

# VOLUMETRIC PROPERTIES OF MIXTURES OF IONIC LIQUID [EMIM]Ac WITH CO<sub>2</sub> AS POTENTIAL PROCESSING FLUIDS FOR LIGNOCELLULOSIC MATERIALS AT HIGH PRESSURES

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**Abstract.** Densities of binary mixtures of 1-ethyl-3-methylimidazolium acetate, [EMIM]Ac and CO<sub>2</sub> with 0; 2.5; 5; 10; 25; 55 wt % CO<sub>2</sub> have been determined at 25, 50, 75 and 100 °C over a pressure range up to 40 MPa using a variable-volume view-cell which permits continuous density determinations. Densities were determined also for a mixture with 95 wt% [EMIM]Ac + 5 wt% microcrystalline cellulose (Avicel) and a mixture with 85.4 wt% [EMIM]Ac + 10.1 wt% CO<sub>2</sub> and 4.5 wt% Avicel at these temperatures and pressures. The densities were correlated with pressure (P) at each temperature fitting the data to a function of the form  $\rho = A + BP^{-1} + CP + DP^{-2} + EP^m$  where A, B, C, D, E and m are adjustable parameters. These functions were then used to determine the isothermal compressibilities for each mixture. In the [EMIM]Ac + CO<sub>2</sub> mixtures, at a given temperature compressibilities were observed to increase with increasing CO<sub>2</sub> content in the mixture. In mixtures containing Avicel, compressibilities are found to increase in the direction of 5 wt% Avicel; 5 wt% CO<sub>2</sub>; 4.5 wt% Avicel + 10.1 wt% CO<sub>2</sub>, and 10 wt% CO<sub>2</sub>.

**Keywords:** Ionic liquid, Cellulose, [EMIM]Ac, Carbon Dioxide, Avicel

## 1. Introduction

Since the first publication by Rogers and co-workers [1], which reported that cellulose could be dissolved in room temperature ionic liquids such as 1-butyl-3-methylimidazolium chloride or 1-butyl-3-methylimidazolium bromide, there has been intense research activity in exploring the possibilities for processing of lignocellulosic materials as well as polymers using ionic liquids as reviewed in recent publications [2-6]. Among the applications are converting lignocellulosic materials to biofuels [7, 8], regenerating and solution spinning of cellulose [9, 10], and derivatization of cellulose [3], or pretreatment of biomass for further modifications [11]. Some challenges presented with the use of ionic liquids are their high viscosities and limitations in their recovery and recycle in a given process.

Among the various ionic liquids that have been explored, the acetate-based ionic liquids, and in particular 1-butyl-3-methylimidazolium acetate, [BMIM]Ac, and 1-ethyl-3-methylimidazolium acetate, [EMIM]Ac, have been shown to be the most effective solvents for cellulose and also for lignin, and as a result most of the recent research activity has been focused on these type of ionic liquids for applications pertaining to biomass processing and modifications [6, 9, 10, 12-14].

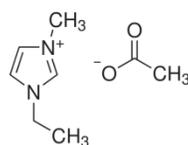
We have recently started a research program to explore the properties of binary and ternary mixtures of these acetate-based ionic liquids with carbon dioxide as well as some selected organic solvents to explore further their effectiveness in possible processing applications of lignocellulosic polymers. A literature search showed that the available information on these mixtures at high pressures is extremely limited, or lacking. One study reports on the solubility of CO<sub>2</sub> in [BMIM]Ac in the temperature range from 283-348 K up to only 2 MPa [15]. Another study reports on the solubility of CO<sub>2</sub> in [BMIM]Ac but at a low pressure of 0.1 MPa [16]. Only one study has reported CO<sub>2</sub> solubility in [BMIM]Ac at high pressures, up to 76 MPa, at temperatures up to 363 K [17]. There is no data reported for mixtures involving [EMIM]Ac. There is no prior

report on the miscibility of lignocellulosic materials in mixtures of acetate based ionic liquids with carbon dioxide at high pressures. Modulation of miscibility and /or phase separation of polymeric constituents of biomass such as cellulose in ionic liquid + CO<sub>2</sub> mixtures and using pressure as a tuning parameter can potentially offer new processing opportunities while lowering the viscosity of the medium.

We are now reporting on the volumetric properties and compressibility of [EMIM]Ac and its mixtures with CO<sub>2</sub> at temperatures up to 373 K and pressures up to 40 MPa. Volumetric data are also reported for mixtures of [EMIM]Ac + Avicel and [EMIM]Ac + Avicel + CO<sub>2</sub>. The data have been generated with a new experimental methodology which permits continuous recording of density of mixtures as a function of pressure at a given temperature [18]. The continuous density data are then described as a function of pressure by fitting to an equation of state from which isothermal compressibilities are determined.

