352	0.083	1.36910	−0.0002	1059	1212.1	7.1	0.9499	0.7364	0.089	1.36985	−0.0000	1063	1202.5	5.1
1	0.7404	0	1.36597	0	1035	1268.6	0	1	0.7404	0	1.36896	0	1060	1202.4	0
		MTBE (1) + Octane (2)								MTBE (1) + Nonane (2)					
0	0.7026	0	1.39768	0	1193	999.2	0	0	0.7178	0	1.40562	0	1227	925.1	0
0.0719	0.7042	0.097	1.39601	0.0004	1189	1013.1	−0.7	0.0584	0.7184	0.072	1.40401	0.0005	1219	937.4	−3.9
0.1232	0.7054	0.162	1.39471	0.0006	1177	1022.8	−1.4	0.1200	0.7191	0.139	1.40232	0.0011	1210	950.2	−8.1
0.2154	0.7077	0.266	1.39238	0.0009	1165	1041.1	−1.8	0.2020	0.7201	0.223	1.39999	0.0018	1197	968.8	−12.3
0.3137	0.7105	0.331	1.38984	0.0012	1152	1061.1	−1.8	0.3122	0.7217	0.299	1.39661	0.0024	1180	994.7	−16.9
0.4216	0.7138	0.395	1.38686	0.0013	1137	1083.4	−1.5	0.4143	0.7234	0.349	1.39320	0.0028	1164	1020.8	−19.1
0.5024	0.7166	0.406	1.38457	0.0013	1126	1100.3	−1.0	0.5078	0.7252	0.370	1.38994	0.0029	1148	1045.8	−20.1
0.6074	0.7206	0.393	1.38150	0.0013	1112	1122.8	0.2	0.6053	0.7274	0.357	1.38634	0.0029	1132	1073.4	−19.5
0.7064	0.7248	0.348	1.37848	0.0011	1098	1144.0	1.3	0.7070	0.7300	0.324	1.38222	0.0025	1114	1104.6	−16.5
0.8079	0.7296	0.268	1.37523	0.0007	1085	1165.2	1.8	0.8064	0.7330	0.252	1.37805	0.0020	1096	1136.1	−12.6
0.9022	0.7347	0.139	1.37217	0.0004	1072	1184.4	1.8	0.9036	0.7364	0.149	1.37359	0.0011	1078	1169.4	−6.3
0.9473	0.7373	0.071	1.37069	0.0002	1066	1193.0	1.3	0.9549	0.7385	0.067	1.37116	0.0006	1068	1187.0	−2.9
1	0.7404	0	1.36896	0	1060	1202.4	0	1	0.7404	0	1.36896	0	1060	1202.4	0
						T = 288.15 K									
		MTBE (1) + Hexane (2)								MTBE (1) + Heptane (2)					
0	0.6646	0	1.37802	0	1123	1192.8	0	0	0.6879	0	1.39005	0	1174	1055.3	0
0.0656	0.6688	0.131	1.37753	−0.0001	1118	1196.5	6.9	0.0655	0.6906	0.086	1.38930	0.0004	1166	1064.4	3.3
0.1102	0.6717	0.216	1.37715	−0.0002	1115	1198.4	11.0	0.0973	0.6919	0.134	1.38882	0.0005	1163	1068.3	4.3
0.1971	0.6777	0.325	1.37636	−0.0005	1109	1200.4	17.3	0.2082	0.6968	0.254	1.38691	0.0006	1151	1083.0	9.2
0.2993	0.6851	0.411	1.37549	−0.0007	1102	1201.1	22.9	0.3092	0.7015	0.352	1.38486	0.0004	1141	1095.7	13.0
