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Densities and Viscosities of MTBE + Heptane or Octane at $p = 0.1$ MPa from (273.15 to 363.15) K

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This work presents atmospheric density and viscosity values for methyl *tert*-butyl ether + heptane or octane over the whole range of compositions from (273.15 to 363.15) K. A vibrating tube densimeter is used for the density measurements, and a Cannon-Fenske viscosimeter is used for the viscosity measurements. Excess molar volumes have been calculated from the density measurements and represented with a Redlich−Kister equation. The root-mean-square deviation of the excess molar volumes from the literature values is 0.018 $\text{cm}^3\cdot\text{mol}^{-1}$. We also have represented our kinematic viscosity values with a three-body McAllister equation.

Introduction

Knowledge of densities and viscosities of pure substances and mixtures is necessary for the design of chemical processes. Also, a need always exists to have accurate experimental densities and viscosities of liquids to develop new theories that probe the interactions between molecules of dissimilar size and polarity. With these data, we can develop accurate predictive models useful in the chemical industry.

Methyl *tert*-butyl ether (MTBE) is a volatile, flammable, and colorless liquid that is relatively soluble in water. It also is used medically to dissolve gallstones. MTBE has been a gasoline additive at low levels since 1979, replacing tetraethyl lead to increase octane rating and reduce engine knocking. Since 1992, MTBE has been used at higher concentrations in some gasolines to fulfill oxygenate dictates, but MTBE has begun to be phased out because of groundwater contamination. Accurate experimental densities and viscosities for MTBE + hydrocarbons can guide correlations of oxygenates + gasoline. In 1992, Marsh et al.[1] reviewed the thermophysical property measurements (excess volume, vapor−liquid equilibrium (VLE), excess enthalpy, and infinite dilution activity coefficient) of MTBE with different hydrocarbons. It is surprising that only two authors had measured the density of MTBE with heptane and that no data had appeared for MTBE with octane. Pinnick et al.[2] report excess volumes for MTBE + heptane from (243.15 to 333.14) K at pressures of (0.34, 1.72, and 4.85) MPa. Domańska[3] calculates the excess volumes of heptane with MTBE at (298.15 and 308.15) K at atmospheric pressure. Rodríguez et al.[4] has measured densities, the refractive index, and speed of sound of binary mixtures of MTBE + hexane, heptane, octane, and nonane at (288.15, 293.15, and 298.15) K. To the best of our knowledge, experimental viscosity data do not exist for the systems in this paper.

In this work, densities have been measured with a vibrating densimeter for the binary mixtures of MTBE + heptane and MTBE + octane over the entire composition range from (273.15 to 343.15) K and from (273.15 to 363.15) K, respectively. Also, the kinematic viscosity of these mixtures has been measured over the whole composition range using a Cannon-Fenske viscosimeter from (273.15 to 313.15) K for the heptane mixture and from (273.15 to 333.15) K for the octane mixture. Excess molar volumes are calculated using Redlich−Kister-type equations, and we have compared our results with predictions of densities from Peng−Robinson (PR) EOS[5] and the Prigogine−Flory−Patterson[6−8] (PFP) theory. The kinematic viscosity has been correlated to a three-body McAllister equation[9] only for mixtures and conditions where component viscosities were measured. We have generated dynamic viscosity values from our kinematic viscosity results using our density measurements.

Experimental

Apparatus and Procedures. We have described our vibrating tube densimeter (Anton Paar, model DMA 5000) earlier.[10] The repeatability in the density and temperature measurements provided by the manufacturer is $\pm\ 1\cdot10^{-6}\ \text{g}\cdot\text{cm}^{-3}$ and ± 0.001 K, respectively. The uncertainty of the thermometer and the density measurements is ± 0.01 K on ITS-90 and $\pm\ 5\cdot10^{-6}\ \text{g}\cdot\text{cm}^{-3}$, respectively. We believe the uncertainty in the density measurements is less than $\pm\ 3\cdot10^{-5}\ \text{g}\cdot\text{cm}^{-3}$. Using a propagation error formula,[11] the uncertainty in the excess volume is less than 0.008 $\text{cm}^3\cdot\text{mol}^{-1}$.

The kinematic viscosity is measured using a Cannon-Fenske viscosimeter, size 25, with flow ranges of $(0.5\cdot10^{-6}$ to $2\cdot10^{-6})$ $\text{m}^2\cdot\text{s}^{-1}$. The measurements follow ASTM 445. The viscosimeter resides in a Polyscience constant-temperature water bath controlled within ± 0.01 K. A digital thermometer is used to measure the temperature with an accuracy of 0.01 K. The efflux time was measured manually using a digital stopwatch within an accuracy of 0.01 s. Each datum is an average of at least five runs with a maximum deviation in the kinematic viscosity of ± 0.1 %. The viscosity resulted from multiplying the time by the calibration constant of the viscosimeter and by the density

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Table 1. Comparison between Experimental Densities and Literature Values for MTBE, Heptane, and Octane

