

Compressed-liquid Densities of the Binary Mixture Dimethyl Carbonate + Heptane at Three Compositions*

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Abstract

Compressed-liquid densities of the binary system dimethyl carbonate + heptane have been measured with a vibrating-tube densimeter over the temperature and pressure ranges of 270 K to 470 K, and 1 MPa to 50 MPa at three compositions of the mixture. The measurements are part of an effort to better understand the molecular interactions of polar/non-polar mixtures. These types of mixtures often exhibit very non-ideal behavior. By measuring the mixture at three compositions and over a large range of temperature and pressure, the non-ideality can be assessed. There are no high-pressure liquid density data for this binary system in the literature, thus data reported here could only be compared to literature data at atmospheric pressure to establish their quality. The majority of literature data agree well with the presented results which have a maximum expanded uncertainty of $1.63 \text{ kg}\cdot\text{m}^{-3}$ (for the composition with the greatest mole fraction of dimethyl carbonate). The non-ideality for the mixture, in the temperature, pressure and composition range of this study was found to be minimal. This is rationalized by considering the molecular sizes, shapes, and charge distributions of the pure components and the attractive parts of their intermolecular force fields as they are reflected in the temperature ranges of their vapor pressure curves.

Keywords

Binary mixture; Compressed liquid; Density; Dimethyl Carbonate; Equation of State; Heptane; Vibrating-tube densimeter

1. Introduction

As a pure fluid, dimethyl carbonate (DMC) is widely used in the electrolyte solution of lithium ion batteries,¹ in the synthesis of pharmaceuticals and industrial chemicals,² and as a lubricant with HFC refrigerants.³ These are just a few of its applications. Dimethyl carbonate has such a large number of current and potential applications that it is estimated that by 2025 its global market will reach \$553 million.²

Dimethyl carbonate however, is seldom utilized as a pure fluid, and it is a polar molecule. Polar molecules mixed with non-polar molecules often lead to azeotropy in their vapor-liquid equilibria and minima in the concentration dependencies of their densities, speeds of sound, viscosities and other properties. It is thus important to understand and be able to predict how dimethyl carbonate will interact with other molecules in a given application. Several researchers have measured thermophysical properties of dialkyl carbonate + n-alkane mixtures.⁴⁻¹³ Such data facilitate the development of molecular models that can be used to predict thermophysical properties of those systems and similar systems.

In this work, the binary mixture of dimethyl carbonate + heptane was chosen for study because there are no wide-ranging liquid density data in the literature. The density data that do exist, are at atmospheric pressure and in a limited temperature range. The measurements presented herein, greatly expand the temperature and pressure range of density data available for this mixture. In addition to expanding the available data for dialkyl carbonate + n-alkane mixtures, measuring the densities of the dimethyl carbonate + heptane mixture at three compositions and over a large range of temperature and pressure, allows an assessment of the polar/non-polar molecular interactions of this system.

2. Material and Methods

The pure fluids dimethyl carbonate (CAS # 616-38-6) and heptane (CAS # 142-82-5) used to make the mixtures studied in this work were purchased from Sigma-Aldrich Corporation.[§] Purity analyses of the samples (as received from the manufacturer) were performed in our laboratories by gas chromatography (GC) with mass spectrometry (MS). Conditions of the GC-MS (single quad) method were a 5% phenyl dimethylpolysiloxane stationary phase, 0.25 μm film, temperature program from 50 °C at 3 °C per minute to 90 °C, then at 6 °C per minute to 170 °C, 100:1 split injector isothermal at 325 °C, 168.7 kPa constant pressure, and m/z range 32-550 Da. Karl-Fischer analysis was also performed on each of the samples prior to mixture preparation to determine the water content. Results of the analysis are shown in Table 1.

	Manufacturer	GC/MS raw area count [%]	Impurity, raw area count [%]	Karl Fischer water content [$\mu\text{g/g}$]
Dimethyl carbonate	Sigma-Aldrich	99.9	propane or CO ₂ ,* 0.1	10 \pm 20
Heptane	Sigma-Aldrich	99.07	2-methylhexane, 0.24 3-methylhexane, 0.34 methylcyclohexane, 0.36	19 \pm 20

Table 1. Results of analyses of dimethyl carbonate and heptane used to prepare mixtures. *The analysis could not resolve if the impurity was propane or carbon dioxide.

The binary mixtures of dimethyl carbonate + heptane measured in this work were prepared gravimetrically in 300 mL stainless steel cylinders. The balance used in the preparation of the mixtures has a precision of 0.1 mg. The mass of each component in the mixture was measured incorporating the double-substitution weighing scheme of Harris and Torres.¹⁴ Weighings were repeated four times to determine the mass of each mixture component. Three samples were prepared at mole fractions of dimethyl carbonate (x_1) of 0.101, 0.301 and 0.600. The total mass of each of the mixtures was 199 g, 215 g and 226 g from lowest to highest mole fraction of dimethyl

[§] In order to describe materials and experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturers' names or labels. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular product or equipment is necessarily the best available for the purpose.

carbonate. Prior to measurements, samples underwent a series of freeze, evacuate, and thaw cycles to remove air. Based upon the weighings and degassing of samples, the expanded uncertainty in the composition of the prepared samples was estimated to be 0.001 mole fraction ($k=2$).

3. Experimental

Densities of the compressed test liquids were measured with the automated densimeter used in our previous studies.¹⁵ The core of the apparatus is a commercial vibrating-tube densimeter. To minimize the uncertainty in the measurements, more accurate measurements of temperature and pressure and a specialized thermostat for precise temperature control have been implemented (see reference 15 for details). The temperature range of the instrument is 270 K to 470 K with pressures up to 50 MPa. The calibration fluids used in this study were toluene (99.92 % purity) and 99.999 % pure propane. Toluene was measured from 270 K to 470 K at pressures ranging from 0.5 MPa to 50 MPa covering a density range of $681 \text{ kg}\cdot\text{m}^{-3}$ to $917 \text{ kg}\cdot\text{m}^{-3}$. Propane was measured from 4 MPa to 50 MPa covering a density range of $263 \text{ kg}\cdot\text{m}^{-3}$ to $767 \text{ kg}\cdot\text{m}^{-3}$. Density values for the toluene and propane were calculated with the REFPROP database¹⁶. The calibration data were correlated with the equation of May et al.¹⁷ The toluene data were fit by the calibration equation with an absolute average deviation (AAD) of $0.23 \text{ kg}\cdot\text{m}^{-3}$ and the propane data with an AAD of $0.12 \text{ kg}\cdot\text{m}^{-3}$. The influence of the calibration liquids and of the formulations to correlate their densities on the accuracy of the measurement results with vibrating-tube densimeters has been addressed in a separate publication.¹⁸

