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Densities and Excess Molar Volumes of Methyl *tert*-Butyl Ether and Ethyl *tert*-Butyl Ether with Hydrocarbons from 255.4 to 333.2 K

Adisak Jangkamolkulchai,* Gregory C. Allred, and William R. Parrish

Phillips Petroleum Company, Bartlesville, Oklahoma 74004

This paper reports densities of methyl *tert*-butyl ether and ethyl *tert*-butyl ether from 255.4 to 333.2 K, at pressures up to 8.3 bar, and densities and excess molar volumes of (1) binary mixtures of (2,2,4-trimethylpentane or toluene) + (methyl *tert*-butyl ether or ethyl *tert*-butyl ether) at 288.7 K, and atmospheric pressure, (2) mixtures of gasoline + (methyl *tert*-butyl ether or ethyl *tert*-butyl ether) at 288.7, 299.8, and 310.9 K, at pressures up to 8.3 bar, and (3) ternary mixtures of 34.0 mass % toluene in 2,2,4-trimethylpentane + (methyl *tert*-butyl ether or ethyl *tert*-butyl ether) at 288.7 K, and atmospheric pressure. Excess molar volumes for all mixtures studied are small (less than 0.46% of the total mixture molar volume). Mixtures of methyl *tert*-butyl ether or ethyl *tert*-butyl ether with 2,2,4-trimethylpentane show positive excess molar volumes, while mixtures of methyl *tert*-butyl ether or ethyl *tert*-butyl ether with toluene have negative excess molar volumes. Excess molar volumes for 2,2,4-trimethylpentane + toluene + (methyl *tert*-butyl ether or ethyl *tert*-butyl ether) are qualitatively similar to those for gasoline + (methyl *tert*-butyl ether or ethyl *tert*-butyl ether); excess molar volumes are positive for those mixtures containing methyl *tert*-butyl ether and negative for mixtures containing ethyl *tert*-butyl ether.

Introduction

The recently passed Clean Air Act mandates that oxygenates be blended with gasoline in specific geographic regions to reduce carbon monoxide emissions from motor vehicles. The Environmental Protection Agency (EPA) has granted waivers to use ethanol and methanol (with cosolvent) as fuel additives, but alcohol–gasoline blends are susceptible to splitting into two phases if water is present. Also, because they have relatively high polarity, alcohols can significantly increase the volatility of the fuel. This would force refiners to reduce the amount of butanes in gasoline.

Both methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE) have high octane numbers, are less polar than alcohols, and do not alter gasoline volatility. Therefore, they are considered good alternatives to alcohols. To ensure fair trade of ether + gasoline mixtures, the density of the mixture needs to be known accurately. Limited density data are available for pure MTBE and ETBE (*1–3*), but we know of no published data for these ethers with hydrocarbons. This paper reports densities for pure MTBE and ETBE from 255.4 to 333.2 K, at pressures to 8.3 bar. Also, we report mixture densities and excess molar volumes for binary mixtures of (2,2,4-trimethylpentane (TMP) or toluene) + (MTBE or ETBE) at 288.7 K, ternary mixtures of TMP + toluene + (MTBE or ETBE) at 288.7 K, up to 20 mol % ethers, and mixtures of gasoline + (MTBE or ETBE) at 288.7, 299.8, and 310.9 K, up to 18 mol % ethers.

Experimental Section

All densities were measured with an Anton-Paar DMA 602 HT vibrating-tube densimeter. This technique requires two density standards; we used freshly boiled, deionized, distilled water and dry nitrogen. The density of water was calculated from the correlation given by Kell (*4*), and that of nitrogen by the modified Berthelot equation given by Ott et al. (*5*). *n*-Pentane was used as a standard at temperatures below 276 K. The density of *n*-pentane was calculated with the correlation given by Kratzke et al. (*6*). The temperature was measured with a thermistor thermometer (Digitec HT5510) inserted into a thermowell in the glass densimeter cell. The densimeter temperature was known to within ±0.1 K and was held constant within ±0.01 K. Pressurization of the densimeter was achieved by interfacing a pressurized nitrogen line and densimeter through a thick-wall glass capillary tube, using $^1/_8$-in. stainless steel tubing and fittings. The capillary minimizes diffusion of nitrogen into the liquid samples. Because the vibrational period of the densimeter remained constant, no diffusion effect was observed during a course of a run (typically 10–15 min per sample). The pressure in the densimeter was known to within ±0.05 bar.