## 2. Materials

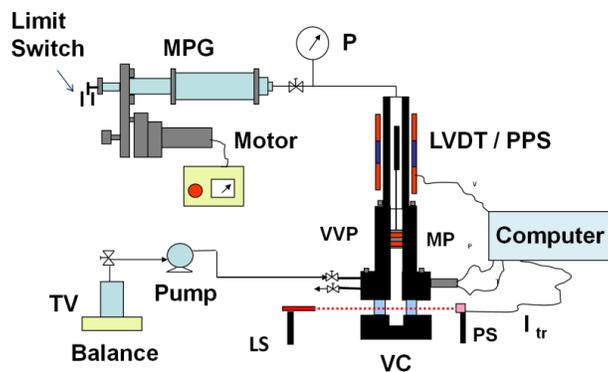
The ionic liquid 1-ethyl-3-methylimidazolium acetate, [EMIM]Ac,



was BASF-grade obtained from Sigma-Aldrich with a stated purity > 90 %. Avicel, which is microcrystalline cellulose powder with ~ 50 µm particle size, was also obtained from Sigma Aldrich. Carbon dioxide with 99.8 % purity was obtained from Airgas.

## 3. Experimental System

Measurements have been carried out in a high pressure variable-volume view-cell equipped with two sapphire windows for visual observations or optical real-time recording of the transmitted light intensities. The cell is equipped with a movable piston, the position of which is recorded with a long stroke-length linear variable differential transformer (LVDT). The piston position, thus the internal volume of the cell, is changed by applying pressure to the back side of the piston with the aid of a pressure generator. Ethanol is used as the pressurizing fluid. The pressure generator has been motorized in-house and the pressure in the system can be increased or decreased at controlled rates. Figure 1 is a schematic of the overall system. As the pressure is altered, the position of the piston is recorded in real time with a dedicated computer. From the initial mass loading and the internal volume of the cell at any given moment, the densities are evaluated. Densities are determined with accuracies within 1 %.



**Figure 1.** Schematic diagram of the experimental system. VC=view cell, MPG= motorized pressure generator; LVDT/PPS = Linear variable differential transformer/piston position sensor; VVP = variable-volume part of the view cell; MP = movable piston; LS = light source; PS = Photosensor; I<sub>tr</sub> = Transmitted light intensity; TV = transfer vessel

## 4. Results and Discussions

### 4.1 [EMIM]Ac + CO<sub>2</sub> Mixtures

Densities and compressibilities of pure [EMIM]Ac and its mixtures with 2.5, 5, 10, 25, 54.6 wt % CO<sub>2</sub> were determined at 25, 50, 75, and 100 °C over a pressure range up to about 40 MPa. Figure 2 shows the density data for pure [EMIM]Ac at these temperatures. As would be expected densities are lowered with temperature and increase with pressure.

The density data were fitted by a least square analysis to the following isothermal equation of state

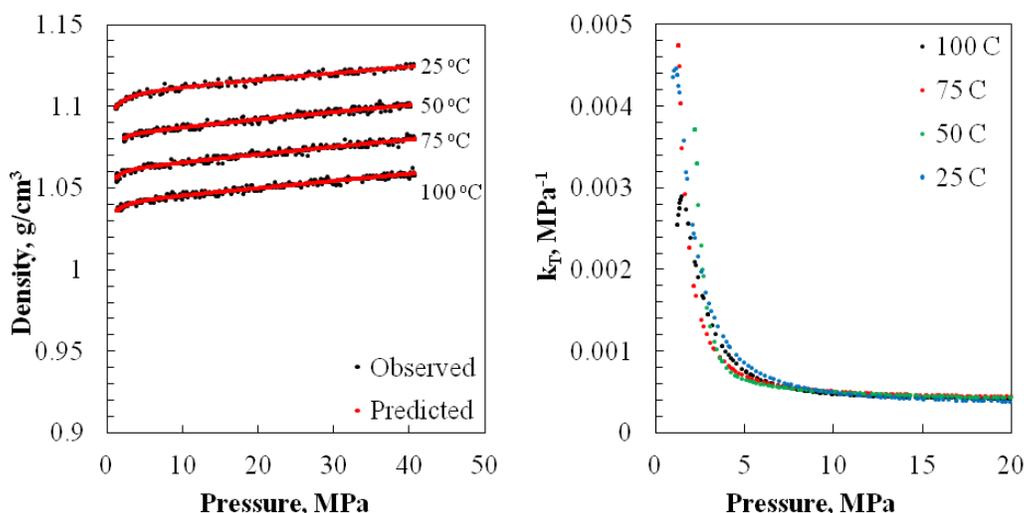
$$\rho = A + BP^{-1} + CP + DP^{-2} + EP^m$$