The mixture with a mole fraction of $x_1 = 0.101$ DMC was measured at temperatures from 270 K to 470 K, while the other two compositions (higher in mole fraction of DMC) were measured from 290 K to 470 K to avoid the triple point of DMC near 277 K. All the mixtures were measured up to 50 MPa along each isotherm, with the lowest pressures being 1 MPa up to 430 K and 2 MPa at higher temperatures to avoid the two-phase region. Each mixture was measured from lowest to highest temperature in 20 K increments and from highest to lowest pressure along each isotherm. After one complete set of measurements was finished at a given composition, the measured sample was removed

from the instrument and the instrument was evacuated. A second load of the sample was then introduced into the system. Measurements were repeated for all the points originally measured at dimethyl carbonate mole fractions (x_1) equal to 0.101 and 0.600. For the mole fraction 0.301, measurements were repeated for all the points from 290 K to 390 K. Data reported here are all from the first set of measurements.

Uncertainty

The overall combined uncertainty ($k = 2$) in density has been calculated for each of the mixture compositions. These uncertainties are $0.71 \text{ kg}\cdot\text{m}^{-3}$, $1.23 \text{ kg}\cdot\text{m}^{-3}$, $1.63 \text{ kg}\cdot\text{m}^{-3}$ for the dimethyl carbonate mole fractions (x_1) of 0.101, 0.301, 0.600, respectively. This uncertainty was calculated with the root sum of squares method and includes the density equivalent of the uncertainties associated with the equations of state for both propane and toluene (as calculated with REFPROP¹⁶), temperature, pressure, mixture composition, and repeatability of the measurements. It is impossible to be certain that the mixture composition in the U-tube during measurements is that of the bulk mixture composition of the prepared sample. To address this, the difference in density of the repeated measurements from the original measurements were used to represent the composition uncertainty. The average of the standard deviations of the original and the repeated measurements for each composition, was considered to represent the uncertainty in the composition.

4. Results

Tables 2 to 4 list the measured density values of three compositions of compressed-liquid dimethyl carbonate (DMC) + heptane. A total of 370 data points are reported for these mixtures.

270 K		290 K		310 K		330 K		350 K		370 K	
Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ
MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³
49.99	758.5	49.96	744.8	49.99	731.5	50.02	718.5	50.01	705.5	50.03	692.1
45.00	755.7	45.01	741.8	44.99	728.2	45.01	714.9	45.00	701.5	44.99	687.8
40.00	752.9	39.99	738.6	40.00	724.9	40.02	711.2	40.01	697.4	39.99	683.2
34.99	749.9	34.99	735.4	34.98	721.3	34.99	707.2	35.01	693.0	35.00	678.5
29.98	746.8	29.99	732.0	30.00	717.6	30.00	703.1	29.99	688.5	29.98	673.4
25.01	743.6	25.00	728.5	25.00	713.7	24.98	698.7	24.99	683.6	25.00	668.0
19.98	740.3	19.98	724.8	19.99	709.6	19.98	694.1	19.97	678.4	19.97	662.2
15.01	736.9	14.98	720.9	15.00	705.2	14.99	689.2	14.99	672.8	15.00	655.9
10.00	733.3	9.99	716.8	9.99	700.6	9.99	683.9	10.00	666.8	9.99	648.9
5.01	729.5	5.00	712.5	5.00	695.7	5.01	678.2	5.00	660.2	5.00	641.2
2.99	727.9	2.99	710.7	3.01	693.6	3.01	675.8	3.00	657.3	3.03	637.8
1.00	726.3	0.99	708.9	1.00	691.5	1.01	673.2	1.00	654.4	1.00	634.3
390 K		410 K		430 K		450 K		470 K			
Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ		
MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³		
50.00	679.1	50.02	666.2	49.99	653.5	49.99	640.9	49.96	628.2		
45.01	674.4	45.00	661.1	45.01	648.0	45.01	635.0	45.00	621.8		
40.02	669.5	39.98	655.8	40.00	642.2	39.99	628.6	39.99	614.9		
35.00	664.3	34.99	650.0	34.99	635.9	34.99	621.7	34.99	607.3		
29.99	658.7	30.00	643.9	30.00	629.1	30.00	614.2	29.98	599.0		
24.99	652.6	25.01	637.2	24.99	621.6	25.00	605.9	25.00	589.7		
19.98	646.1	19.98	629.8	19.99	613.3	20.00	596.5	19.99	579.0		
14.99	638.9	14.99	621.6	15.00	603.9	15.00	585.8	15.00	566.6		
9.98	630.9	9.98	612.4	10.00	593.1	9.99	573.0	9.99	551.3		
4.97	621.8	5.00	601.5	4.99	580.0	5.00	556.9	4.98	530.6		
2.99	617.8	2.99	596.5	2.98	573.9	2.98	549.1	2.99	519.7		
0.99	613.4	1.01	591.1	1.02	567.0	1.02	539.6				

Table 2: Compressed-liquid densities of the binary system dimethyl carbonate (x_1) + heptane (x_2) measured along isotherms from 270 K to 470 K. $x_1 = 0.101$. The combined expanded uncertainties U_c are $U_c(T) = 30$ mK, $U_c(p) = 0.01$ MPa, *average of standard deviations of repeat measurements* = 0.23 kg·m⁻³, $U_c(\rho) = 0.71$ kg·m⁻³ (level of confidence = 0.95).