Table I gives sources, purities as received from the suppliers, measured densities, and published densities for all the chemicals used in this study. Compositional analysis of gasoline was performed by using a gas chromatographic technique, and the results are summarized in Table II. The molecular weight of the gasoline was determined to be 107, using a freezing point depression technique. We distilled the ethyl *tert*-butyl ether under nitrogen in a column packed with glass helices and discarded the first 20% and the last 10% of each distillation batch. The purity of distilled ethyl *tert*-butyl ether was chromatographically checked and found to be better than 99 mol %. Other chemicals were used as received. Because of its high vapor pressure, gasoline was kept under nitrogen atmosphere, at 273 K. We degassed all chemicals just prior to use by placing the unopened containers in an ultrasonic bath for approximately 30 min.

Mixtures were prepared by mass in evacuated, 15-mL glass vials with Teflon-lined rubber septum caps. The vapor space in the vials was minimized to reduce compositional changes in the samples due to evaporation. The vials were reweighed before each sample was withdrawn, and the mole fraction of each component in the liquid phase was corrected for evaporation by using the measured liquid density, the ideal gas law, and ideal solution behavior. The total correction to the mole fraction was always less than 0.000 06. Reported values are average mole fraction and density for two or three density determinations on each mixture.

The excess molar volume

$$V^E = V - (x_1V_1 + x_2V_2) \tag{1}$$

was obtained from the density ρ of each mixture according to the relation

$$V^E = (x_1M_1 + x_2M_2)/\rho - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \tag{2}$$

where V is the molar volume of the mixture, x_i is the mole fraction, M_i is the molecular weight, and ρ_i is the density of pure component i.

We used a Monte Carlo error analysis method to estimate reproducibility in mixture mole fraction, density, and excess

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* To whom correspondence should be addressed.

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Table I. Sources, Purities, and Densities of Chemicals

chemical	source	purity/(mol %)	density/(g cm^{-3}) measured	density/(g cm^{-3}) published	T/K	P/bar
MTBE[a]	Aldrich	99.8	0.7453_0	0.7453[b]	288.7	1.01
ETBE[c]	Phillips	98.0	0.7451_1	0.7456[b]	288.7	1.01
TMP[d]	Fisher	99.5	0.6953_0	0.6955[e]	288.7	1.01
toluene	Fisher	99.5	0.8708_9	0.8710[e]	288.7	1.01
n-pentane	Fisher	99.5	0.6303_4	0.6305[e]	288.7	1.01
gasoline	Phillips	*f*	0.7597_3		288.7	1.01
			0.7602_3		288.7	7.17
			0.7501_6		299.8	1.01
			0.7507_3		299.8	7.31
			0.7407_6		310.9	1.38
			0.7418_9		310.9	8.27

[a] Methyl *tert*-butyl ether. [b] Data taken from ref 4, at 288.2 K. [c] Ethyl *tert*-butyl ether. [d] 2,2,4-Trimethylpentane. [e] Data taken from ref 9. [f] Compositional analysis is given in Table II.