	ρ/g·cm^{-3}		ρ/g·cm^{-3}		ρ/g·cm^{-3}	
T/K	this work	lit.	this work	lit.	this work	lit.
	MTBE		Heptane		Octane	
273.15	0.76134		0.70075	0.700673[12]	0.71858	
278.15	0.75614		0.69659	0.696567[12]	0.71461	
283.15	0.75102		0.69242	0.692397[12]	0.71062	0.71064[22]
288.15	0.74585	0.7457[4]	0.68822	0.688204[12]	0.70662	
293.15	0.74065	0.7404[4]	0.68400	0.683988[12]	0.70261	0.70256[23] 0.70255[24]
298.15	0.73540	0.7353[4] 0.73517[4]	0.67975	0.67977[12]	0.69857	0.69856[25]
303.15	0.73010		0.67548	0.675485[12]	0.69452	0.69445[26] 0.69459[27]
308.15	0.72482	0.72726[3]	0.67119	0.671193[12]	0.69044	0.6905[28]
313.15	0.71942		0.66686	0.666869[12]	0.68635	0.68628[29] 0.6865[28]
318.15			0.66250	0.662515[12]	0.68223	0.68221[30]
323.15			0.65811	0.658127[12]	0.67809	0.6783[31]
328.15			0.65368	0.6536[21]	0.67392	0.673786[32] 0.67448[27]
333.15			0.64922	0.649242[12]	0.66971	0.669607[32] 0.6707[33]
338.15			0.64472	0.644739[12]	0.66551	0.665397[32]
343.15			0.64017	0.640193[12]	0.66124	0.661158[32]
348.15			0.63558	0.635600[12]	0.65696	0.656884[32]
353.15			0.63041	0.630954[12]	0.65263	0.652571[32]
358.15			0.62634	0.626261[12]	0.64826	0.648225[32]
363.15					0.64385	0.643833[32]

of the sample. Using the propagation of error formula,[11] the estimated accuracy of the dynamic viscosity is ± 0.004 mPa·s.

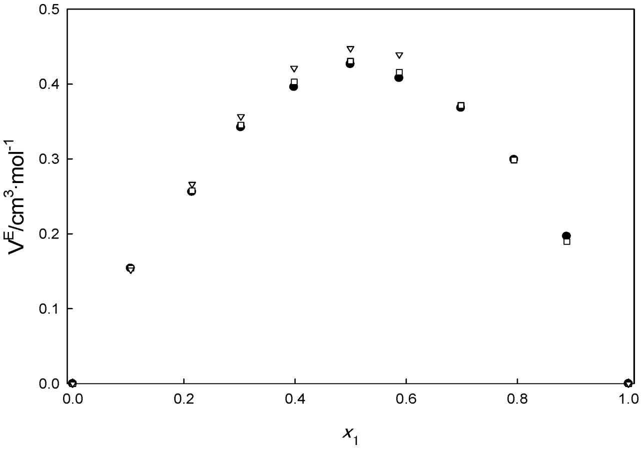

Figure 1. Temperature dependence of the excess molar volume for MTBE (1) + heptane (2): ●, 273.15 K; □, 298.15 K; ▽, 318.15 K.

Chemicals. Sigma Aldrich Co. supplied the MTBE and octane with stated purities of better than 99.8 mol % and 99 mol %, respectively. J. T. Baker provided the heptane with a stated purity of 99.6 mol %. The confirmed purities of the samples from the manufacturer (certificates of analysis) are 99.96 mol %, 99.44 mol %, and 99.6 mol % for MTBE, octane, and heptane, respectively. The pure components are used as received. Using an analytical balance (Ohaus Model AS120S), we prepared the mixtures gravimetrically with a precision of ± 0.1 mg. The overall uncertainty in the mole fractions is less than ± 0.002.

Table 2. Experimental Densities and Excess Molar Volumes for MBTE (1) + Heptane (2)

