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# Densities of Mixtures of Heptane + Methyl 1,1-Dimethylethyl Ether at Temperatures between 243.16 and 333.14 K

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This paper reports densities and excess volumes of binary mixtures of heptane and methyl 1,1-dimethylethyl ether (methyl *tert*-butyl ether, MTBE) at 243.16, 278.15, 288.17, 293.10, 313.14, and 333.14 K. Data were obtained at 0.34, 1.72, and 4.83 MPa. Mixture compositions were between 5 and 95 mol %. Equimolar excess volumes are about 0.4 $cm^3 \cdot mol^{-1}$ and are weak functions of temperature and pressure.

## Introduction

With government mandates for including oxygenates (alcohols or ethers) in motor fuels, there is a need to develop accurate density tables for custody transfer purposes. Under contract to the American Petroleum Institute, this laboratory obtained accurate densities of mixtures of four different gasolines with each of six oxygenates including methyl 1,1-dimethylethyl ether (methyl *tert*-butyl ether, MTBE). Results will be reported in a forthcoming paper.

Densities of binary mixtures of MTBE with gasoline components are needed to guide density correlations for gasoline + oxygenate mixtures. Densities of binary mixtures of MTBE with gasoline, toluene, and 2,2,4-trimethylpentane are given by Jangkamolkulchai et al. (1991). Kumaran et al. (1993) report densities for mixtures of MTBE with $C_6$ hydrocarbons. However, we know of no previous work involving binary mixtures of heptane with MTBE.

This paper gives densities of binary mixtures of heptane with MTBE, obtained at the same temperatures and pressures as the gasoline + oxygenate data mentioned previously. Heptane + MTBE densities were obtained at 243.16, 278.15, 288.17, 293.10, 313.14, and 333.14 K and at 0.34, 1.72, and 4.83 MPa. Ambient pressure could not be used because bubble point pressures for these mixtures exceed 0.1 MPa at the higher temperatures.

## Experimental Section

Table 1 gives the sources and purities of the compounds used in this study. All reagents were used as received. The table also compares our densities of heptane and MTBE with literature values. Our data were extrapolated in pressure and interpolated in temperature for the comparison. Agreement is within ±0.1%.

All density measurements were made using Anton-Paar DMA 512 vibrating-tube densimeters. To minimize potential problems of fractionation, the sample was charged one time to six densimeters connected in series. All but the 288.17 and 293.10 K densimeters were immersed in constant temperature baths. The 288.17 and 293.10 K densimeters were temperature controlled by flowing coolant from constant temperature baths through the jackets of the densimeters. The tubing between each bath and densimeter was insulated to help maintain constant temperature. All baths had a long-term stability of ±0.005 K or better. However, the 288.17 and 293.10 K densimeters had a stability of ±0.01 K as measured inside the densimeter cell. Temperature indicators were calibrated against a platinum resistance thermometer with a calibration traceable to the National Institute of Standards and Technology. The calibration used the IPTS-68 temperature scale, but the temperatures were corrected to the ITS-90 temperature scale (Goldberg and Weir, 1992). The estimated uncertainty in the temperature is ±0.02 K. Pressure was measured using a 0–1000 psi double-revolution Hiese gauge calibrated against a dead weight gauge. The estimated maximum uncertainty in the pressure is ±0.014 MPa. System pressures, 0.34, 1.72, and 4.83 MPa, were set by adjusting the volume of the liquid-full system via a hand-driven, positive displacement pump containing pentane. The pump was located downstream of the densimeters to prevent sample contamination.

**Table 1. Reagents and Densities**

| reagent | source | % water | % purity | $\varrho/(g \cdot cm^{-3})$ this work[a] | $\varrho/(g \cdot cm^{-3})$ lit. | *T*/K |
|---|---|---|---|---|---|---|
| nitrogen | Linde | | | | | |
| pentane | Fisher | 0.003 | 99.6 | | | |
| heptane | Fisher | 0.004 | 99.6 | $0.6802_9$ | 0.67957[b] | 298.15 |
| MTBE | Aldrich | 0.01 | 99.8 | $0.7461_1$ | $0.7453_0$[c] | 288.7 |

[a] The densities were extrapolated to 0.10 MPa and interpolated to the literature temperature. [b] Treszczanowicz and Benson (1977). [c] Jangkamolkulchai et al. (1991).