Table II. Compositional Analysis of Gasoline in Weight Percent

no. of carbons	saturates[a] *i*-par	saturates[a] *n*-par	saturates[a] naph	unsaturates[a] *i*-par	unsaturates[a] *n*-par	unsaturates[a] naph	aromat[a]	totals
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	3.74	0.51	0.46	0.53	0.45	0.07	0.00	5.76
6	11.88	1.35	1.40	1.36	0.72	0.43	1.24	18.38
7	8.51	1.35	1.71	1.23	0.44	0.41	5.63	19.28
8	12.49	0.52	1.29	0.81	0.25	0.21	10.40	25.97
9+	5.19	0.58	1.45	0.86	0.51	0.09	15.35	24.03
totals	41.81	4.31	6.31	4.79	2.37	1.21	32.62	93.42
polynaphthenes								0.09
component(s) with bp > 473 K								6.49
total								100.00

[a] Abbreviations: *i*-par, isoparaffinics; *n*-par, normal paraffinics; naph, naphthenics; aromat, aromatics.

Table III. Densities of Methyl *tert*-Butyl Ether (MTBE) and Ethyl *tert*-Butyl Ether (ETBE)

T/K	P/bar	ρ/(g cm^{-3}) MTBE	ρ/(g cm^{-3}) ETBE
255.4	1.01	0.7796_8	0.7791_3
	7.03	0.7807_9	0.7804_1
266.5	1.01	0.7686_2	0.7682_2
	7.03	0.7691_4	0.7687_0
274.8	1.01	0.7600_4	0.7597_4
	7.03	0.7607_8	0.7604_0
280.9	1.01	0.7533_2	0.7531_6
283.2	1.01	0.7509_3	0.7507_7
	7.17	0.7516_6	0.7514_3
285.9	1.01	0.7481_1	0.7479_9
288.7	1.01	0.7453_0	0.7451_1
	7.17	0.7461_0	0.7458_8
299.8	1.01	0.7337_9	0.7337_3
	7.31	0.7344_8	0.7344_1
310.9	1.38	0.7217_8	0.7220_9
	8.27	0.7227_7	0.7229_1
322.0	1.38	0.7095_9	0.7101_3
	8.27	0.7106_6	0.7111_8
333.2	1.72	0.6971_1	0.6981_0
	8.27	0.6982_5	0.6991_7

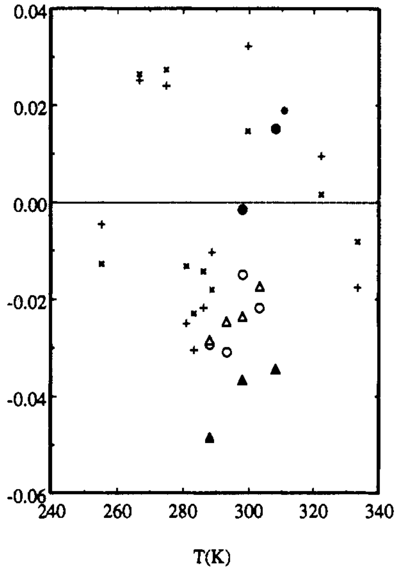

Figure 1. Deviation between smoothed (eq 3) and measured atmospheric pressure densities: (+,×) MTBE and ETBE, respectively, from Table III; (△,○) MTBE and ETBE, respectively, from ref 1; (▲,●) MTBE and ETBE, respectively, from ref 2.

molar volume based on the standard deviations of the principal independent variables. The relative standard deviations of the independent variables were estimated as 0.02%, 0.001%, 0.5%, 0.001%, and 0.0003% for mixture component mass, density of water, density of nitrogen, densimeter vibrational period for nitrogen, and densimeter vibrational period for liquid, respectively. The resulting estimated standard deviations of the calculated quantities were 0.000 03, 0.000 02 g cm^{-3}, and 0.0034 cm^3 mol^{-1} for mole fractions, mixture densities, and excess molar volumes, respectively. Because of the compositional uncertainities in the gasoline caused by evaporation of volatile components, the resulting estimated standard deviations of the calculated densities and excess molar volumes were 0.000 05 g cm^{-3} and 0.010 cm^3 mol^{-1}, respectively.