x_1	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}
	T = 273.15 K		T = 278.15 K		T = 283.15 K		T = 288.15 K		T = 293.15 K	
0.0000		0.0000		0.0000		0.0000		0.0000		0.0000
0.1042	0.70519	0.1540	0.70096	0.1527	0.69672	0.1532	0.69245	0.1538	0.68815	0.1540
0.2146	0.71040	0.2559	0.70609	0.2535	0.70176	0.2550	0.69740	0.2561	0.69302	0.2568
0.3024	0.71467	0.3421	0.71030	0.3384	0.70590	0.3403	0.70147	0.3419	0.69702	0.3432
0.3982	0.71973	0.3959	0.71527	0.3915	0.71079	0.3947	0.70628	0.3968	0.70173	0.3999
0.4996	0.72544	0.4265	0.72090	0.4203	0.71632	0.4237	0.71172	0.4261	0.70709	0.4279
0.5875	0.73085	0.4079	0.72622	0.4008	0.72155	0.4050	0.71686	0.4083	0.71213	0.4122
0.6985	0.73808	0.3681	0.73334	0.3586	0.72856	0.3626	0.72376	0.3655	0.71892	0.3677
0.7940	0.74480	0.2992	0.73996	0.2876	0.73508	0.2908	0.73017	0.2931	0.72522	0.2958
0.8890	0.75200	0.1967	0.74705	0.1824	0.74207	0.1847	0.73704	0.1858	0.73198	0.1877
1.0000		0.0000		0.0000		0.0000		0.0000		0.0000
	T = 298.15 K		T = 303.15 K		T = 308.15 K		T = 313.15 K		T = 318.15 K	
0.0000		0.0000		0.0000		0.0000		0.0000		0.0000
0.1042	0.68383	0.1541	0.67949	0.1542	0.67512	0.1543	0.67071	0.1531	0.66628	0.1520
0.2146	0.68862	0.2575	0.68418	0.2582	0.67971	0.2619	0.67519	0.2648	0.67065	0.2662
0.3024	0.69254	0.3453	0.68802	0.3472	0.68348	0.3515	0.67889	0.3540	0.67426	0.3566
0.3982	0.69716	0.4030	0.69255	0.4065	0.68791	0.4141	0.68323	0.4179	0.67851	0.4211
0.4996	0.70242	0.4307	0.69772	0.4332	0.69298	0.4408	0.68820	0.4449	0.68338	0.4477
0.5875	0.70737	0.4159	0.70257	0.4193	0.69773	0.4296	0.69285	0.4343	0.68792	0.4393
0.6985	0.71404	0.3716	0.70911	0.3756	0.70414	0.3885	0.69912	0.3940		
0.7940	0.72023	0.2985	0.71519	0.3018	0.71011	0.3134				
0.8890	0.72687	0.1895	0.72172	0.1914						
1.0000		0.0000		0.0000		0.0000		0.0000		0.0000
	T = 323.15 K		T = 328.15 K		T = 333.15 K		T = 338.16 K		T = 343.16 K	
0.0000										
0.1042	0.66180		0.65727		0.65274		0.64813		0.64327	
0.2146	0.66608		0.66146		0.65677		0.65207			
0.3024	0.66960		0.66489		0.66013					
0.3982	0.67375		0.66893							
0.4996	0.67850									
0.5875										
0.6985										
0.7940										
0.8890										
1.0000										

Table 3. Experimental Densities and Excess Molar Volumes for MBTE (1) + Octane (2)

x_1	ρ / $g{\cdot}cm^{-3}$	V_m^E / $cm^3{\cdot}mol^{-1}$	ρ / $g{\cdot}cm^{-3}$	V_m^E / $cm^3{\cdot}mol^{-1}$	ρ / $g{\cdot}cm^{-3}$	V_m^E / $cm^3{\cdot}mol^{-1}$	ρ / $g{\cdot}cm^{-3}$	V_m^E / $cm^3{\cdot}mol^{-1}$	ρ / $g{\cdot}cm^{-3}$	V_m^E / $cm^3{\cdot}mol^{-1}$
	$T = 273.15$ K		$T = 278.15$ K		$T = 283.15$ K		$T = 288.15$ K		$T = 293.15$ K	
0.0000		0.0000		0.0000		0.0000		0.0000		0.0000
0.1059	0.72115	0.1771	0.717106	0.1738	0.713046	0.1718	0.708972	0.1704	0.704884	0.1694
0.2123	0.724203	0.2881	0.720082	0.2822	0.715938	0.2798	0.711779	0.2776	0.707601	0.2761
0.3019	0.727065	0.3520	0.722866	0.3447	0.718644	0.3423	0.714403	0.3402	0.710139	0.3393
0.4099	0.730835	0.4078	0.726533	0.3991	0.722208	0.3970	0.717859	0.3954	0.713488	0.3941
0.5053	0.734583	0.4175	0.730183	0.4072	0.725756	0.4056	0.721306	0.4037	0.716833	0.4018
0.6005	0.738614	0.4160	0.734106	0.4046	0.729573	0.4029	0.725009	0.4018	0.720419	0.4007
0.6934	0.742992	0.3805	0.738371	0.3675	0.733719	0.3668	0.729044	0.3645	0.724332	0.3636
0.7967	0.748318	0.3202	0.743560	0.3055	0.738766	0.3054	0.733942	0.3043	0.729066	0.3066
0.8975	0.754329	0.1931	0.749420	0.1768	0.744471	0.1772	0.739489	0.1763	0.734467	0.1761
1.0000		0.0000		0.0000		0.0000		0.0000		0.0000
	$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K		$T = 313.15$ K		$T = 318.15$ K	
0.0000		0.0000		0.0000		0.0000		0.0000		0.0000
0.1059	0.700768	0.1684	0.696633	0.1676	0.692484	0.1654	0.688303	0.1640	0.684108	0.1586
0.2123	0.703393	0.2748	0.699177	0.2706	0.694926	0.2702	0.690652	0.2670	0.686345	0.2634
0.3019	0.705856	0.3359	0.701546	0.3331	0.697212	0.3322	0.692842	0.3300	0.688444	0.3256
0.4099	0.709092	0.3912	0.704666	0.3889	0.700213	0.3898	0.695728	0.3867	0.691207	0.3826
0.5053	0.712324	0.4002	0.707798	0.3958	0.703231	0.3981	0.698629	0.3955	0.693985	0.3925
0.6005	0.715799	0.3984	0.711146	0.3958	0.706458	0.3993	0.701736	0.3962	0.696968	0.3927
0.6934	0.719586	0.3621	0.714806	0.3598	0.709988	0.3647	0.705127	0.3632	0.700224	0.3600
0.7967	0.724172	0.3051	0.719238	0.3032	0.714261	0.3100	0.709240	0.3090	0.704169	0.3070
0.8975	0.729408	0.1751	0.724303	0.1740	0.719151	0.1828	0.713950	0.1832	0.708696	0.1823
1.0000		0.0000		0.0000		0.0000		0.0000		0.0000
	$T = 323.15$ K		$T = 328.15$ K		$T = 333.15$ K		$T = 338.15$ K		$T = 343.15$ K	
0.0000										
0.1059	0.679876		0.675617		0.671333		0.667018		0.662680	
0.2123	0.682017		0.677665		0.673250		0.668815		0.664349	
0.3019	0.684017		0.679549		0.675046		0.670514		0.665923	
0.4099	0.686655		0.682067		0.677434		0.672758		0.668038	
0.5053	0.689306		0.684587		0.679825					
0.6005	0.692159		0.687304		0.682397					
0.6934	0.695271		0.690272							
0.7967	0.699039									
0.8975										
1.0000										
	$T = 348.15$ K		$T = 353.15$ K		$T = 358.15$ K		$T = 363.15$ K			
0.0000										
0.1059	0.658279		0.653843		0.649405		0.644850			
0.2123	0.659830		0.655280		0.650681		0.646031			
0.3019	0.661299		0.656638		0.651917		0.647140			
0.4099										
0.5053										
0.6005										
0.6934										
0.7967										
0.8975										
1.0000										