To prevent sample flashing, the samples were charged into the system using dry nitrogen at about 0.5 MPa while the pressure in the system was maintained at approximately 0.4 MPa using a dome-loaded back-pressure regulator. The sample charge vessel was configured with a dip tube to draw sample from the bottom of a 110 $cm^3$ bottle inside the vessel. Sufficient liquid always remained in the bottle to prevent nitrogen from entering the densimeters. The system was charged to provide a liquid-full system.

All mixtures were prepared by mass in clean 110 $cm^3$ bottles. To minimize fractionation, the samples were filled to leave less than 3 $cm^3$ vapor space. The estimated maximum uncertainty in the mole fraction is 0.0001 in the minor component. Mixtures were homogenized by placing the closed sample containers in an ultrasonic bath for 10 min.

Densities of the mixtures were determined from the vibrational period of the densimeter using the relation

$$\varrho = \varrho_r + k(\tau^2 - \tau_r^2) \tag{1}$$

where $\varrho$ is the density and $\tau$ is the vibrational period of the densimeter. The subscript, r, refers to a reference standard, and $k$ is the calibration constant, obtained from

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**Table 2. Densities and Excess Volumes of $x$ MTBE + $(1 - x)$ Heptane as a Function of Mole Fraction, Temperature, and Pressure**