0.4007	0.6928	0.454	1.37471	−0.0009	1097	1199.2	26.0	0.4109	0.7067	0.398	1.38284	0.0002	1130	1107.2	15.5
0.4958	0.7003	0.467	1.37407	−0.0009	1093	1195.8	27.3	0.5147	0.7124	0.413	1.38062	−0.0001	1121	1117.8	16.9
0.5868	0.7078	0.444	1.37354	−0.0009	1089	1190.5	26.4	0.6044	0.7176	0.413	1.37891	−0.0002	1112	1126.1	17.2
0.6892	0.7166	0.384	1.37302	−0.0008	1086	1182.9	23.9	0.6919	0.7231	0.372	1.37723	−0.0003	1105	1133.5	16.9
0.8185	0.7282	0.270	1.37244	−0.0006	1083	1169.7	17.0	0.7933	0.7299	0.297	1.37541	−0.0003	1097	1139.0	13.5
0.9133	0.7372	0.138	1.37215	−0.0003	1082	1157.9	9.8	0.8954	0.7373	0.185	1.37361	−0.0002	1089	1143.7	9.1
0.9769	0.7433	0.056	1.37198	−0.0001	1082	1148.6	3.6	0.9485	0.7414	0.109	1.37274	−0.0001	1086	1144.5	5.2
1	0.7457	0	1.37194	0	1083	1143.8	0	1	0.7457	0	1.37194	0	1083	1143.8	0
		MTBE (1) + Octane (2)								MTBE (1) + Nonane (2)					
0	0.7066	0	1.40010	0	1214	960.8	0	0	0.7216	0	1.40792	0	1247	891.1	0
0.0660	0.7081	0.094	1.39843	0.0002	1205	972.6	−0.3	0.0467	0.7222	0.039	1.40662	0.0004	1240	900.2	−2.7
0.1023	0.7090	0.135	1.39751	0.0003	1200	978.8	−0.8	0.1030	0.7228	0.121	1.40510	0.0009	1232	911.1	−6.1
0.2050	0.7116	0.258	1.39494	0.0006	1187	997.6	−0.7	0.1971	0.7241	0.202	1.40237	0.0015	1218	930.4	−10.5
0.3058	0.7145	0.338	1.39230	0.0008	1173	1016.3	−0.5	0.3060	0.7257	0.300	1.39920	0.0023	1201	954.6	−13.8
0.4053	0.7176	0.402	1.38968	0.0010	1160	1035.0	−0.0	0.4078	0.7275	0.352	1.39585	0.0026	1185	978.0	−16.2
0.5022	0.7210	0.426	1.38699	0.0010	1147	1053.7	0.9	0.5005	0.7294	0.373	1.39272	0.0028	1171	1000.6	−17.0
0.5982	0.7247	0.427	1.38427	0.0010	1134	1072.1	1.7	0.6019	0.7317	0.385	1.38905	0.0028	1154	1027.0	−16.2
0.7044	0.7294	0.367	1.38114	0.0009	1120	1092.1	2.4	0.7046	0.7345	0.348	1.38508	0.0025	1136	1055.4	−13.7
0.8066	0.7344	0.284	1.37811	0.0007	1107	1111.3	2.8	0.8057	0.7377	0.279	1.38080	0.0019	1118	1084.8	−9.9
0.9021	0.7396	0.173	1.37504	0.0003	1095	1128.1	2.1	0.9052	0.7415	0.154	1.37635	0.0010	1100	1115.2	−4.6
0.9504	0.7425	0.096	1.37351	0.0002	1089	1136.4	1.7	0.9545	0.7435	0.096	1.37407	0.0005	1091	1130.4	−1.9
1	0.7457	0	1.37194	0	1083	1143.8	0	1	0.7457	0	1.37194	0	1083	1143.8	0