where A, B, C, D, E and m are adjustable parameters and P is pressure. The parameters are given in Table 1 for densities expressed as g/cm<sup>3</sup> and pressures are in MPa. This form of correlation was previously used in the literature to describe the pressure dependence of the density of argon and mixtures of helium and nitrogen [19]. This equation captures the features of the variation of density at both the low and high pressures and over very wide ranges of pressure. Figure 2 and Table 1 show that the data are indeed well represented by an equation of this form with correlation coefficient values typically higher than 0.99. Densities show the expected decrease with temperature and increase with pressure.

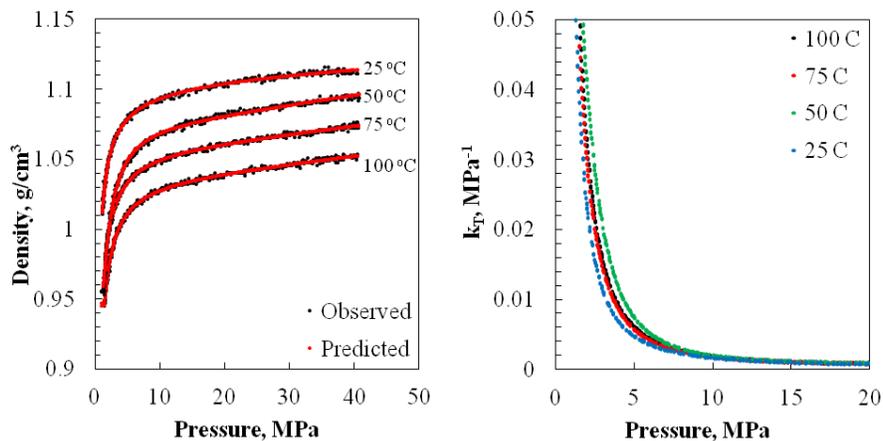
From these equations the isothermal compressibilities have been determined using the thermodynamic relationship,  $k_T = (1/\rho) [\partial\rho/\partial P]_T$ . Figure 2 also shows the values of the compressibilities. They are observed to decrease with pressure but level off around 0.00045 MPa<sup>-1</sup> above 10 MPa. Temperature dependence of compressibility does not seem to be strong for this ionic liquid.

Figures 3- 7 show the density and compressibility data for the [EMIM]Ac + CO<sub>2</sub> mixture with 2.5, 5, 10, 25 and 54.6 wt% CO<sub>2</sub> respectively. Densities show a greater dependence on pressure at low pressures and the compressibilities now display a higher degree of sensitivity to temperature. As shown in the figures, compressibilities increase with temperature at a given pressure, but at pressures above about 25 MPa, they tend to merge and level off around 0.002 MPa<sup>-1</sup>, values which are significantly higher than that for the pure ionic liquid. These solutions were homogeneous and did not display any liquid-liquid phase separation.

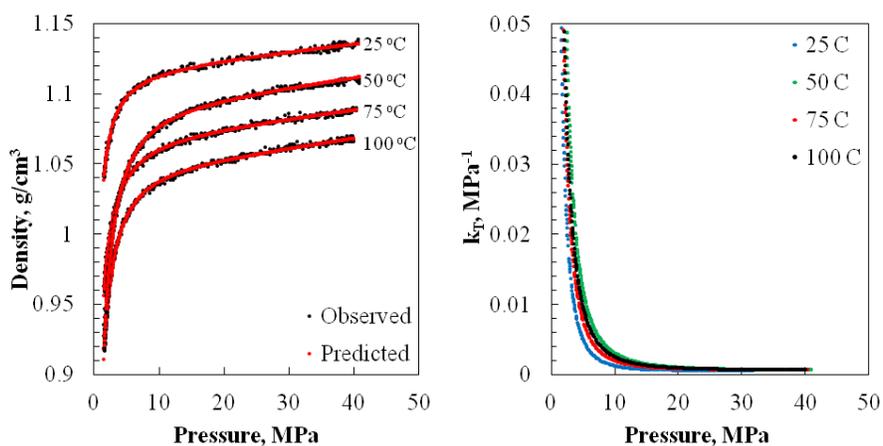
Figures 8-11 compare the densities and compressibilities of these mixtures at 25, 50, 75 and 100 °C. As shown, densities are reduced with increasing CO<sub>2</sub> content, which however increase with pressure and approach that of the pure ionic liquid. Also seen in the figures is that compressibilities become higher as the CO<sub>2</sub> content in the mixture is increased.