Results and Discussion

Densities of pure MTBE and ETBE are given in Table III. These data are correlated as a function of temperature by using second-order polynomial expansion

$$\rho/(\text{g cm}^{-3}) = \sum_i A_i (T/\text{K})^{i-1} \qquad i = 1, 2, 3 \tag{3}$$

where T is temperature. Coefficients A_i for atmospheric density

Table IV. Coefficients of Equation 3 for Densities of Methyl *tert*-Butyl Ether (MTBE) and Ethyl *tert*-Butyl Ether (ETBE) at 1 bar

compound	A_1	$10^4 A_2$	$10^6 s(A_2)$[a]	$10^7 A_3$	$10^8 s(A_3)$[a]	n[b]	s[c]/(g cm^{-3})
MTBE	0.9924	−6.587	6.355	−6.827	10.75	11	0.000 02
ETBE	1.0017	−7.402	5.260	−5.134	8.90	11	0.000 02

[a] Estimated standard deviation of coefficient determined from regression. [b] Number of data points, each of which is an average of two or three measurements. [c] Estimated standard deviation of fit.

Table V. Densities and Excess Molar Volumes of Binary Mixtures of (*x*)Ether + ((1 − *x*)2,2,4-Trimethylpentane, (1 − *x*)Toluene, or (1 − *x*)(34 mass % Toluene in 2,2,4-Trimethylpentane)) at 288.7 K and 1.01 bar

methyl *tert*-butyl ether			ethyl-*tert*-butyl ether		
x	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	x	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})
		2,2,4-Trimethylpentane + Ether			
0.0599_9	0.6972_8	0.05_0	0.0558_2	0.6974_4	0.04_8
0.1155_0	0.6991_3	0.10_6	0.1124_4	0.6996_3	0.10_1
0.2085_8	0.7024_2	0.18_9	0.2062_8	0.7034_3	0.17_0
0.3081_8	0.7062_6	0.25_0	0.3093_4	0.7078_5	0.22_2
0.3967_8	0.7100_4	0.27_4	0.4119_7	0.7125_1	0.25_1
0.4991_8	0.7146_8	0.29_8	0.5022_7	0.7168_4	0.25_9
0.5987_8	0.7196_7	0.29_1	0.5977_6	0.7216_6	0.24_9
0.6996_6	0.7252_0	0.26_0	0.6948_6	0.7268_2	0.22_3
0.7940_7	0.7308_9	0.20_5	0.7939_5	0.7324_3	0.16_8
0.8967_7	0.7377_1	0.11_7	0.8916_6	0.7382_8	0.09_4
0.9444_1	0.7411_2	0.06_5	0.9428_9	0.7414_8	0.04_8
		Toluene + Ether			
0.0573_8	0.8635_4	-0.08_0	0.0543_4	0.8631_0	-0.11_5
0.0960_1	0.8585_5	-0.12_3	0.1022_4	0.8563_1	-0.20_4
0.2008_9	0.8451_2	-0.22_9	0.2165_1	0.8405_2	-0.37_5
0.2996_4	0.8325_5	-0.30_2	0.3026_7	0.8289_7	-0.46_8
0.3986_5	0.8200_2	-0.35_0	0.3974_5	0.8165_9	-0.53_2
0.5019_3	0.8070_6	-0.37_5	0.4951_9	0.8041_7	-0.55_6
0.5955_2	0.7953_7	-0.37_1	0.5993_6	0.7913_2	-0.53_7
0.6955_8	0.7829_3	-0.33_6	0.6929_8	0.7800_9	-0.48_1
0.7908_5	0.7711_4	-0.27_1	0.7995_0	0.7676_6	-0.36_8
0.8824_4	0.7599_6	-0.19_7	0.8880_4	0.7575_9	-0.23_5
0.9389_0	0.7529_0	-0.10_8	0.9278_3	0.7531_3	-0.16_1
		34 mass % Toluene in 2,2,4-Trimethylpentane + Ether			
0.0617_1	0.7458_2	0.02_1	0.0537_4	0.7459_5	-0.00_5
0.1194_3	0.7458_0	0.01_9	0.1014_1	0.7459_7	-0.01_6
0.1679_8	0.7457_2	0.02_8	0.1519_9	0.7459_9	-0.02_7
0.2286_6	0.7456_7	0.03_1	0.2049_1	0.7460_1	-0.03_9