290 K		310 K		330 K		350 K		370 K		390 K	
Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ
MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³
49.98	795.8	49.99	781.1	49.99	766.7	49.96	752.2	49.98	737.5	49.98	723.2
44.98	792.7	45.00	777.7	44.99	762.9	45.03	748.1	44.99	733.0	44.99	718.3
39.99	789.4	39.99	774.1	39.98	758.9	40.01	743.7	40.01	728.2	39.99	713.1
35.00	786.0	34.99	770.3	35.00	754.8	35.01	739.1	34.99	723.1	34.99	707.5
29.99	782.5	29.99	766.5	30.00	750.5	29.99	734.3	29.98	717.8	30.00	701.6
25.00	778.8	25.00	762.3	24.99	745.9	24.97	729.1	24.98	712.1	25.00	695.2
19.98	774.9	19.99	758.1	20.00	741.0	20.00	723.7	20.00	705.9	20.01	688.3
14.99	770.9	14.97	753.5	14.98	735.9	15.01	717.9	15.01	699.3	14.99	680.7
9.99	766.7	10.00	748.7	9.99	730.4	9.99	711.5	9.99	691.9	10.03	672.3
4.97	762.2	4.98	743.6	5.00	724.4	5.00	704.5	4.99	683.8	4.99	662.5
2.99	760.3	3.00	741.4	2.98	721.8	2.98	701.5	3.00	680.2	2.98	658.2
0.99	758.4	0.99	739.1	0.98	719.0	0.97	698.1	0.97	676.0	1.00	653.2
410 K		430 K		450 K		470 K					
Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ				
MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³				
50.01	709.0	50.00	695.0	50.00	681.1	50.01	667.2				
45.00	703.6	44.99	689.2	44.99	674.7	45.00	660.3				
40.01	698.0	39.99	682.9	39.99	667.9	39.99	652.9				
34.98	691.8	34.99	676.2	34.99	660.5	34.99	644.8				
29.98	685.2	30.00	668.9	30.03	652.5	30.00	635.8				
25.00	678.1	25.00	661.0	24.99	643.5	24.99	625.8				
20.00	670.3	19.99	652.1	19.98	633.4	20.01	614.3				
14.99	661.5	14.99	642.0	14.99	621.8	14.99	600.7				
9.99	651.6	10.00	630.3	10.02	607.9	9.98	583.9				
5.01	640.1	4.97	616.1	4.99	590.1	4.96	560.7				
3.00	634.7	2.97	609.3	2.99	581.2	3.01	548.1				
0.99	628.0			2.00	576.0	1.97	538.4				

Table 3: Compressed-liquid densities of the binary system dimethyl carbonate (x_1) + heptane (x_2) measured along isotherms from 290 K to 470 K. $x_1 = 0.301$. The combined expanded uncertainties U_c are $U_c(T) = 30$ mK, $U_c(p) = 0.01$ MPa, *average of standard deviations of repeat measurements* = 0.55 kg·m⁻³, $U_c(\rho) = 1.23$ kg·m⁻³ (level of confidence = 0.95).

290 K		310 K		330 K		350 K		370 K		390 K	
Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ
MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³
50.01	898.7	50.01	881.4	49.98	864.5	50.01	847.4	50.00	830.3	50.02	813.5
45.01	895.4	44.98	877.8	44.99	860.5	45.00	843.0	45.01	825.6	45.00	808.2
39.99	892.0	39.97	874.0	39.99	856.4	39.99	838.4	40.02	820.5	39.96	802.7
35.00	888.4	34.99	870.2	34.99	852.1	34.98	833.6	35.00	815.2	34.99	796.8
30.00	884.8	29.99	866.2	29.99	847.6	29.98	828.6	30.01	809.6	29.99	790.6
24.98	881.0	24.99	861.9	24.99	842.8	24.98	823.2	24.99	803.6	25.01	783.9
19.99	877.0	19.99	857.5	19.97	837.8	19.98	817.6	20.00	797.3	20.01	776.7
14.99	872.9	14.98	852.9	14.99	832.5	14.99	811.6	14.99	790.3	14.97	768.7
10.00	868.6	10.00	848.0	9.98	826.9	9.98	805.1	9.99	782.8	10.00	760.0
4.99	864.1	4.99	842.8	4.98	820.9	4.99	798.1	4.99	774.6	5.01	750.2
2.98	862.2	3.00	840.6	2.98	818.3	2.97	795.0	3.01	771.0	2.98	745.9
1.00	860.3	1.00	838.4	1.00	815.7	0.99	791.9	0.99	767.3	0.98	741.3
410 K		430 K		450 K		470 K					
Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ				
MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³	MPa	kg·m ⁻³				
49.98	796.8	50.01	780.2	50.01	763.4	50.04	746.3				
45.00	791.1	45.00	773.9	45.00	756.5	45.00	738.7				
40.00	785.0	40.00	767.2	40.01	749.2	40.00	730.6				
34.98	778.5	34.98	759.9	35.01	741.2	35.01	721.7				
30.00	771.5	29.99	752.2	29.97	732.4	29.98	711.8				
24.98	763.9	25.01	743.7	24.98	722.8	24.99	700.8				
20.00	755.7	20.00	734.3	19.99	712.0	19.99	688.2				
14.98	746.6	14.98	723.7	14.99	699.6	14.98	673.3				
9.99	736.4	9.99	711.5	9.99	685.0	10.00	655.0				
5.00	724.6	5.00	697.1	5.01	666.8	5.00	629.6				
2.98	719.2	3.00	690.4	2.98	657.6	3.00	615.4				
0.99	713.5	1.00	682.9	1.99	652.6	1.99	606.0				

Table 4: Compressed-liquid densities of the binary system dimethyl carbonate (x_1) + heptane (x_2) measured along isotherms from 290 K to 470 K. $x_1 = 0.600$. The combined expanded uncertainties U_c are $U_c(T) = 30$ mK, $U_c(p) = 0.01$ MPa, average of standard deviations of repeat measurements = 0.77 kg·m⁻³, $U_c(\rho) = 1.63$ kg·m⁻³ (level of confidence = 0.95).

Table 5 lists the available density data found in the literature for this mixture. The table shows that while

Author, Year	Mole fraction DMC (x_1)	Temperature range [K]	Pressure range [MPa]
Garcia et al., 1992 [10]	0.05 - 0.9	298.15	0.101
Negadi et al., 1993 [12]	0.1 - 0.9	298.15	0.101
Oh et al., 2006 [9]	0 - 1	298.15	0.101
Prado et al., 1999 [7]	0.03 - 0.95	278.15 - 308.15	0.101
Regueiro, 1999 [13]	0.05 - 0.95	288.15 - 308.15	0.101
Tojo et al., 2004 [5]	0 - 1	293.15 - 318.15	0.1013
Yang et al., 2004 [8]	0 - 1	293.15 - 343.15	“normal atmospheric”

Table 5. Density data available in the literature for the mixture dimethyl carbonate + heptane and the composition, temperature and pressure range of those data.

there are data across the full composition range for the mixture, no data exist at pressures above atmospheric. Figures 1 and 2 are provided to compare our results to those densities available in the literature for this mixture.