Table 3. Root Mean Square Deviations (σ) for Comparison with Literature Data at 298.15 K

system	ref	σ (V_m^E/(cm^3·mol^{-1}))
MTBE (1) + hexane (2)	Kumaran et al.	0.010
MTBE (1) + heptane (2)	Dománska	0.020

precision of $\pm 10^{-5}$. Before each series of measurements, these instruments were calibrated with Millipore quality water and ambient air, respectively, in accordance with the instructions.

3. Results and Discussion

The experimental density, refractive index, and speed of sound values were measured at 288.15 K, 293.15 K, and 298.15 K and atmospheric pressure, as shown in Table 2. The excess molar volumes, changes of refractive index on mixing, isentropic compressibilities (determined by means of the Laplace equation $\kappa_S = \rho^{-1}\cdot u^{-2}$), and deviations in isentropic compressibility $\Delta\kappa_S$ of the binary mixtures are reported in Table 2 for the aforementioned temperatures. The differences between the experimental values in the literature and our results, in terms of root mean square deviations, concerning the binary systems discussed, are shown in Table 3.

Excess molar volumes and changes of refractive indices on mixing of binary mixtures were derived, respectively, from eqs 1 and 2.

$$V_m^E = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{\circ -1}) \quad (1)$$

$$\Delta_{mix} n_D = n_D - \sum_{i=1}^{N} x_i n_{Di}^{\circ} \quad (2)$$

In these equations, ρ is the density of the mixture, n_D is the refractive index of the mixture, and ρ_i° and n_{Di}° are the density and refractive index of the pure components. The deviations in isentropic compressibility values were calculated as

$$\Delta\kappa_S = \kappa_S - \sum_{i=1}^{N} x_i \cdot \kappa_{S,i} \quad (3)$$

where κ_S is the isentropic compressibility of the mixture and $\kappa_{S,i}$ is the isentropic compressibility of the purecom-

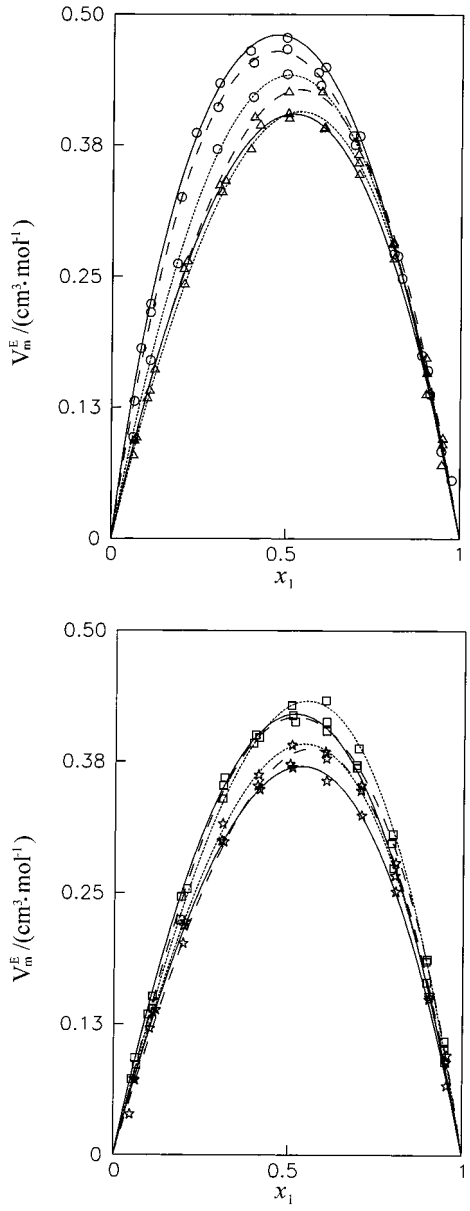

Figure 1. Curves of excess molar volumes V_m^E/(cm^3·mol^{-1}) from Redlich−Kister's equation (eq 7) at 298.15 K (- - -), 293.15 K (—), and 288.15 K (— — —) for (a) (○) MTBE (1) + hexane (2) and (△) MTBE (1) + octane (2) and (b) (□) MTBE (1) + heptane (2) and (☆) MTBE (1) + nonane (2).