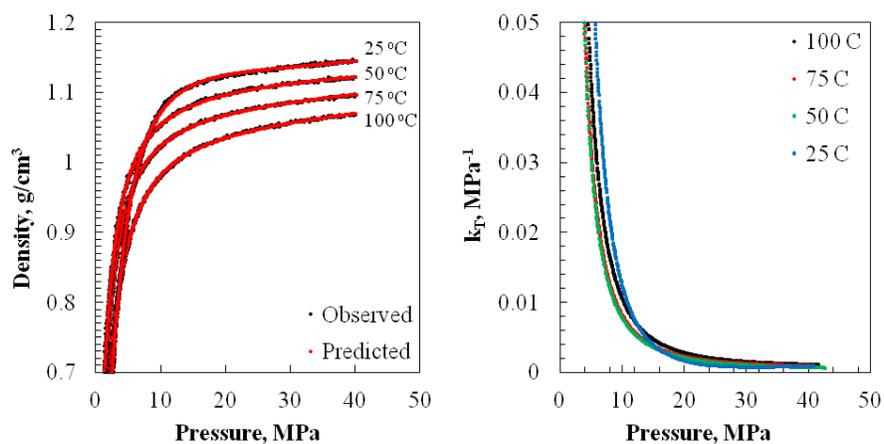
**Figure 2.** Variation of the density (left) and isothermal compressibility (right) of [EMIM]Ac with pressure at 25, 50, 75 and 100 °C.



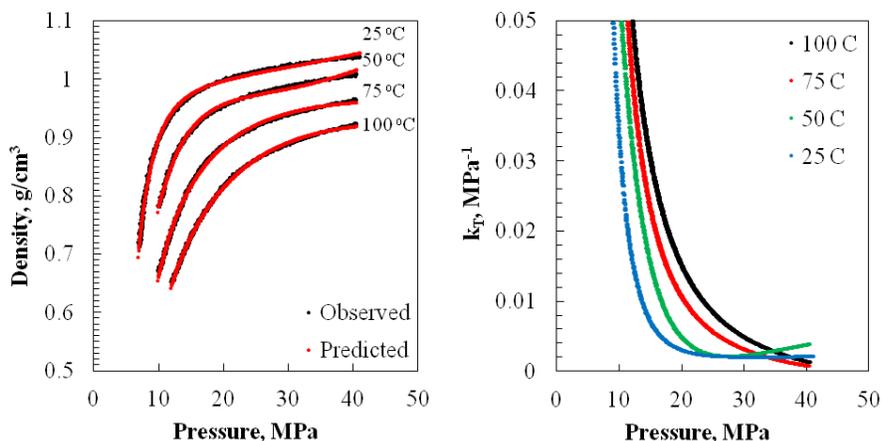
**Figure 3.** Variation of the density (left) and isothermal compressibility (right) of [EMIM]Ac + CO<sub>2</sub> mixture with 2.5 wt% CO<sub>2</sub> with pressure at 25, 50, 75 and 100 °C.



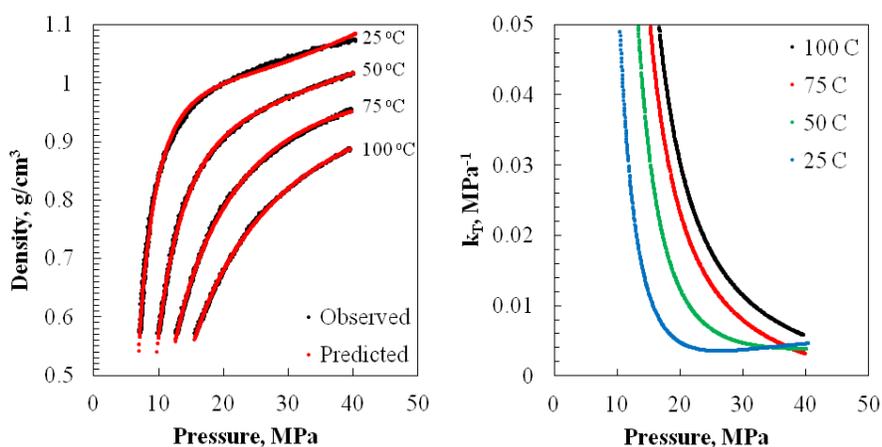
**Figure 4.** Variation of the density (left) and isothermal compressibility (right) of [EMIM]Ac + CO<sub>2</sub> mixture with 5 wt% CO<sub>2</sub> with pressure at 25, 50, 75 and 100 °C.