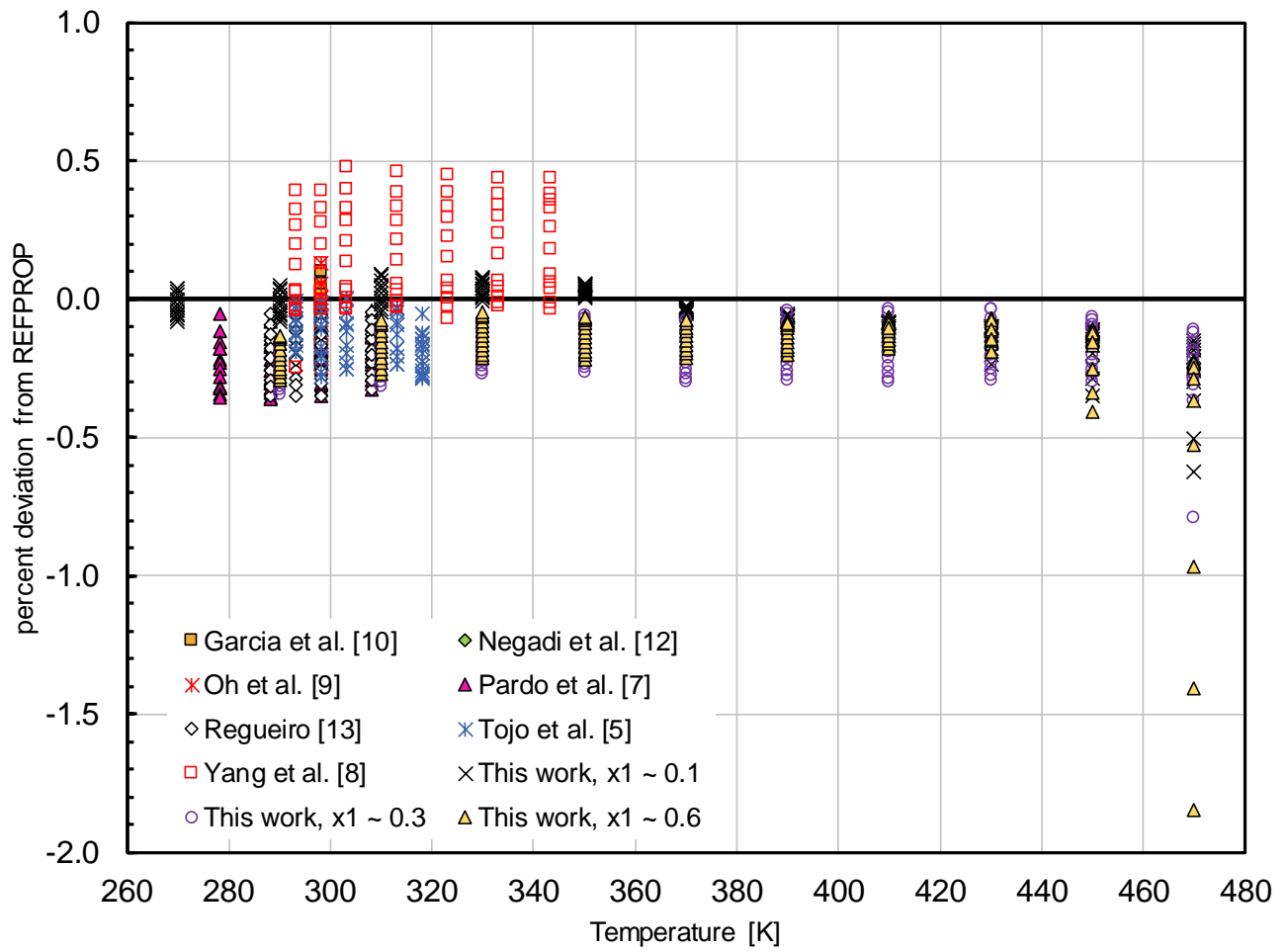


Figure 1. Percent deviation of literature data and data presented herein from predictions by REFPROP^{16, 19} as a function of temperature.