Table 4. Coefficients A_{ij} of Eq 7 and Root Mean Square Deviations (σ)

			MTBE (1) + Hexane (2)				
V_m^E/(cm^3·mol^{-1})	$A_{11} = 1.6895$	$A_{12} = -0.2670$	$A_{13} = -0.0206$	$A_{21} = 0.1124$	$A_{22} = 0.3008$	$A_{23} = 0.0230$	$\sigma = 0.005$
$\Delta_{mix} n_D$	$A_{11} = -0.00177$	$A_{12} = 0.00197$	$A_{13} = 0.00020$	$A_{21} = -0.00328$	$A_{22} = -0.00277$	$A_{23} = -0.00027$	$\sigma = 0.00004$
$\Delta\kappa_S$/(T Pa^{-1})	$A_{11} = 119.751$	$A_{12} = 0.7851$	$A_{13} = -0.0752$	$A_{21} = -3.3570$	$A_{22} = -4.5477$	$A_{23} = -0.3371$	$\sigma = 0.5$
			MTBE (1) + Heptane (2)				
V_m^E/(cm^3·mol^{-1})	$A_{11} = 1.0764$	$A_{12} = -0.1457$	$A_{13} = -0.0126$	$A_{21} = 0.9214$	$A_{22} = 0.2256$	$A_{23} = 0.0193$	$\sigma = 0.006$
$\Delta_{mix} n_D$	$A_{11} = 0.00276$	$A_{12} = 0.00071$	$A_{13} = 0.00014$	$A_{21} = -0.00364$	$A_{22} = -0.00091$	$A_{23} = -0.00019$	$\sigma = 0.00004$
$\Delta\kappa_S$/(T Pa^{-1})	$A_{11} = 33.8167$	$A_{12} = 0.9527$	$A_{13} = 0.0134$	$A_{21} = 46.8574$	$A_{22} = -4.8124$	$A_{23} = -0.3244$	$\sigma = 0.5$
			MTBE (1) + Octane (2)				
V_m^E/(cm^3·mol^{-1})	$A_{11} = 1.1886$	$A_{12} = -0.0760$	$A_{13} = -0.0067$	$A_{21} = 0.6223$	$A_{22} = 0.1234$	$A_{23} = 0.01228$	$\sigma = 0.005$
$\Delta_{mix} n_D$	$A_{11} = 0.00706$	$A_{12} = 0.00009$	$A_{13} = -0.00003$	$A_{21} = -0.00152$	$A_{22} = 0.00004$	$A_{23} = 0.00003$	$\sigma = 0.00002$
$\Delta\kappa_S$/(T Pa^{-1})	$A_{11} = -34.7731$	$A_{12} = 0.6468$	$A_{13} = 0.1327$	$A_{21} = 25.0954$	$A_{22} = -6.6977$	$A_{23} = -0.4495$	$\sigma = 0.4$
			MTBE (1) + Nonane (2)				
V_m^E/(cm^3·mol^{-1})	$A_{11} = 1.0771$	$A_{12} = -0.0391$	$A_{13} = -0.0063$	$A_{21} = 0.6930$	$A_{22} = 0.0990$	$A_{23} = 0.0129$	$\sigma = 0.006$
$\Delta_{mix} n_D$	$A_{11} = 0.00993$	$A_{12} = 0.00011$	$A_{13} = 0.00001$	$A_{21} = 0.00437$	$A_{22} = 0.00028$	$A_{23} = 0.00003$	$\sigma = 0.00003$
$\Delta\kappa_S$/(T Pa^{-1})	$A_{11} = -90.7016$	$A_{12} = -3.9884$	$A_{13} = -0.1821$	$A_{21} = -21.6139$	$A_{22} = -3.7003$	$A_{23} = -0.1108$	$\sigma = 0.3$