Table VI. Densities and Excess Molar Volumes for (*x*)Ether + (1 − *x*)Gasoline

methyl *tert*-butyl ether			ethyl *tert*-butyl ether			
x	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	x	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	P/bar
		T = 288.7 K				
0.1178_8	0.7582_0	0.01_4	0.1003_8	0.7584_3	-0.02_5	1.01
0.1715_3	0.7575_4	0.01_0	0.1522_0	0.7577_4	-0.03_4	1.01
0.1176_6	0.7587_2	0.01_5	0.1033_9	0.7588_6	-0.01_4	7.17
0.1793_0	0.7579_1	0.02_4	0.1553_8	0.7582_2	-0.03_1	7.17
		T = 299.8 K				
0.1156_9	0.7486_7	-0.02_6	0.1028_4	0.7483_0	0.03_9	1.01
0.1723_6	0.7477_9	-0.01_4	0.1516_5	0.7481_0	-0.07_3	1.01
0.1196_8	0.7489_1	0.02_8	0.1043_7	0.7490_7	-0.00_1	7.31
0.1809_2	0.7479_4	0.04_4	0.1559_1	0.7483_4	-0.01_9	7.31
		T = 310.9 K				
0.1171_8	0.7388_5	-0.00_1	0.1035_2	0.7389_7	-0.02_1	1.38
0.1782_5	0.7376_9	0.02_6	0.1565_0	0.7381_0	-0.04_0	1.38
0.1199_2	0.7398_7	0.00_7	0.1027_6	0.7401_0	-0.02_5	8.27
0.1751_8	0.7389_1	0.01_2	0.1565_4	0.7392_1	-0.04_7	8.27

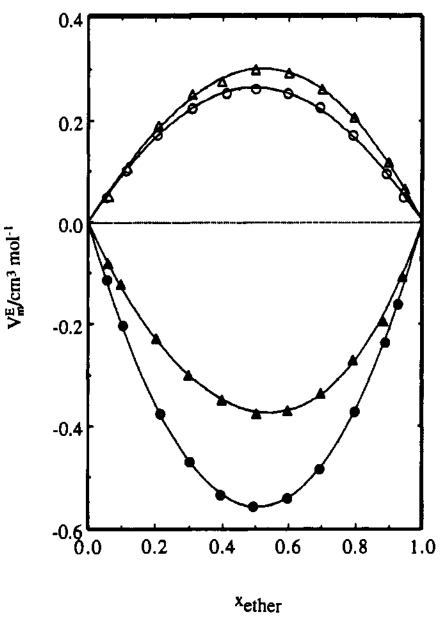

Figure 2. Excess molar volume of binary mixtures of (*x*)ether + ((1 − *x*) TMP or (1 − *x*) toluene) at 288.7 K and 1.01 bar: (-△-,-○-) TMP + (MTBE and ETBE), respectively; (-▲-,-●-) toluene + (MTBE and ETBE), respectively.

data of MTBE and ETBE were determined by linear regression. Coefficients and standard deviations from the regressions are given in Table IV. Deviations between smoothed atmospheric density data calculated from eq 3 and data of ref 1 and 2 are plotted against temperature in Figure 1. Table V shows densities and excess molar volumes for TMP + (MTBE or ETBE), toluene + (MTBE or ETBE), and TMP + toluene + (MTBE or ETBE). Densities and excess molar volumes for mixtures of gasoline + (MTBE or ETBE) are summarized in Table VI. We correlated excess molar volumes for binary mixtures of TMP + (MTBE or ETBE) and toluene + (MTBE or ETBE) as a function of composition using the Redlich–Kister expansion (*8*)

$$V^E/(\mathrm{cm^3\,mol^{-1}}) = x(1-x)\sum_i B_i(1-2x)^{i-1} \qquad i = 1, 2, 3, \ldots \qquad (4)$$

where x is the mole fraction of ether. Coefficients B_i for each binary system were determined by using linear regression. Coefficients and standard deviations from the regressions are given in Table VII.