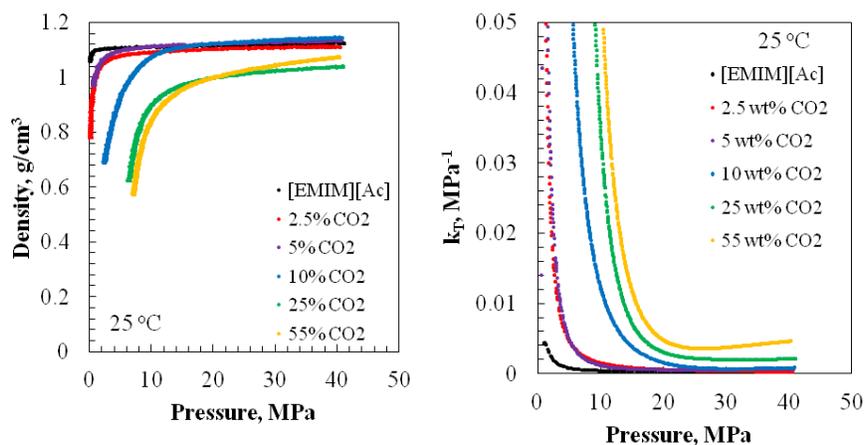
**Figure 5.** Variation of the density (left) and isothermal compressibility (right) of [EMIM]Ac + CO<sub>2</sub> mixture with 10 wt% CO<sub>2</sub> with pressure at 25, 50, 75 and 100 °C.



**Figure 6.** Variation of the density (left) and isothermal compressibility (right) of [EMIM]Ac + CO<sub>2</sub> mixture with 25 wt% CO<sub>2</sub> with pressure at 25, 50, 75 and 100 °C.



**Figure 7.** Variation of the density (left) and isothermal compressibility (right) of [EMIM]Ac + CO<sub>2</sub> mixture with 54.6 wt% CO<sub>2</sub> with pressure at 25, 50, 75 and 100 °C.



**Figure 8.** Comparison of the densities (left) and isothermal compressibilities (right) of [EMIM]Ac + CO<sub>2</sub> mixture with 0; 2.5; 5; 20; 25; and 54.6 wt% CO<sub>2</sub> with pressure at 25 °C.

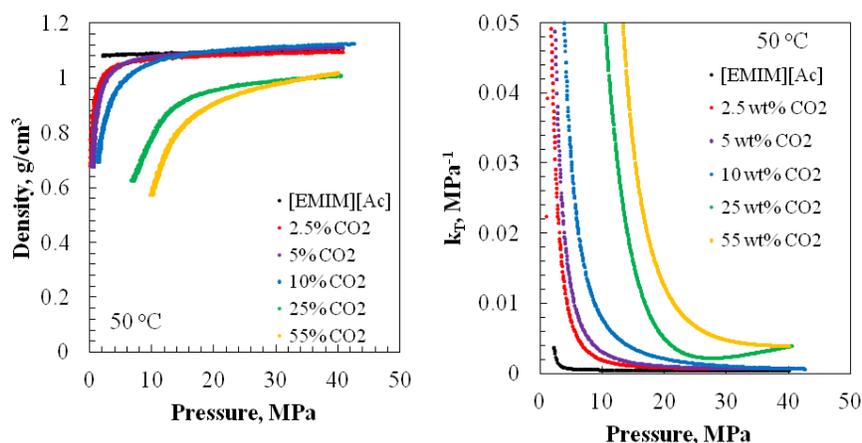


Figure 9. Comparison of the densities (left) and isothermal compressibilities (right) of [EMIM]Ac + CO<sub>2</sub> mixture with 0; 2.5; 5; 20; 25; and 54.6 wt% CO<sub>2</sub> with pressure at 50 °C.