| | 243.16 K | | 278.15 K | | 288.17 K | | 293.10 K | | 313.14 K | | 333.14 K | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $x$ | $\varrho$/(g·cm$^{-3}$) | $V^E$/(cm$^3$·mol$^{-1}$) | $\varrho$/(g·cm$^{-3}$) | $V^E$/(cm$^3$·mol$^{-1}$) | $\varrho$/(g·cm$^{-3}$) | $V^E$/(cm$^3$·mol$^{-1}$) | $\varrho$/(g·cm$^{-3}$) | $V^E$/(cm$^3$·mol$^{-1}$) | $\varrho$/(g·cm$^{-3}$) | $V^E$/(cm$^3$·mol$^{-1}$) | $\varrho$/(g·cm$^{-3}$) | $V^E$/(cm$^3$·mol$^{-1}$) |
| | | | | | | 0.34 MPa | | | | | | |
| 0.0000 | 0.7260 | 0.00 | 0.6973 | 0.00 | 0.6889 | 0.00 | 0.6847 | 0.00 | 0.6676 | 0.00 | 0.6500 | 0.00 |
| 0.0498 | 0.7282 | 0.09 | 0.6993 | 0.10 | 0.6908 | 0.10 | 0.6865 | 0.10 | 0.6693 | 0.10 | 0.6515 | 0.11 |
| 0.1013 | 0.7305 | 0.20 | 0.7013 | 0.20 | 0.6929 | 0.19 | 0.6886 | 0.18 | 0.6712 | 0.20 | 0.6532 | 0.20 |
| 0.1523 | 0.7331 | 0.24 | 0.7037 | 0.24 | 0.6951 | 0.25 | 0.6908 | 0.24 | 0.6732 | 0.26 | 0.6550 | 0.27 |
| 0.2988 | 0.7409 | 0.36 | 0.7107 | 0.38 | 0.7019 | 0.38 | 0.6974 | 0.38 | 0.6794 | 0.39 | 0.6606 | 0.42 |
| 0.5053 | 0.7534 | 0.41 | 0.7220 | 0.45 | 0.7128 | 0.45 | 0.7081 | 0.46 | 0.6892 | 0.48 | 0.6696 | 0.50 |
| 0.7013 | 0.7669 | 0.38 | 0.7343 | 0.40 | 0.7247 | 0.41 | 0.7198 | 0.41 | 0.7001 | 0.43 | 0.6795 | 0.45 |
| 0.8555 | 0.7792 | 0.22 | 0.7455 | 0.24 | 0.7356 | 0.24 | 0.7305 | 0.24 | 0.7100 | 0.26 | 0.6886 | 0.27 |
| 0.8970 | 0.7827 | 0.18 | 0.7487 | 0.19 | 0.7387 | 0.19 | 0.7336 | 0.19 | 0.7128 | 0.21 | 0.6912 | 0.22 |
| 0.9479 | 0.7874 | 0.09 | 0.7529 | 0.10 | 0.7428 | 0.09 | 0.7376 | 0.10 | 0.7166 | 0.10 | 0.6947 | 0.11 |
| 1.0000 | 0.7922 | 0.00 | 0.7573 | 0.00 | 0.7471 | 0.00 | 0.7418 | 0.00 | 0.7206 | 0.00 | 0.6983 | 0.00 |
| | | | | | | 1.72 MPa | | | | | | |
| 0.0000 | 0.7269 | 0.00 | 0.6985 | 0.00 | 0.6902 | 0.00 | 0.6860 | 0.00 | 0.6691 | 0.00 | 0.6518 | 0.00 |
| 0.0498 | 0.7291 | 0.09 | 0.7004 | 0.10 | 0.6921 | 0.10 | 0.6878 | 0.10 | 0.6708 | 0.10 | 0.6533 | 0.11 |
| 0.1013 | 0.7314 | 0.19 | 0.7025 | 0.19 | 0.6942 | 0.20 | 0.6899 | 0.18 | 0.6727 | 0.20 | 0.6550 | 0.20 |
| 0.1523 | 0.7340 | 0.24 | 0.7049 | 0.24 | 0.6964 | 0.24 | 0.6922 | 0.23 | 0.6748 | 0.25 | 0.6569 | 0.27 |
| 0.2988 | 0.7418 | 0.37 | 0.7119 | 0.38 | 0.7033 | 0.38 | 0.6988 | 0.38 | 0.6809 | 0.40 | 0.6625 | 0.41 |
| 0.5053 | 0.7543 | 0.42 | 0.7232 | 0.45 | 0.7143 | 0.43 | 0.7095 | 0.46 | 0.6909 | 0.48 | 0.6716 | 0.50 |
| 0.7013 | 0.7679 | 0.38 | 0.7356 | 0.39 | 0.7262 | 0.40 | 0.7213 | 0.41 | 0.7018 | 0.43 | 0.6816 | 0.44 |
| 0.8555 | 0.7802 | 0.23 | 0.7468 | 0.24 | 0.7370 | 0.25 | 0.7320 | 0.24 | 0.7118 | 0.26 | 0.6908 | 0.27 |
| 0.8970 | 0.7837 | 0.18 | 0.7500 | 0.19 | 0.7401 | 0.19 | 0.7351 | 0.19 | 0.7147 | 0.21 | 0.6934 | 0.22 |
| 0.9479 | 0.7884 | 0.09 | 0.7542 | 0.09 | 0.7442 | 0.10 | 0.7391 | 0.10 | 0.7185 | 0.10 | 0.6969 | 0.11 |
| 1.0000 | 0.7932 | 0.00 | 0.7587 | 0.00 | 0.7485 | 0.00 | 0.7433 | 0.00 | 0.7224 | 0.00 | 0.7006 | 0.00 |
| | | | | | | 4.83 MPa | | | | | | |
| 0.0000 | 0.7289 | 0.00 | 0.7010 | 0.00 | 0.6929 | 0.00 | 0.6888 | 0.00 | 0.6723 | 0.00 | 0.6556 | 0.00 |
| 0.0498 | 0.7311 | 0.09 | 0.7030 | 0.10 | 0.6949 | 0.09 | 0.6907 | 0.10 | 0.6741 | 0.10 | 0.6571 | 0.11 |
| 0.1013 | 0.7334 | 0.18 | 0.7051 | 0.19 | 0.6969 | 0.19 | 0.6928 | 0.18 | 0.6760 | 0.19 | 0.6589 | 0.20 |
| 0.1523 | 0.7360 | 0.23 | 0.7075 | 0.23 | 0.6992 | 0.24 | 0.6951 | 0.22 | 0.6781 | 0.25 | 0.6608 | 0.26 |
| 0.2988 | 0.7439 | 0.36 | 0.7146 | 0.37 | 0.7062 | 0.36 | 0.7018 | 0.37 | 0.6844 | 0.38 | 0.6666 | 0.40 |
| 0.5053 | 0.7564 | 0.41 | 0.7260 | 0.43 | 0.7173 | 0.43 | 0.7127 | 0.44 | 0.6945 | 0.46 | 0.6759 | 0.48 |
| 0.7013 | 0.7701 | 0.36 | 0.7385 | 0.38 | 0.7294 | 0.37 | 0.7245 | 0.39 | 0.7057 | 0.41 | 0.6862 | 0.42 |
| 0.8555 | 0.7825 | 0.22 | 0.7498 | 0.24 | 0.7403 | 0.22 | 0.7354 | 0.23 | 0.7157 | 0.25 | 0.6955 | 0.26 |
| 0.8970 | 0.7859 | 0.18 | 0.7530 | 0.19 | 0.7434 | 0.18 | 0.7384 | 0.19 | 0.7186 | 0.20 | 0.6981 | 0.21 |
| 0.9479 | 0.7906 | 0.09 | 0.7572 | 0.10 | 0.7476 | 0.09 | 0.7425 | 0.10 | 0.7224 | 0.10 | 0.7017 | 0.10 |
| 1.0000 | 0.7955 | 0.00 | 0.7617 | 0.00 | 0.7518 | 0.00 | 0.7468 | 0.00 | 0.7264 | 0.00 | 0.7054 | 0.00 |