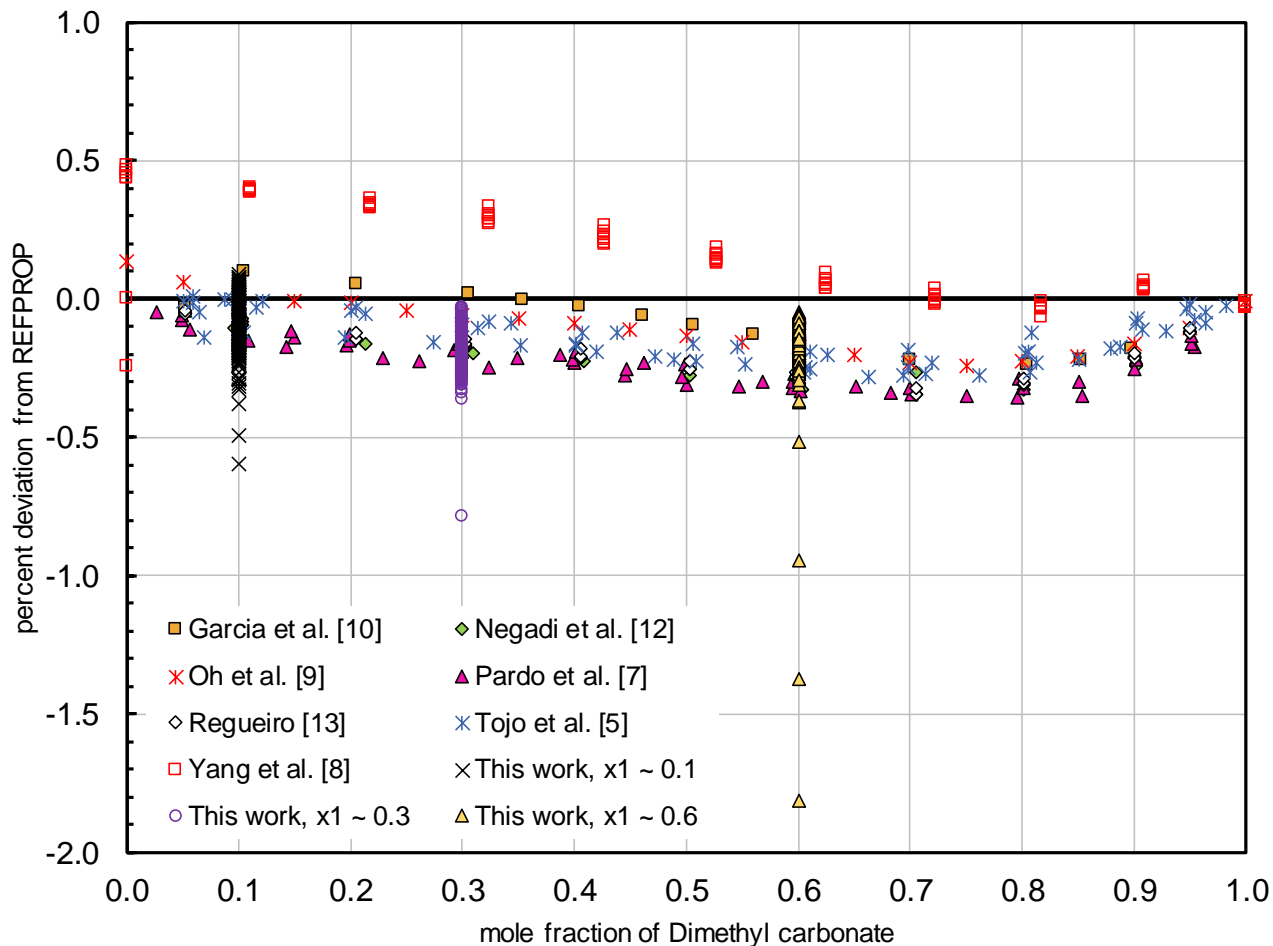


Figure 2. Percent deviation of literature data and data presented herein from predictions by REFPROP^{16, 19} as a function of mole fraction of dimethyl carbonate.

The densities shown for Negadi et al.¹² and Pardo et al.⁷ were derived from reported excess molar volumes. The baseline of both figures is the value predicted by REFPROP¹⁶ at the temperature, pressure and composition of the measured data. Figure 1 shows percent deviations as a function of temperature, while figure 2 shows those deviations as a function of mole fraction of dimethyl carbonate (x_1).

Figure 3 illustrates the measured densities as a function of composition along three isotherms at pressures of 3 and 50 MPa for each temperature.

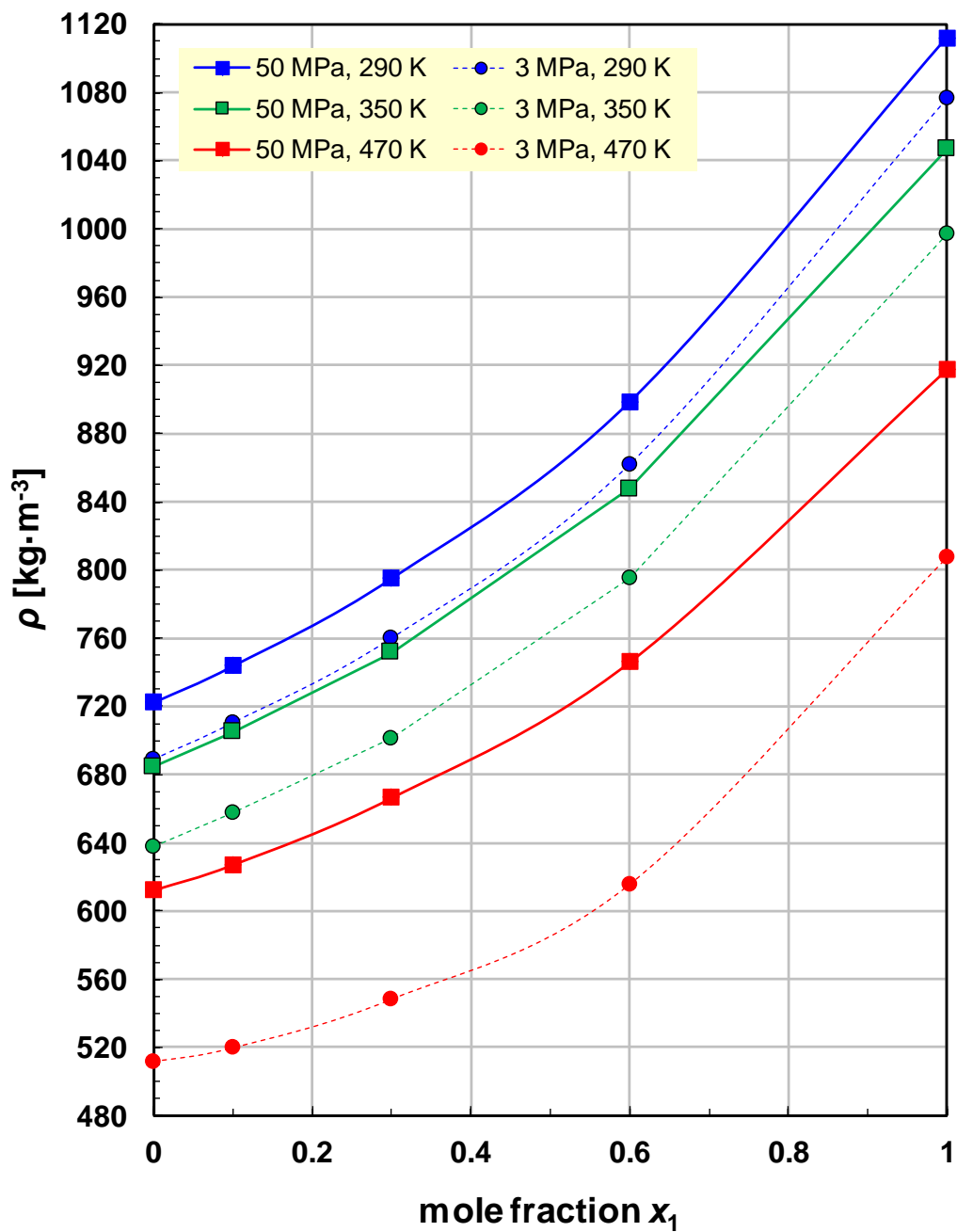


Figure 3. Density isobars at 50 MPa and 3 MPa of the pure components and of three compositions of the system dimethyl carbonate (1) + heptane (2). Pure fluid densities were calculated with REFPROP.^{16, 20, 21} Smoothed lines between points are drawn to guide the readers' eye.

The slope of the curves is slightly greater at the lower temperatures; this indicates that, for this mixture, density is more strongly dependent on composition at lower temperatures. Figure 4 depicts the excess molar volumes of selected isotherms at the lowest pressure measured along the given isotherm.

The excess molar volumes were calculated from the measured density data with equation 1

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1^*} - \frac{x_2 M_2}{\rho_2^*}$$

where x_1 and x_2 are the mole fractions and M_1 and M_2 are the molecular weights of dimethyl carbonate (1) and heptane (2) respectively. The measured density of the mixture at a given temperature and pressure is ρ , and ρ_1^* and ρ_2^* are the pure fluid densities as calculated with REFPROP^{16, 20, 21} at that temperature and pressure.