Results and Discussion

The density of water was measured before those of the mixtures to check the calibration of the densimeter. If the water error exceeded 0.01 $kg{\cdot}m^{-3}$, the equipment was recalibrated. Also, the density and viscosity of the pure components was measured and compared with literature values. Table 1 presents the comparison for the density measurements. The values reported by Ramos-Estrada et al.[12] for *n*-heptane agree within an average absolute percentage deviation of 0.009 %. We also have compared our densities for MTBE to those from Rodríguez et al.,[4] and the agreement between the sets of data is within 0.02 %. For octane, we compared our measurements to those in the TRC database, and our values agree within 0.03 % as seen in Table 1. We measured the liquid density of two mixtures of MTBE with heptane and octane from (273.15 to 343.15) K and from (273.15 to 363.15) K, respectively. Our densities agree with density measurements from Rodríguez et al.[4] within an average percentage value of 0.04 %. Tables 2 and 3 contain our density measurements for MTBE + heptane and MTBE + octane, respectively.

From our density values, we have calculated the excess molar volume using

$$V_m^E = \frac{\sum_i x_i M_{W,i}}{\rho} - \sum_i x_i V_i^o \tag{1}$$

where ρ is the experimental mixture density; x_i is the mole fraction of component *i*; V_i^o is the molar volume of pure component *i*; and $M_{W,i}$ is the molecular weight of component *i*. Tables 2 and 3 contain the calculated excess molar volume for MTBE + heptane and MTBE + octane, respectively. Figures 1 and 2 show that the excess molar volumes of MTBE with heptane and with octane present positive deviations from ideality at the temperatures in this work. These positive deviations could be due to the breaking of the self-association of the ether

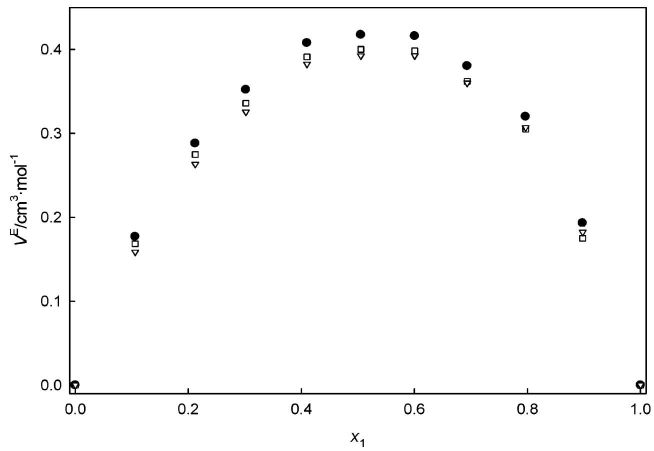

Figure 2. Temperature dependence of the excess molar volume for MTBE (1) + octane (2): ●, 273.15 K; □, 298.15 K; ▽, 318.15 K.

allowing a smaller packing effect as suggested by Domańska.[3] This smaller packing effect decreases for octane. The temperature dependence of the excess molar volumes for the system MTBE + heptane is weaker than that for MTBE + octane; however, the mixture with heptane is more nonideal than that with octane.