Excess molar volumes at 288.7 K and smooth curves calculated from eq 4 for (TMP or toluene) + ether binary systems are shown in Figure 2. Excess molar volumes of ternary mixtures of 34 wt % toluene in TMP, which approximately represents the aromatic content of gasoline, + (MTBE or ETBE) are shown in Figure 3. Figures 4 and 5 are plots of excess molar volumes of gasoline + (MTBE or ETBE) mixtures.

Pure component densities for MTBE and ETBE differ by less than 0.15% over the temperature range examined. However, the effect of temperature on density is slightly greater for MTBE than ETBE, as can be seen from data in Table III. The densities of the two ethers are equal at approximately 298.7 K (calculated from the fitting equations). Densities of MTBE and ETBE at 8 bar are within 0.16% of their atmospheric densities.

Both MTBE and ETBE exhibit positive excess molar volumes when mixed with TMP. Conversely, mixtures of MTBE and ETBE with toluene show negative excess molar volumes. Excess molar volumes of ternary mixtures of TMP + toluene + (MTBE or ETBE) show some unusual behavior, as shown in

Table VII. Coefficients of Equation 4 at 288.7 K

mixture	B_1	$s(B_1)^a$	B_2	$s(B_2)^a$	B_3	$s(B_3)^a$	n^b	s^c/(cm^3 mol^{-1})
TMP + MTBE	1.1951	0.0005	−0.1177	0.0008	−0.0569	0.0011	11	0.0052
TMP + ETBE	1.0459	0.0003	0.0042	0.0004	−0.0831	0.0005	11	0.0031
toluene + MTBE	−1.4870	0.0006	0.2217	0.0009	−0.2240	0.0013	11	0.0057
toluene + ETBE	−2.2239	0.0001	0.0729	0.0002	−0.1063	0.0002	11	0.0018

[a] Estimated standard deviation of coefficient determined from regression. [b] Number of data points, each of which is an average of two or three measurements. [c] Estimated standard deviation of fit.

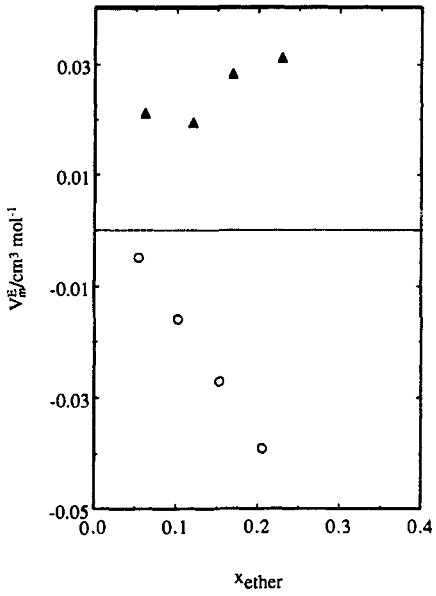

Figure 3. Excess molar volume of (x)ethers + (1 − x)(34 wt % toluene) in TMP at 288.7 K and 1.01 bar: (▲) MTBE; (O) ETBE.