**Table 3. Coefficients of Eq 4 and Standard Deviation of the Fit**[a]

| | 0.34 MPa | | | 1.72 MPa | | | 4.83 MPa | | |
|---|---|---|---|---|---|---|---|---|---|
| $T$/K | $a_0$ | $a_2$ | $\sigma$/(cm$^3$·mol$^{-1}$) | $a_0$ | $a_2$ | $\sigma$/(cm$^3$·mol$^{-1}$) | $a_0$ | $a_2$ | $\sigma$/(cm$^3$·mol$^{-1}$) |
| 243.16 | 1.669<br>(0.035) | 0.445<br>(0.112) | 0.011 | 1.689<br>(0.023) | 0.377<br>(0.073) | 0.007 | 1.643<br>(0.023) | 0.379<br>(0.073) | 0.007 |
| 278.15 | 1.797<br>(0.025) | 0.379<br>(0.081) | 0.008 | 1.794<br>(0.020) | 0.314<br>(0.066) | 0.007 | 1.733<br>(0.023) | 0.352<br>(0.072) | 0.007 |
| 288.17 | 1.823<br>(0.027) | 0.323<br>(0.087) | 0.009 | 1.747<br>(0.028) | 0.479<br>(0.089) | 0.009 | 1.710<br>(0.024) | 0.289<br>(0.076) | 0.008 |
| 293.10 | 1.850<br>(0.024) | 0.193<br>(0.076) | 0.008 | 1.838<br>(0.031) | 0.157<br>(0.100) | 0.010 | 1.771<br>(0.029) | 0.220<br>(0.092) | 0.009 |
| 313.14 | 1.913<br>(0.032) | 0.364<br>(0.103) | 0.010 | 1.913<br>(0.027) | 0.346<br>(0.087) | 0.009 | 1.831<br>(0.024) | 0.362<br>(0.077) | 0.008 |
| 333.14 | 2.012<br>(0.026) | 0.378<br>(0.083) | 0.008 | 1.984<br>(0.027) | 0.375<br>(0.087) | 0.009 | 1.888<br>(0.023) | 0.414<br>(0.074) | 0.008 |

[a] Values in parentheses are estimated standard deviations of the coefficients. Note that the coefficient $a_1$ was not used because it was statistically insignificant in all regressions.

two reference standards. For our work we used nitrogen (Ott et al., 1971) and pentane (Kratzke et al., 1985). Our measurements on pure toluene agree with those of Dymond et al. (1988) and Muringer et al. (1985) to better than ±0.1%. An estimated precision in the density was calculated from the standard deviation of $\tau$ values for pentane used in the calibration. On the basis of seven replicate measurements, the standard deviation for the data measured at 243.16 K was ±0.05%, but at the other temperatures the standard deviation was less than ±0.01%.