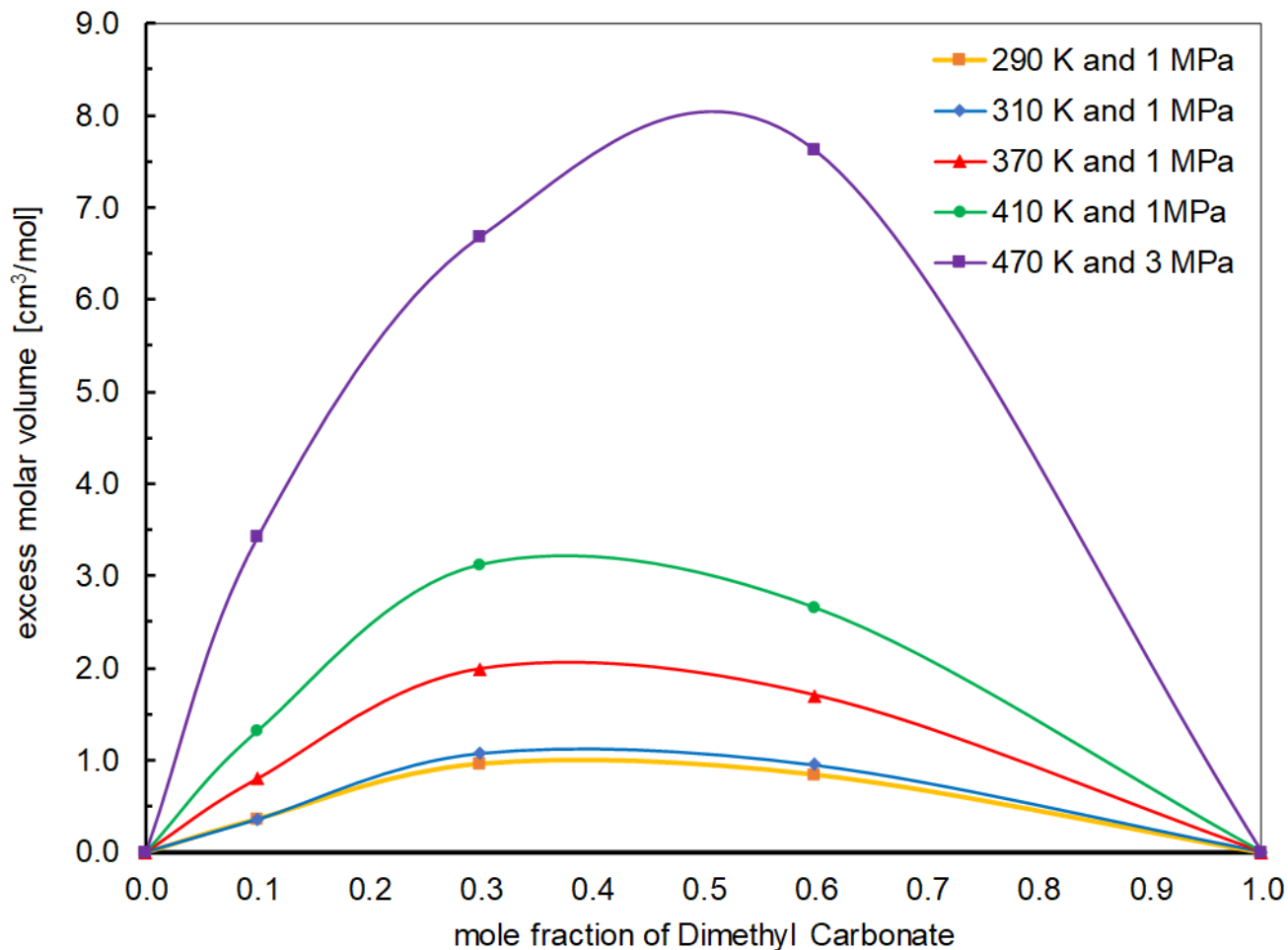


Figure 4. Excess molar volumes along selected isotherms. Pressures are the lowest pressure measured for the given isotherm. “Smoothed lines” between isothermal data have been drawn to aid in comparing the magnitude of excess molar volumes along isotherms.

5. Discussion

To understand the mixture results presented in this work, it is helpful to first examine some of the pure fluid characteristics of dimethyl carbonate and heptane. Figure 5 is an illustration designed to give a general understanding of the differences in the size, shape and charge distribution of the two molecules.