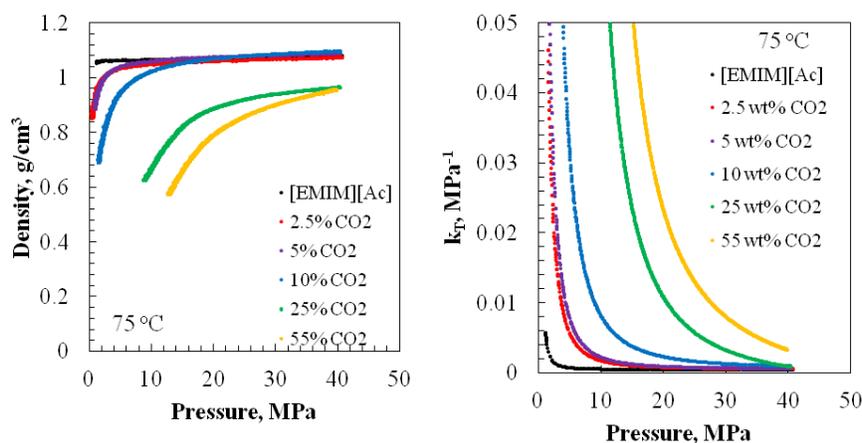


Figure 10. Comparison of the densities (left) and isothermal compressibilities (right) of [EMIM]Ac + CO<sub>2</sub> mixture with 0; 2.5; 5; 20; 25; and 54.6 wt% CO<sub>2</sub> with pressure at 75 °C.

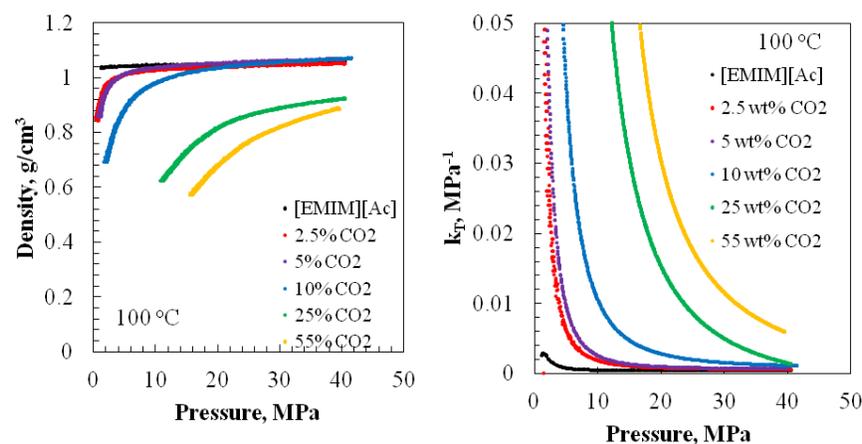
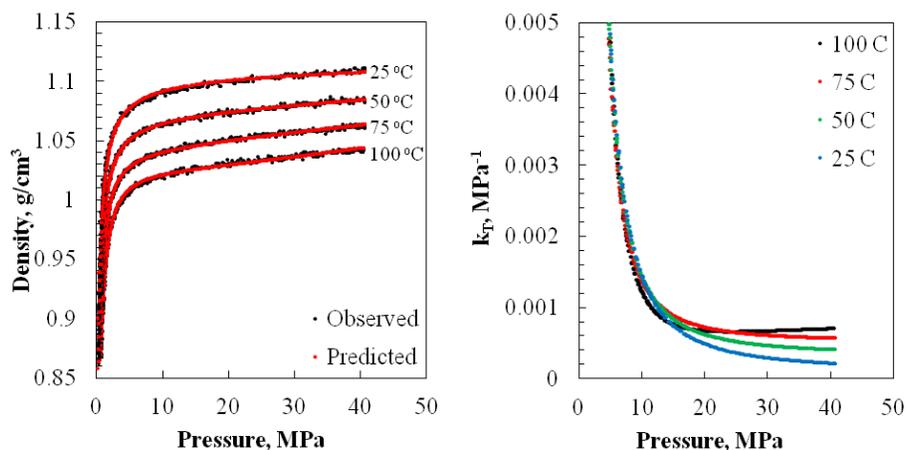