## Results and Discussion

Table 2 presents densities of the pure components and mixtures as well as the excess molar volumes

$$V^E = V - (x_1V_1 + x_2V_2) \tag{2}$$

computed from

$$V^E = (x_1M_1 + x_2M_2)/\varrho - (x_1M_1/\varrho_1 + x_2M_2/\varrho_2) \tag{3}$$

where $V$ and $\varrho$ are the molar volume and density of the mixture, respectively, and $x_i$ is the mole fraction, $M_i$ is the molecular weight, and $\varrho_i$ is the density of pure component $i$. The estimated standard deviation of $V^E$ is ±0.1 cm$^3$·mol$^{-1}$ at 243.16 K and ±0.03 cm$^3$·mol$^{-1}$ at the other temperatures.

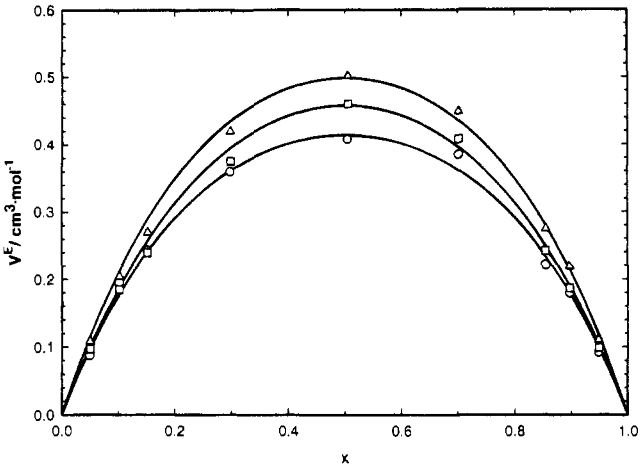

**Figure 1.** Excess volumes of $x$ MTBE + $(1 - x)$ heptane as a function of composition at 243.16 (○), 293.10 (□), and 333.14 K (△).

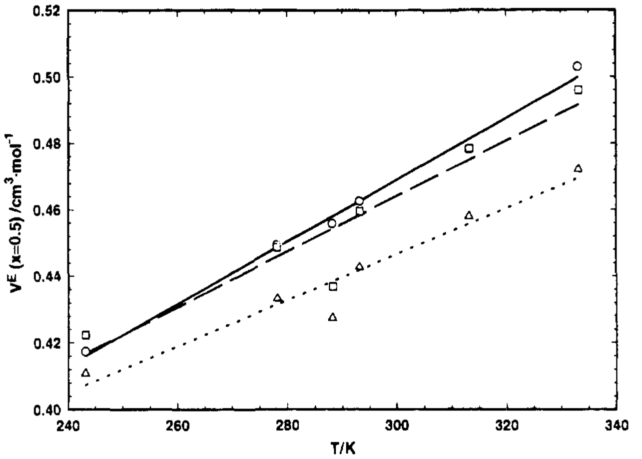

**Figure 2.** Equimolar excess volumes, $V^E$ ($x$ = 0.5), as a function of pressure at 0.34 (○), 1.72 (□) and 4.83 MPa (△).

Table 3 presents the regression coefficients obtained by fitting the excess volumes to the Redlich-Kister equation (Redlich and Kister, 1948)

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x(1-x)\sum_{i=0}^{2} a_i(1-2x)^i \qquad (4)$$

where $x$ refers to the mole fraction of MTBE. For these mixtures, the $a_1$ coefficient was always statistically insignificant. This implies that the excess volume curve is completely symmetrical around the equimolar value and that there are no strong interactions between the two compounds. Figure 1 shows the compositional dependence of excess volumes for three temperatures at 0.34 MPa.

Figure 2 shows the effects of temperature and pressure on the equimolar excess volume calculated from $a_0$ values in Table 3. This plot shows the weak pressure dependence over the range studied as well as the weak, linear temperature dependence.

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