The excess molar volume is represented with a Redlich−Kister-type equation

$$V_m^E/\text{cm}^3\text{·mol}^{-1} = x_1x_2\sum a_i(x_1 - x_2)^i \qquad (2)$$

where V_m^E is the excess molar volume and a_i are the coefficients for the calculated excess molar volumes. The values of the parameters at each temperature together with their standard deviations from the fit are in Table 4. The standard deviation has been calculated as

$$\sigma = \left[\frac{\sum((V_m^E)_i^{\text{exptl}} - (V_m^E)_i^{\text{calcd}})^2}{n - m}\right]^{1/2} \qquad (3)$$

where n is the number of excess molar volumes; m is the number of adjusted parameters; and superscripts exptl and calcd represent experimental and calculated values. Our excess molar volume results for MTBE + heptane are compared to those from Rodriguez et al.[4] and Domańska.[3] Figure 3 shows the excess molar volumes at 298.15 K and the root-mean-square deviations of our results from the results of these authors are (0.013 and 0.018) cm^3·mol^{-1}, respectively. For the octane mixture, the root-mean-square deviation of our excess molar volumes with respect to Rodriguez et al.[4] is 0.015 cm^3·mol^{-1}.

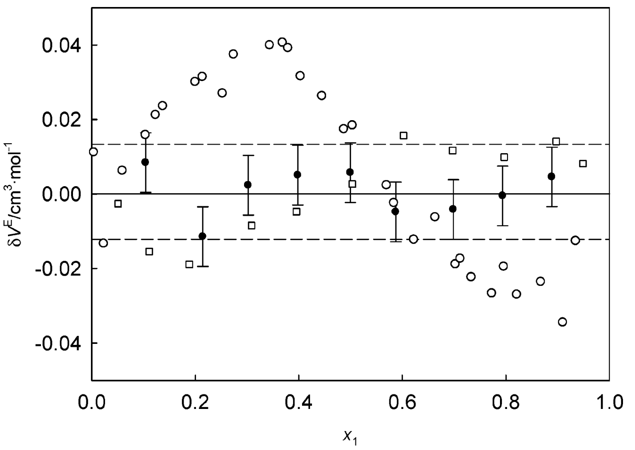

Figure 3. Fractional deviations $\delta V_m^E = V_m^E(\text{exptl}) - V_m^E(\text{calcd})$ of the excess molar volumes of MTBE (1) + heptane (2) at T = 298.15 K from values calculated from the Redlich−Kister equation: ○, Domańska;[3] □, Rodríguez et al.;[4] ●, this work; error bars represent the uncertainty; dash line represents 2σ.

We have compared our calculated results at 298.15 K with those obtained from densities using the Peng−Robinson (PR) EOS and the Prigogine−Flory−Patterson Theory[6−8] (PFP). For the EOS, conventional van der Waals mixing rules are used without an interaction parameter. For the PFP theory, Awwad and Jabra[13] have reported the excess molar volume

$$\frac{V_m^E}{x_1v_1^* + x_2v_2^*} = \frac{(\tilde{V}_m^{1/3} - 1)\tilde{V}_m^{2/3}}{(4/3)\tilde{V}_m^{-1/3} - 1}\psi_1\sigma_2\frac{X_{12}}{p_1^*} - \frac{(\tilde{V}_1 - \tilde{V}_2)^2(14\tilde{V}_m^{-1/3}/9 - 1)}{((4/3)\tilde{V}_m^{-1/3} - 1)\tilde{V}_m}\psi_1\psi_2 + \frac{(\tilde{V}_1 - \tilde{V}_2)(p_1^* - p_2^*)}{p_2^*\psi_1 + p_1^*\psi_2}\psi_1\psi_2 \qquad (4)$$

where according to Van and Patterson,[8] the first term, ΔV_{inter}, is a contribution caused by the interaction between the two components; the second term, ΔV_F, is the contribution from the

Table 4. Parameters for the Redlich−Kister Equation for the Excess Molar Volume

T/K	a_0	a_1	a_2	σ/cm^3·mol^{-1}	T/K	a_0	a_1	a_2	σ/cm^3·mol^{-1}
	MTBE + Heptane					MTBE + Octane			
273.15	1.67	0.21	0.12	0.009	273.15	1.68	0.17	0.48	0.004
278.15	1.65	0.15	0.05	0.008	278.15	1.64	0.12	0.39	0.005
283.15	1.67	0.17	0.04	0.008	283.15	1.63	0.13	0.39	0.005
288.15	1.68	0.18	0.04	0.008	288.15	1.62	0.13	0.38	0.005
293.15	1.69	0.19	0.04	0.007	293.15	1.62	0.14	0.39	0.006
298.15	1.70	0.20	0.03	0.007	298.15	1.61	0.15	0.39	0.006
303.15	1.71	0.21	0.03	0.008	303.15	1.60	0.15	0.39	0.006
308.15	1.75	0.26	0.07	0.008	308.15	1.60	0.2	0.43	0.006
313.15	1.77	0.27	0.07	0.008	313.15	1.59	0.2	0.43	0.006
318.15	1.78	0.29	0.07	0.008	318.15	1.58	0.22	0.41	0.005

Table 5. Pure Component Parameters for the PFP Theory at 298.15 K

substance	α·10^{-3}/K^{-1}	γ/J·cm^{-3}·K^{-1}	v/cm^{-3}·mol^{-1}	v_i^*/cm^{-3}·mol^{-1}	p_i^*/J·cm^{-3}	T_i^*/K	s_2/s_1
MTBE (1) +	1.438[a]	0.8508[18]	119.87	90.05	449.5	4364.1	−
heptane (2)	1.253[a]	0.8597[17]	147.41	113.62	431.4	4653.3	0.9254
octane (2)	1.158[a]	0.8944[15]	163.52	127.83	431.8	4840.3	0.8898

[a] Evaluated from experimental densities.