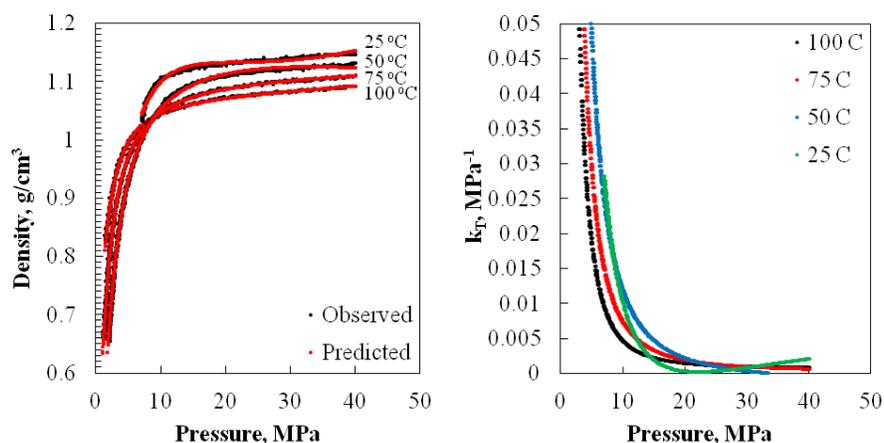
Figure 11. Comparison of the densities (left) and isothermal compressibilities (right) of [EMIM]Ac + CO<sub>2</sub> mixture with 0; 2.5; 5; 20; 25; and 54.6 wt% CO<sub>2</sub> with pressure at 100 °C.

#### 4.2 [EMIM]Ac + Avicel + CO<sub>2</sub> Mixtures

Figure 12 shows the density and compressibility of the mixture of the ionic liquid with 5 wt% Avicel at different temperatures. This solution was initially prepared at ambient pressure by heating the mixture to 100 °C to dissolve the cellulose. The solution was then loaded into the view cell. Figure 13 shows the data for this mixture after adding CO<sub>2</sub> to the system, that resulted in a mixture with a composition of 84.5 wt% [EMIM]Ac, 4.5 wt% Avicel, and 10.1 wt% CO<sub>2</sub>.

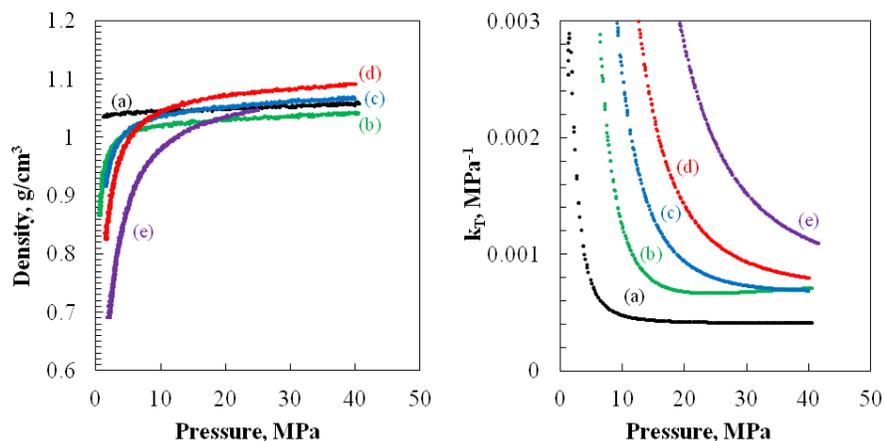


**Figure 12.** Variation of the density (left) and isothermal compressibility (right) of [EMIM]Ac + Avicel mixture with 5 wt% Avicel with pressure at 25, 50, 75 and 100 °C.



**Figure 13.** Variation of the density (left) and isothermal compressibility (right) of 85.4 wt% [EMIM]Ac + 4.5 wt% Avicel + 10.1 wt% CO<sub>2</sub> with pressure at 25, 50, 75 and 100 °C.

Figure 14 is a comparison of [EMIM]Ac, and its mixtures with 5wt% Avicel; 5wt% CO<sub>2</sub>; and 5wt% Avicel + 10.1wt% CO<sub>2</sub> and 10 wt% CO<sub>2</sub> at 100 °C. Distinct differences are displayed especially in the compressibility behavior. The mixture containing 5 wt% Avicel is more compressible than pure ionic liquid, and the mixture containing 5 wt% CO<sub>2</sub> is more compressible than that with Avicel. Higher compressibilities are noted for the mixture containing both CO<sub>2</sub> and Avicel and even higher for the mixture that contains only 10 wt% CO<sub>2</sub>. Densities are lowered when Avicel is added to the ionic liquid, but with addition of CO<sub>2</sub>, densities increase and display a crossover. Interestingly, the density of the mixture containing both Avicel and CO<sub>2</sub> seems to become slightly higher than the densities of [EMIM]Ac and its mixtures with Avicel or CO<sub>2</sub> as pressure is increased, yet compressibilities of the [EMIM]Ac + Avicel + CO<sub>2</sub> solution were found to be lower than those of the solution containing only 10 wt% CO<sub>2</sub>.