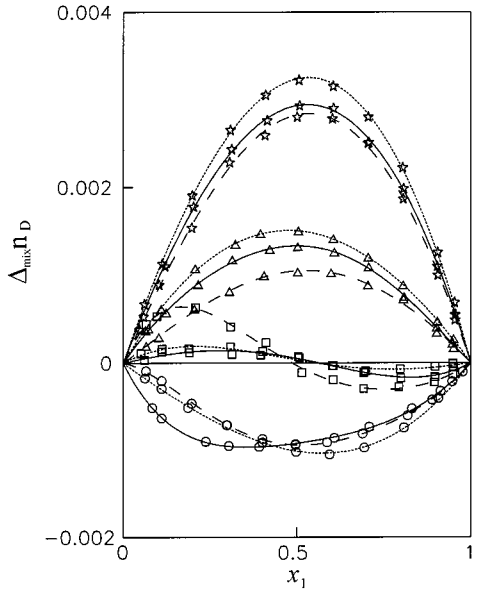

Figure 2. Curves of changes of refractive index on mixing $\Delta_{mix}n_D$ from Redlich−Kister's equation (eq 7) at 298.15 K (- - -), 293.15 K (—), and 288.15 K (— — —) for (○) MTBE (1) + hexane (2), (□) MTBE (1) + heptane (2), (△) MTBE (1) + octane (2), and (☆) MTBE (1) + nonane (2).

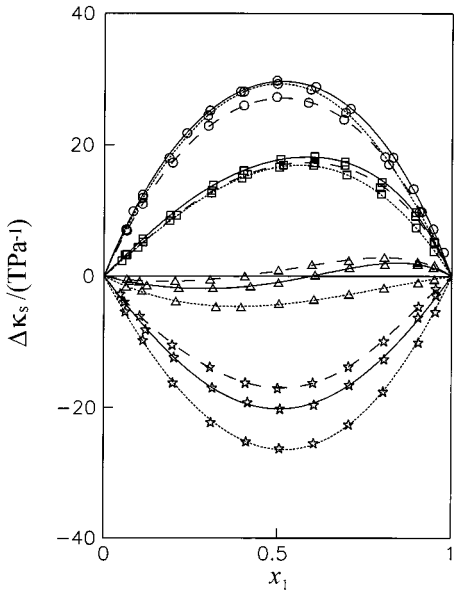

Figure 3. Curves of deviation in isentropic compressibility $\Delta\kappa_S$/(T Pa^{-1}) from Redlich−Kister's equation (eq 7) at 298.15 K (- - -), 293.15 K (—), and 288.15 K (— — —) for (○) MTBE (1) + hexane (2), (□) MTBE (1) + heptane (2), (△) MTBE (1) + octane (2), and (☆) MTBE (1) + nonane (2).

ponent. Excess isentropic compressibilities (Sastry et al., 1996) are calculated by applying the equation

$$\kappa_S^E = \kappa_S - \kappa_S^{id} \tag{4}$$

where κ_S^{id} was calculated by the following relation

$$\kappa_S^{id} = \sum_i \phi_i\{\kappa_{S,i} + T\cdot V_i\cdot(\alpha_i)^2/C_{p,i}\} - T\cdot(\sum_i x_i\cdot V_i)\cdot(\sum_i \phi_i\cdot\alpha_i)^2/(\sum_i x_i\cdot C_{p,i}) \tag{5}$$