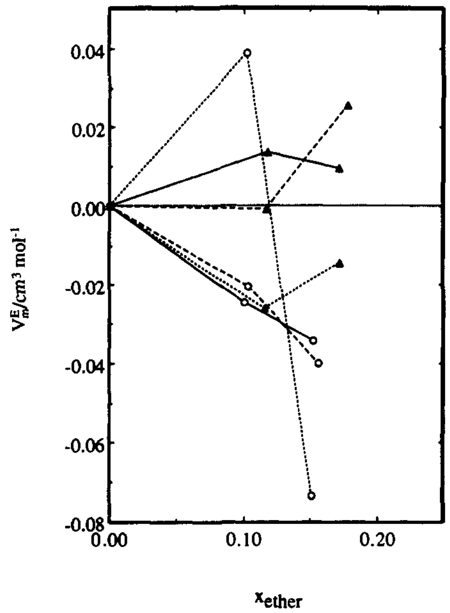

Figure 4. Excess molar volume of (x)ethers + (1 − x)gasoline: (▲) MTBE; (O) ETBE; (—) 288.7 K and 1.01 bar; (- -) 299.8 K and 1.01 bar; (– –) 310.9 K and 1.38 bar.

Figure 3. The ternary mixture with MTBE exhibits positive excess molar volumes with two extreme values over the composition range examined: one at approximately 7 mol % MTBE and the other at approximately 23 mol % MTBE. Furthermore, excess molar volumes of the ternary mixture with ETBE are negative and do not extrapolate to zero, suggesting a possibility of having positive values at very low concentrations. These trends are qualitatively similar to those found in gasoline + (MTBE or ETBE) mixtures, as shown in Figures 4 and 5.

It should be noted that scattering of data for gasoline mixtures, as seen in Figure 4, may be due largely to compositional uncertainty of gasoline, specifically evaporation of some light ends (C4 or C5 hydrocarbons) from gasoline. This is based on the fact that densities of gasoline mixtures at 8 bar, taken at a later period of this study, behave more smoothly. This is presumably because the gasoline contains fewer light ends. Regardless of this uncertainty, the overall trend of excess molar volumes of gasoline mixtures is qualitatively similar to that of ternary mixtures.

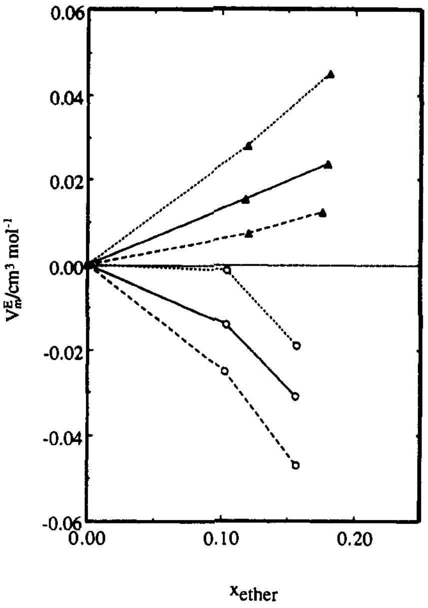

Figure 5. Excess molar volume of (x)ethers + (1 − x)gasoline: (▲) MTBE; (O) ETBE; (—) 288.7 K and 7.17 bar; (- -) 299.8 K and 7.31 bar; (– –) 310.9 K and 8.27 bar.

Conclusions

Excess molar volumes at 288.7 K for binary mixtures of TMP + (MTBE or ETBE) are positive and less than 0.3 cm^3 mol^{-1}, with ETBE being slightly lower. Binary mixtures of toluene + (MTBE or ETBE) show relatively larger negative excess molar volumes (less than −0.6 cm^3 mol^{-1}). Excess molar volumes of these four mixtures are small (less than 0.46% of the total mixture molar volumes). Excess molar volumes of ternary mixtures of TMP + toluene + (MTBE or ETBE) exhibit both positive and negative excess molar volumes over the composition range studied. These results are qualitatively similar to those of gasoline mixtures.

Finally, EPA mandates that no more than 15 vol % of oxygenates can be blended in the fuels. Over this range, the excess molar volumes of (MTBE or ETBE) + gasoline mixtures are less than 0.05% of the total mixture molar volume. This means that, for custody-transfer purposes, the excess volume correction can be ignored when the densities of (MTBE or ETBE) + gasoline mixtures are computed.

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Registry No. TMP, 540-84-1; MTBE, 1634-04-4; ETBE, 637-92-3; toluene, 108-88-3.

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