**Figure 14.** Comparison of densities (left) and isothermal compressibilities (right) of (a) [EMIM]Ac, (b) [EMIM]Ac + 5 wt% Avicel, (c) [EMIM]Ac + 5 wt% CO<sub>2</sub>, (d) [EMIM]Ac + 10.1 wt% CO<sub>2</sub> + 4.5 wt% Avicel and (e) [EMIM]Ac + 10 wt% CO<sub>2</sub> at 100 °C.

## 5. Conclusions

Densities of the ionic liquid [EMIM]Ac and its mixtures with carbon dioxide and microcrystalline cellulose, Avicel, can be correlated by an equation of state of the form  $\rho = A + BP^{-1} + CP + DP^{-2} + EP^m$  over a wide pressure range. Compressibilities are found to display strong dependence and increase with the CO<sub>2</sub> and or Avicel content of the mixtures.

## Acknowledgements

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**Table 1.** Parameters of the density pressure correlations  $\rho = A + BP^{-1} + CP + DP^{-2} + EP^m$

Mixture Composition (wt%)		Parameters						
IL / CO <sub>2</sub> / Avicel	T (°C)	A	B	C	D	E	m	R <sup>2</sup>
100 / 0 / 0	25	3.3767	-0.0148	0.0004	0.0053	-2.2685	-0.0001	0.9648
	50	1.0848	-0.0347	0.0004	9.1164	-9.1147	-2.0067	0.9563
	75	1.6613	-0.0038	0.0004	-0.0016	-0.6013	-0.0011	0.9654
	100	1.0409	-1.6099	0.0004	0.0127	1.5915	-0.9954	0.9621
97.5 / 2.5 / 0	25	2.0095	-0.0906	0.0001	0.0080	-0.9254	-0.0078	0.9957
	50	1.0633	5.8149	0.0007	0.2357	-6.1697	-1.0222	0.9964
	75	1.8936	-0.1674	0.0006	0.0445	-0.8259	0.0044	0.9978
	100	1.8495	-0.1753	0.0006	0.0442	-0.8020	0.0048	0.9968
95 / 5 / 0	25	1.1159	3.9594	0.0005	0.0817	-4.1410	-1.0092	0.9961
	50	1.9337	-0.4222	0.0009	0.1384	-0.7908	0.0183	0.9971
	75	1.9163	-0.2468	0.0007	0.0752	-0.8241	0.0078	0.9968
	100	1.8303	-0.3464	0.0009	0.1336	-0.7354	0.0191	0.9975
90 / 10 / 0	25	3.7671	-3.4838	0.0047	2.9443	-1.9960	0.0842	0.9983
	50	1.1318	-0.8136	0.0003	11.3323	-10.9785	-1.9885	0.9971
	75	1.6977	-1.0203	0.0008	0.5372	-0.5498	0.0277	0.9979
	100	1.0185	-1.9199	0.0009	1.2477	0.4710	-0.5477	0.9986
75 / 25 / 0	25	3.8374	3.9834	0.0023	-31.3218	-3.1873	-0.0195	0.9964
	50	-0.2944	96.2982	0.0132	205.2652	-217.8183	-1.3071	0.9976
	75	1.1371	-4.0247	-0.0018	-5.3275	-33.8677	-4.6345	0.9986
	100	0.6727	-7.0006	-0.0033	11.8395	0.4595	0.0466	0.9992
45 / 55 / 0	25	4.4243	0.1718	0.0124	-33.9452	-2.7731	0.0867	0.9960
	50	4.4866	-4.1079	0.0102	-37.0659	-2.5360	0.1062	0.9989
	75	3.4861	1.0411	-0.0058	-31.7530	-3.9701	-0.1469	0.9993
	100	3.2046	1.7141	-0.0042	-31.6088	-4.1222	-0.1742	0.9993
95 / 0 / 5	25	1.1079	0.8729	0.0001	0.0038	-0.9841	-0.9728	0.9823
	50	1.0725	-0.1218	0.0004	255.4491	-255.4275	-2.0000	0.9883
	75	1.0424	-0.0650	0.0006	10.4692	-10.5020	-1.9955	0.9929
	100	-0.2943	-0.1888	0.0010	0.0418	1.3599	-0.0117	0.9890
85.4 / 10.1 / 4.5	25	2.7222	-4.9039	0.0160	5.4779	-0.6493	0.3170	0.9818
	50	1.2219	-1.6968	-0.0014	9.9106	-8.8873	-2.0267	0.9975
	75	1.7850	-0.9427	0.0004	0.4192	-0.6249	0.0182	0.9962
	100	1.0552	-1.9077	0.0008	0.5214	1.1353	-0.8312	0.9971

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