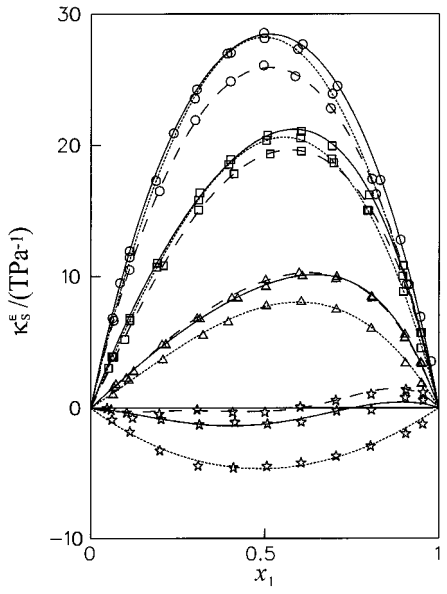

Figure 4. Curves of excess isentropic compressibility κ_S^E/(T Pa^{-1}) from Redlich−Kister's equation (eq 7) at 298.15 K (- - -), 293.15 K (—), and 288.15 K (— — —) for (○) MTBE (1) + hexane (2), (□) MTBE (1) + heptane (2), (△) MTBE (1) + octane (2), and (☆) MTBE (1) + nonane (2).

Table 5. Partial Excess Molar Volumes at Infinite Dilution of the Binary Mixtures at 298.15 K

T/K	$\bar{V}_1^{E,\infty}$/(cm^3·mol^{-1})	$\bar{V}_2^{E,\infty}$/(cm^3·mol^{-1})
	MTBE (1) + Hexane (2)	
298.15	1.726	1.808
293.15	2.582	1.631
288.15	2.273	1.857
	MTBE (1) + Heptane (2)	
298.15	1.360	2.067
293.15	1.576	1.783
288.15	1.324	2.234
	MTBE (1) + Octane (2)	
298.15	1.377	1.861
293.15	1.502	1.731
288.15	1.467	1.940
	MTBE (1) + Nonane (2)	
298.15	1.289	1.823
293.15	1.272	1.678
288.15	1.143	1.908

ϕ_i is defined by the relation

$$\phi_i = x_i\cdot V_i/(\sum_j x_j\cdot V_j) \tag{6}$$

The values of V_i and α_i were calculated from the densities, and $C_{p,i}$ was calculated from the literature compilations (Daubert and Danner, 1984). This magnitude will be compared graphically with the deviation in isentropic compressibility later on.

All properties were fitted as a function of the mole fraction and temperature to a polynomial of the form

$$\Delta Q_{ij} = x(1-x)\sum_{i=1}^{2}\sum_{j=1}^{2} A_{ij}x^{(i-1/2)}(T - 298.15\ \text{K})^{j-1} \tag{7}$$

where ΔQ_{ij} is the excess property, x is the mole fraction, T is the temperature, and A_{ij} is the fitting parameter. The degree of this equation was optimized by applying Marquardt's algorithm (Marquardt, 1963). The correlation parameters calculated using eq 7 are listed in Table 4,

Table 6. Characteristic Parameters of Pure Components for Flory Theory at 298.15 K

component	V/(cm^3·mol^{-1})	α_i/kK^{-1}	κ_T/(T Pa^{-1})	V^*/(cm^3·mol^{-1})	P^*/(J·cm^{-3})	T^*/K	X_{12}/(J·cm^{-3})
MTBE	119.88[a]	1.423[b]	1690.6[b]	90.20[b]	442.9[b]	4385[b]	
hexane	131.55[a]	1.387[c]	1703.9[c]	99.54[c]	424.2[c]	4436[c]	14.79[b]
heptane	147.49[a]	1.256[c]	1460.6[c]	113.60[c]	431.9[c]	4648[c]	15.06[g]
octane	163.53[a]	1.164[c]	1302.4[c]	127.70[c]	436.8[c]	4827[c]	15.24[h]
nonane	179.66[a]	1.070[d]	1178.4[e]	142.37[f]	431.07[f]	5043[f]	15.45[h]

[a] This work. [b] Wang et al. (1993). [c] Wang et al. (1989). [d] Evaluated from experimental density. [e] Evaluated from κ_S. [f] Estimated from Flory's equation; Abe and Flory (1965). [g] Tong et al. (1996). [h] Interpolated from the equation $x_{12} = f(n)$, n being the number of carbons in the alkane; Wang et al. (1989) (decane $x_{12} = 15.65$).

together with the root mean square deviations (σ). This deviation is calculated by applying the following expression

$$\sigma = \left(\frac{\sum_{i}^{n_{DAT}} (z_{exp} - z_{pred})^2}{n_{DAT}} \right)^{1/2} \quad (8)$$

where property values and the number of experimental data points are represented by z and n_{DAT}, respectively.