Dimethyl carbonate + n-Heptane

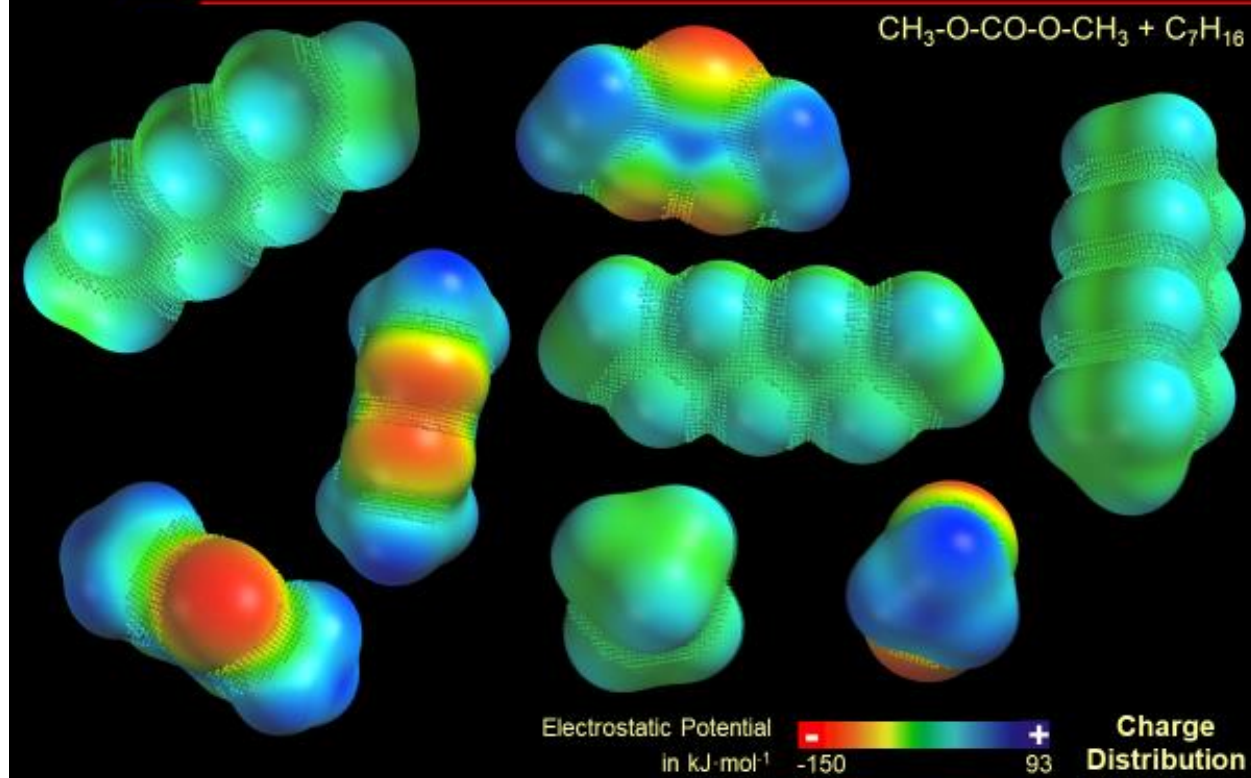


Figure 5. Equimolar mixture of four DMC molecules and four heptane molecules in various views to illustrate their sizes and shapes. The color scale indicates the charge distribution in the molecules. See text for more details.

The dimethyl carbonate molecules are shown in the cis-cis orientation as that has been documented as the predominant conformation for the molecule in the liquid phase.²² In an equimolar mixture, four dimethyl carbonate molecules and four heptane molecules are arranged in various views to convey an idea of how they interact. The molecules are shown in terms of isosurfaces of their electron density distributions at a value of $0.002 \text{ electrons}\cdot\text{au}^{-3}$ (with 1 atomic unit = 0.05292 nm being the Bohr radius of hydrogen). This surface encloses more than 99 % of a molecule. As explained in detail in our previous work²³, SPARTAN 10 version 1.1.0²⁴ was used to calculate the electron density distributions and the electrostatic potentials *ab initio* with density functional theory at the B3LYP level and with the 6-311++G** basis set.²⁵ Dots on the electron density isosurfaces mark those parts of the surface that are inaccessible by other molecules of the same species.²⁶ Thus, they indicate the approximate void volume

between the molecules. This is of particular interest in the context of density measurements. The electrostatic potential is mapped on the isosurfaces so that the color scale indicates the charge distribution in the molecules. While heptane is nonpolar, DMC has a non-uniform charge distribution and is polar. The double-bonded oxygen atom is a center of negative charge (most intense red color). The ether oxygen atoms have lower negative charges (shown as orange to yellow). The methyl-groups are centers of positive charge (blue). Electrostatic attractions between these centers of opposite charges orient the DMC molecules and induce structure in the liquid. In the mixture, the nonpolar heptane molecules hinder these attractions sterically and prevent the full orientation of the DMC molecules.

An indicator of the strength of van der Waals and electrostatic attractions among molecules is the range of the vapor pressure curve from the triple point to the critical point. This follows from the fact that without an attractive part of the intermolecular potential, no liquid phase can be formed and the length of the vapor pressure curve is zero.^{27, 28} This is evidenced by the fact that the pVT-relationships for purely repulsive hard or soft spheres reduce to lines and are not three-dimensional as for real fluids with repulsions and attractions.^{29, 30} Figure 6 depicts the vapor pressure curves for dimethyl carbonate and heptane from their triple points to their critical points.

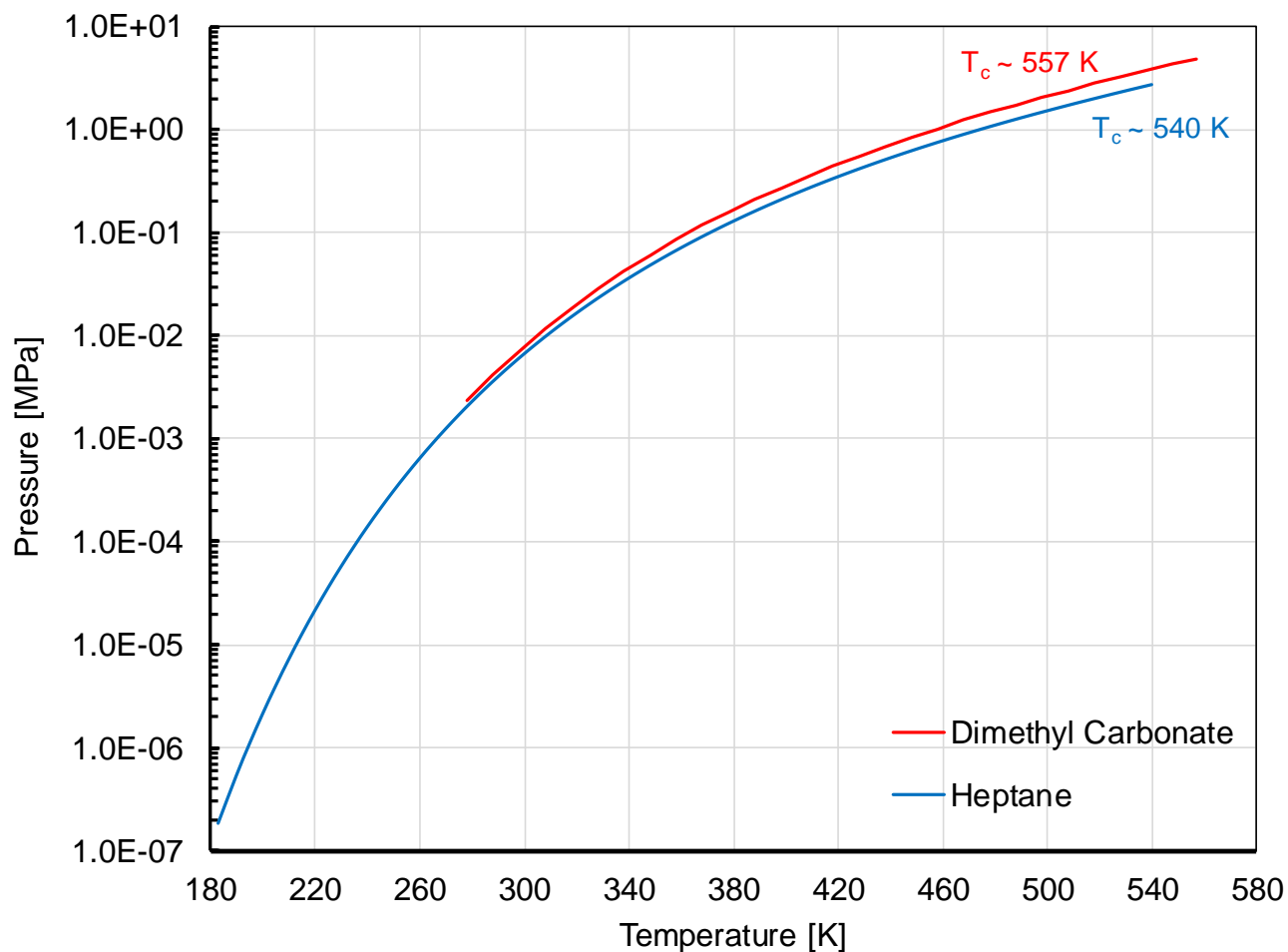


Figure 6. Vapor pressure curves for dimethyl carbonate and heptane from their triple points to their critical points. Values calculated with REFPROP.^{16, 20, 21}