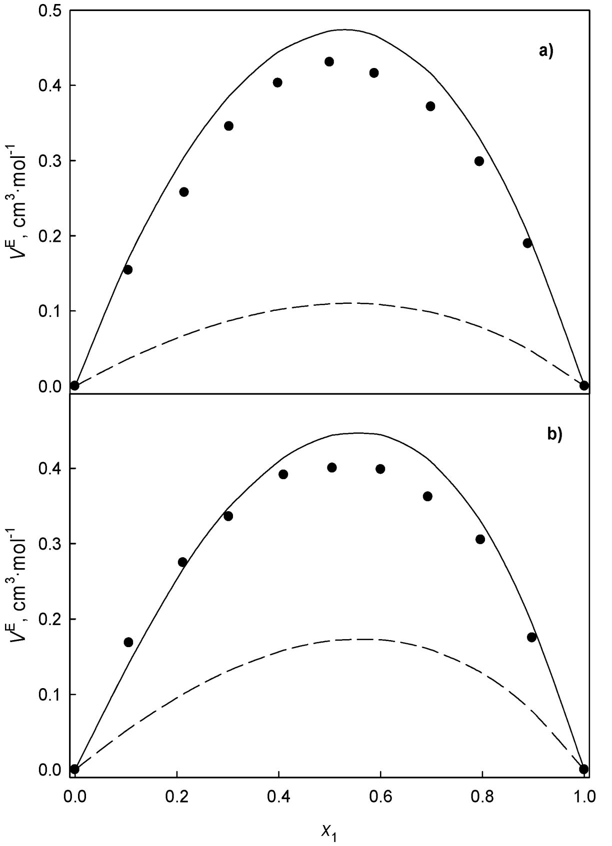

Figure 4. Prediction of the excess molar volume at 298.15 K of (a) MTBE (1) + heptane and (b) MTBE (1) + octane. In both graphs: −, PFP theory; --, using densities from PR EOS; ●, this work.

difference of free volumes of the two components; and the third term, ΔV_{p*}, is the contribution from the internal pressure. In eq 4, the subscript *i* represents the pure component; x_i is the molar fraction; v_i^* is the characteristic molar volume; p_i^* is the characteristic pressure; ψ_i is the contact energy fraction; θ_i is the surface fraction; and $\tilde{V}_i$ is the reduced volume. Also, X_{12} is the interaction parameter of the mixture and $\tilde{V}_m$ is the reduced volume. Expressions for ψ_i, θ_i, $\tilde{V}_m$, and $\tilde{V}_i$ are given elsewhere.[14,15]

In this work, we have calculated X_{12} from excess enthalpy values as suggested by Lam et al.[16] We have used an alternative expression for the excess enthalpy

$$\frac{H^E}{x_1U_1^* + x_2U_2^*} = (-\tilde{U}_m + \tilde{T}_m\tilde{C}_p)\psi_1\theta_2\frac{X_{12}}{p_1^*} + \tilde{V}_m(\tilde{V}_1 - \tilde{V}_2)^2\psi_1\psi_2(1 - \tilde{C}_p((14/9)\tilde{V}_m^{-1/3} - 1)) \quad (5)$$

where $\tilde{U}_m$ is the reduced energy of the mixture; $U_i^* = p_i^* v_i^*$ is the reduction energy parameter according to Van and Patterson;[8] $\tilde{C}_p$ is the reduced heat capacity; and $\tilde{T}_m$ is the reduced temperature. From this expression, we calculate a value of X_{12} after an iterative procedure using

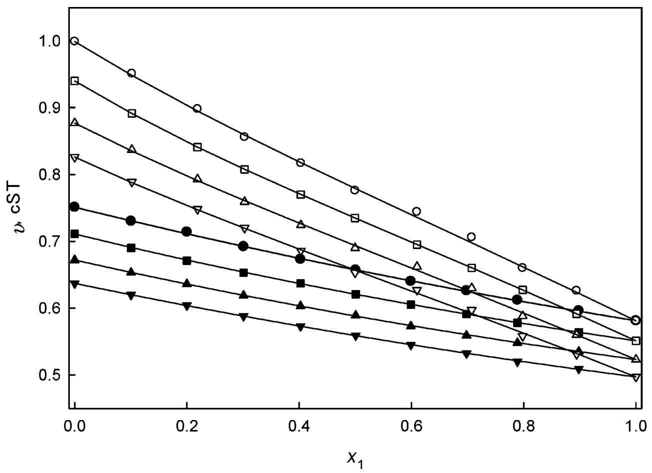

Figure 5. Composition dependence of the kinematic viscosities: solid symbols are for MTBE (1) + heptane (2), and hollow symbols are for MTBE (1) + octane (2). The line corresponds to the McAllister equation.