The fitted curves, as well as the excess changes on mixing and deviation values from 288.15 K to 298.15 K, are shown in Figures 1−4. Excess molar volumes are positive over the whole composition range. Changes of refractive index on mixing are positive for the binary mixture methyl *tert*-butyl ether + octane or nonane. However, if the binary mixture is methyl *tert*-butyl ether + hexane, the changes of refractive index on mixing are negative. For the binary mixture methyl *tert*-butyl ether + heptane the fitted curve of changes of refractive index on mixing is sigmoidal in nature with an initial positive region followed by a negative lobe at low alcohol mole fraction. The deviation in isentropic compressibilities is positive for the binary systems methyl *tert*-butyl ether + hexane or heptane and negative for the binary mixtures methyl *tert*-butyl ether + octane at the above temperatures or nonane at 298.15 K. The excess isentropic compressibilities are positive, except for that of the binary methyl *tert*-butyl ether + nonane at 298.15 K. For the binary mixture methyl *tert*-butyl ether + octane from 288.15 K to 293.15 K the deviation in isentropic compressibilities is sigmoidal, and for the binary methyl *tert*-butyl ether + nonane the excess isentropic compressibilities have the same behavior.

Positive excess molar volumes are observed when the mixture is ether + alkane. The magnitude and sign of excess molar volumes are a reflection of the type of interactions taking place in the mixture. This is exhibited in the mixtures discussed here, which range from 0.370 to 0.480 (cm^3·mol^{-1}). The trend would seem to indicate a less effective packing effect for an ether and normal hydrocarbon mixture. We should take into account the fact that, when the mixture is methyl *tert*-butyl ether + nonane (the highest length of chain of hydrocarbon), the packing effect is better than that for methyl *tert*-butyl ether + hexane.

In Table 5, values of limiting partial excess molar volumes at 298.15 K, calculated for the Redlich−Kister equation (Canosa et al., 1997) as a function of mole fraction, for the four binary mixtures are shown. In general terms, a positive trend is observed corresponding to the binary mixture methyl *tert*-butyl ether + alkanes. These results suggest the different packing of molecules depending on the length of the main chains.

4. Theory

The thermodynamic behavior of binary mixtures has been explained using the Prigogine−Flory and Prigogine−Flory−Patterson predictions, following Awwad *et al.* and Van *et al.*, respectively. In this work, these theories have been useful in predicting the excess molar volumes of the binary mixtures. Table 6 shows the characteristic parameters of pure components and X_{12} used in these theories, some of them being obtained from the literature cited and others correlating our experimental values. A comparison of the calculated and the experimental excess properties for the above mixtures shows that both theories are able to describe excess molar volumes. These results are shown in Table 7.

Table 7. Root Mean Square Deviations (σ) of Prediction Results of Excess Molar Volumes for Binary Systems' (1) Prigogine−Flory and (2) Prigogine−Flory−Patterson Theories at 298.15 K

system	$\sigma_1(V_m^E$/(cm^3·mol^{-1}))	$\sigma_2(V_m^E$/(cm^3·mol^{-1}))
MTBE (1) +		
hexane (2)	0.033	0.014
heptane (2)	0.035	0.017
octane (2)	0.044	0.024
nonane (2)	0.048	0.041

Registry Numbers Supplied by the Author: Methyl *tert*-butyl ether, 2426-08-6; hexane, 110-54-3; heptane, 142-82-5; octane, 111-65-9; nonane, 111-84-2.

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