Table 6 lists the temperature values for the triple point, boiling point, critical point and the temperature range of the vapor pressure curves for dimethyl carbonate and heptane.

	Dimethyl Carbonate	Heptane
Triple point T_t [K]	277.06	182.55
Normal Boiling point T_b [K]	363.26	371.55
Critical Temperature T_c [K]	557.0	540.2
Range of vapor pressure curve $T_c - T_t$ [K]	279.94	357.65

Table 6. Triple point, boiling point and critical point temperatures of dimethyl carbonate and heptane as given in REFPROP.¹⁶

While the two molecules have similar boiling points and critical temperatures, their triple point temperatures and the range of their vapor pressure curves are very different. The vapor pressure curve of the non-polar heptane covers a much larger temperature range than that of the highly polar dimethyl carbonate. Thus, the polarity of dimethyl carbonate does not result in higher attractions between the molecules. Rather, and similar to carbon dioxide which is known for its extremely short vapor pressure curve, the negative charge concentration on the electronegative oxygen atoms effects higher repulsions between the dimethyl carbonate molecules while electrostatic attractions between the oppositely charged parts of the molecule obviously contribute less to their interactions. This will have to be considered in the interpretation of the measured mixture densities.

Because the mixture data presented herein is compared to other density data using the predictions of REFPROP¹⁶, knowledge of the pure fluid equations for dimethyl carbonate and heptane found in REFPROP¹⁶ are helpful. The Zhou et al.²⁰ equation is used for dimethyl carbonate. It is based on many density data in the saturated state, but few in the compressed-liquid state. In fact, the compressed-liquid density data for dimethyl carbonate that are available in the literature only go up to 353 K in temperature. The density uncertainty of the Zhou et al.²⁰ equation is 0.1% at temperatures less than 400 K, with greater uncertainties at temperatures above that. A new equation of state for heptane has recently been formulated by Tenji et al.²¹ Uncertainties in liquid densities for that equation range from 0.03 % to 0.05 % at temperatures from 250 K to 390 K. Above 390 K and up to 440 K, the uncertainty increases to 0.2 %. For the remainder of the temperature and pressure range of this study, the uncertainty of the heptane equation is less than 1 %.

The Helmholtz equation utilized in REFPROP¹⁶ to predict mixture properties is based on equations of state for the pure components combined at the reduced temperature and density of the mixture.³¹ The mixing parameters (found in REFPROP¹⁶) for the dimethyl carbonate + heptane binary mixture were formulated by Cullimore and Lemmon.¹⁹ For the mixture studied herein, both the equation of state for dimethyl carbonate and that for heptane are limited (or have greater uncertainties) at temperatures above

400 K. It is thus understandable why figure 1 shows the greatest deviations at the higher temperatures of this study, particularly 470 K. Most of the deviations of the densities from this work are below 0.5 %. The average absolute deviations (AAD) from REFPROP^{16, 19} are 0.06 %, 0.15 % and 0.17 % for mole fractions dimethyl carbonate (x_1) of 0.101, 0.301, and 0.600 respectively. The deviations from this work that are above 0.5 % occur at points measured at 470 K and at pressures of 5 MPa and below.

In addition to the lack of highly-accurate equations of state (at temperatures above approximately 400 K) for the pure fluids in the dimethyl carbonate + heptane mixture, the polar/non-polar interactions make accurately modeling the mixture more difficult. There is a known azeotrope for this mixture, documented by Rodriguez et al.³² in 2002. It occurs at atmospheric pressure, at 355.4 K and at a mole fraction of dimethyl carbonate of 0.6069. This may help explain why both the data presented here and the literature data as shown in figure 2 have the greatest deviations around x_1 equal to 0.6.

Figures 3 and 4 are helpful in developing an understanding of the non-ideality of this mixture. Figure 3 shows that while the density behavior of the mixture becomes less ideal as temperature is increased, there are no density maxima or minima in the temperature and pressure range of this study as we observed them with mixtures of 2,2,4-trimethylpentane with the associating alcohols ethanol and 2-butanol.²³ Figure 4 (excess molar volumes of isotherms as a function of mole fraction of dimethyl carbonate) gives an understanding of the molecular interactions of the dimethyl carbonate and heptane molecules. At elevated temperatures, the increase in molar volume is indicative of the attractions between the dimethyl carbonate molecules being reduced and greater void volumes in the mixture in general.

6. Conclusions

Compressed-liquid densities of three compositions of the mixture dimethyl carbonate + heptane have been measured over a temperature range of 270 K to 470 K with pressures to 50 MPa. The data presented here are the only available density data for the binary mixture at temperatures above 343 K and pressures

above atmospheric. The data presented here are in good agreement with most of the literature data, but generally lower than the data of Yang et al.⁸ and the predictions of REFPROP.^{16, 19} The deviations of our data that are above 0.5 % are all at 470 K; well above where the pure fluid equations of state for dimethyl carbonate and heptane are no longer highly accurate. Those same points (at 470 K) are also at a temperature well above where any literature data exist, indicating that the mixture model could potentially be improved by the inclusion of the data presented in this work.

Measuring the densities of three compositions of the dimethyl carbonate + heptane mixture over a large temperature and pressure range in this study allows for more detailed examination of the non-ideality of the mixture. Our results indicate that this polar/non-polar mixture is not particularly non-ideal because the polarity of dimethyl carbonate does not result in electrostatic attractions nor hydrogen bonding. It is important to be aware of this ambiguity of polarity and not assume globally that polarity always results in higher attractions between molecules. Many examples of this ambiguity can be found among hydrocarbons at various degrees of fluorination.³³

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