$$\tilde{T}_m = \frac{(\varphi_1 p_1^* \tilde{T}_1 + \varphi_2 p_2^* \tilde{T}_2)}{(\varphi_1 p_1^* + \varphi_2 p_2^* - \varphi_1\theta_2 X_{12})} \quad (6)$$

and

$$\tilde{V}_m^{-1} = \psi_1\tilde{V}_1^{-1} + \psi_2\tilde{V}_2^{-1} \quad (7)$$

In eq 6, φ_i is the segment or the hard core volume fraction of component *i* and $\tilde{T}_i$ is the reduced temperature of component *i*. With a value of X_{12}, we can calculate the excess volume using eq 4. We have calculated the thermal expansion coefficient using

$$\alpha = v_i^{-1}\left(\frac{\partial v_i}{\partial T}\right)_p \quad (8)$$

where v_i is the specific volume. This coefficient is needed in the calculation of the reduced volume, temperature, and pressure. Results appear in Table 5. For the thermal pressure coefficient needed in the evaluation of the reduced pressure of the pure components, a correlation proposed by Liu and Lee[17] has been used for heptane and a value from Orwoll and Flory[15] has been used for octane. The thermal pressure coefficient for MTBE comes from a correlation based upon corresponding states by Lee and Lui.[18] Heats of mixing at 298.15 K come from Tong et al.[19] and Zhu et al.[20] for MTBE + heptane and MTBE + octane, respectively. Table 5 contains the parameters for the pure substances, and Table 6 presents a comparison of the excess molar volume experimental to the prediction from PFP for an equimolar mixture at 298.15 K. The root-mean-square deviation of the PFP theory with respect to the calculated excess molar volumes is 0.04 cm^3·mol^{-1} for both mixtures, and the root-mean-square deviation of the excess volume using densities from the PR EOS with respect to the calculated excess volumes in this work is 0.25 cm^3·mol^{-1}. This deviation could be due to the fact that no interaction parameter has been used. Figure 4 shows a comparison of the calculated excess molar volumes to the prediction from both models.

Table 6. Comparison between the Calculated and Predicted Excess Molar Volumes at 298.15 K and x_1 = 0.5

system	$(H^E)_{exptl}$ J·mol^{-1}	X_{12} J·cm^{-3}	ΔV_{inter} cm^{-3}·mol^{-1}	ΔV_{p*} cm^{-3}·mol^{-1}	ΔV_F cm^{-3}·mol^{-1}	$(V_m^E)_{PFP}$ cm^{-3}·mol^{-1}	$(V_m^E)_{exptl}$ cm^{-3}·mol^{-1}	$(V_m^E)_{PR}$ cm^{-3}·mol^{-1}
MTBE (1) +								
heptane	415.7[19]	16.6	0.4798	0.0348	−0.0423	0.4723	0.4307	0.1055
octane	430.2[20]	17.5	0.4947	0.0556	−0.1061	0.4441	0.4002	0.1688

Table 7. Comparison between Experimental Viscosities and Literature Values for MTBE, Heptane, and Octane

	η/mPa·s					
T/K	this work	lit.	this work	lit.	this work	lit.
	MTBE		Heptane		Octane	
273.15	0.443		0.526	0.521[35]	0.718	0.712[37]
278.15	0.417		0.495		0.671	
283.15	0.392		0.465		0.623	0.616[38]
288.15	0.370	0.4008[34]	0.438		0.584	0.579[39]
293.15			0.415	0.417[35]	0.545	0.546[40]
298.15			0.392	0.3912[21]	0.514	0.5184[41]
303.15			0.372	0.3707[5]	0.486	0.487[37]
308.15			0.354		0.459	0.457[42]
313.15			0.336	0.337[36]	0.434	0.433[40]
318.15					0.415	0.414[27]
323.15					0.394	0.3928[43]
328.15					0.375	0.3706[27]
333.15					0.357	0.355[38]

Table 8. Parameters for the McAllister Equation

$\frac{T}{\text{K}}$	$\frac{\upsilon_{12}\cdot 10^{-6}}{\text{m}^2\cdot\text{s}^{-1}}$	$\frac{\upsilon_{21}\cdot 10^{-6}}{\text{m}^2\cdot\text{s}^{-1}}$	$\frac{\sigma\cdot 10^{-6}}{\text{m}^2\cdot\text{s}^{-1}}$
	MTBE (1) + Heptane (2)		
273.15	0.6292	0.6855	$1.2\cdot 10^{-3}$
278.15	0.5943	0.6459	$5.9\cdot 10^{-4}$
283.15	0.5627	0.6124	$6.3\cdot 10^{-4}$
288.15	0.5347	0.5825	$5.0\cdot 10^{-4}$
	MTBE (1) + Octane (2)		
273.15	0.7366	0.8423	$4.5\cdot 10^{-3}$
278.15	0.6996	0.7878	$3.6\cdot 10^{-3}$
283.15	0.6582	0.7475	$3.7\cdot 10^{-3}$
288.15	0.6241	0.7079	$3.2\cdot 10^{-3}$

We have measured the kinematic viscosities of MTBE, heptane, and octane and have converted them to dynamic viscosities using our experimental density measurements. Table 7 contains the experimental viscosity measurements and a comparison to literature sources. We found a viscosity value at 283.15 K for pure MTBE. This value disagrees with our measurement within 8 %. To resolve this disagreement, the viscosity value was measured using an automated microviscometer (Anton Paar AMVn). The measured viscosity value was 0.369 mPa·s. This disagreement could be due to a difference in the purity because they used a sample with less purity (< 99 mol %) than ours. Also, the kinematic viscosity of MTBE + heptane and MTBE + octane has been measured from (273.15 to 303.15) K and from (273.15 to 333.15) K. To the best of our knowledge, no viscosity measurements exist for these mixtures. The experimental measurements have been correlated using a three-body McAllister[9] equation

$$\ln \upsilon_m = x_1^3 \ln \upsilon_1 + 3x_1^2x_2 \ln \upsilon_{12} + 3x_1x_2^2 \ln \upsilon_{21} + x_2^3 \ln \upsilon_2 - \ln\left(x_1 + x_2\frac{M_2}{M_1}\right) + 3x_1^2x_2 \ln\left[\left(2 + \frac{M_2}{M_1}\right)/3\right] + 3x_1x_2^2 \ln\left[\left(1 + 2\frac{M_2}{M_1}\right)/3\right] + x_2^3 \ln\left(\frac{M_2}{M_1}\right) \quad (9)$$

where subscript i refers to the pure component i; x_i is the molar composition; υ_i is the kinematic viscosity; M_i is the molecular weight; and υ_{12} and υ_{21} are adjustable parameters that represent the interaction between molecules 1 and 2. Table 8 contains the values of υ_{12} and υ_{21} from (273.15 to 288.15) K, and Figure 5 presents the composition behavior of eq 9. Dynamic viscosities of these mixtures appear at different temperatures and compositions in Tables 9 and 10. Viscosity deviations for these mixtures are negative but practically zero, so they behave like an ideal solution for equilibrium thermodynamic properties.

Conclusions

Atmospheric liquid densities of binary systems of MBTE have been measured over the entire composition range from (273.15 to 343.15) K for a heptane mixture and from (273.15 to 363.15) K for an octane mixture. The new density measurements agree with those in the literature within 0.05 %. The excess molar volumes for these mixtures have positive deviations from ideality for the temperatures covered in this work. We have

Table 9. Experimental Viscosities for MTBE (1) + Heptane (2)

	η/mPa·s								
T/K	$x_1 = 0.1004$	$x_1 = 0.1998$	$x_1 = 0.3008$	$x_1 = 0.4024$	$x_1 = 0.5007$	$x_1 = 0.5989$	$x_1 = 0.6981$	$x_1 = 0.7887$	$x_1 = 0.898$
273.15	0.515	0.507	0.494	0.485	0.476	0.468	0.462	0.456	0.448
278.15	0.484	0.474	0.464	0.456	0.448	0.440	0.433	0.427	0.421
283.15	0.455	0.446	0.437	0.429	0.422	0.414	0.408	0.403	0.397
288.15	0.429	0.421	0.413	0.405	0.398	0.391	0.385	0.380	0.375
293.15	0.406	0.398	0.390	0.383	0.376	0.369	0.364	0.359	
298.15	0.384	0.377	0.370	0.363	0.357				
303.15	0.365	0.358	0.351	0.344					
308.15	0.347	0.340							
313.15	0.330								

Table 10. Experimental Viscosities for MTBE (1) + Octane (2)

	η/mPa·s								
T/K	$x_1 = 0.1019$	$x_1 = 0.2189$	$x_1 = 0.3026$	$x_1 = 0.4029$	$x_1 = 0.4995$	$x_1 = 0.6099$	$x_1 = 0.7072$	$x_1 = 0.7981$	$x_1 = 0.8941$
273.15	0.685	0.651	0.622	0.597	0.570	0.549	0.525	0.494	0.472
278.15	0.638	0.607	0.583	0.559	0.534	0.514	0.492	0.462	0.442
283.15	0.597	0.568	0.545	0.523	0.501	0.483	0.462	0.435	0.417
288.15	0.559	0.533	0.514	0.492	0.471	0.454	0.435	0.410	0.393
293.15	0.525	0.501	0.483	0.464	0.445	0.428	0.411	0.388	0.372
298.15	0.495	0.473	0.455	0.439	0.420	0.405	0.388	0.367	0.367
303.15	0.468	0.447	0.430	0.414	0.397	0.382			
308.15	0.443	0.425	0.409	0.393	0.376	0.362			
313.15	0.420	0.402	0.387	0.374	0.358				
318.15	0.398	0.381	0.367	0.355					
323.15	0.377	0.361	0.349						
328.15	0.359	0.344							
333.15	0.342								

correlated these properties using Redlich−Kister-type equations. Also, our results show that the PFP theory predicts more closely the excess molar volume behavior for these mixtures than using densities from the PR EOS. The disagreement of the EOS could be due to the fact that no interaction parameter is considered in the calculation of the densities. Both models correctly predict positive deviations, but the PFP theory agrees closely with the experimental data within 0.04 $cm^3\cdot mol^{-1}$.

We also have measured the viscosities of both systems at temperatures between (273.15 and 333.15) K and correlated our results with the McAllister equation. We have not found any other experimental values in the literature.

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