Measurement of relative static permittivity and solvatochromic parameters of binary and ternary CO$_2$-expanded green solvents

Jingwen Cui$^a$, Mynta Norberg$^a$, Martin Andersson$^b$, Lena Klintberg$^b$, Margareta Sandahl$^a$, Larissa P. Cunico$^a$, Charlotta Turner$^{a,*}$

$^a$ Lund University, Department of Chemistry, Centre for Analysis and Synthesis (CAS), P.O. Box 124, SE-22100 Lund, Sweden

$^b$ Uppsala University, Centre of Natural Hazards and Disaster Science (CNDS), Department of Engineer Sciences, Division of Microsystem Technology, Box 534, SE-75121 Uppsala, Sweden

**HIGHLIGHTS**

- Experimental data for relative static permittivity and solvatochromic parameters.
- Large range of dielectric properties obtained for one-phase CO$_2$-expanded liquids.
- Ternary green solvent mixtures with CO$_2$ + ethanol/ethyl lactate + glycerol/water.
- Novel data for relative static permittivity of CXLs using an in-line microchip.
- Relative static permittivity of up to 75 with CO$_2$ + ethyl lactate + water.

**GRAPHICAL ABSTRACT**

**ABSTRACT**

CO$_2$-expanded liquids (CXLs) is a class of solvent systems giving relatively low viscosity in comparison to neat organic solvents. The challenge is to achieve a high overall polarity of the CXL, despite the presence of compressed liquid CO$_2$. In this study, the relative static permittivity ($\varepsilon_r$) was measured for binary and ternary one-phase mixtures of CO$_2$ + green solvent using an in-line microfluidic device. In addition, Kamlet-Taft solvatochromic parameters were experimentally determined, allowing the characterization of the polarizability, acidity, and basicity. Novel data is shown for binary and ternary systems of CO$_2$ expanded ethanol and ethyl lactate, with or without glycerol or water added, at moderate conditions of pressure and temperature (8 MPa and 35 °C). One-phase CXLs systems of a wide relative permittivity range (7.7–75.3) at lowered viscosity were enabled, by mixing different green solvents with CO$_2$.

1. Introduction

The replacement of conventional solvents with green solvents is not always a viable option due to the limiting physicochemical properties such as high viscosity of the latter. A possible solution is the use of alternative options of green solvents that include supercritical fluids, ionic liquids, and switchable solvents [1]. However, the knowledge of the physicochemical properties of such options of green solvents are still scarce in literature. Supercritical fluids, in specific carbon dioxide (CO$_2$), has the advantage of being available at low cost, chemically...
inert, renewable and environmentally sustainable [2]. CO₂-expanded liquids (CXLs) mainly differ from commonly used supercritical fluid mixtures in that the organic solvent is present in higher amounts than the CO₂ (molar fractions >0.5) and that moderate conditions of pressure and temperature are used. Controlling the fraction of CO₂ and the conditions of temperature and pressure of CXLs, allows for the tuning of its physicochemical properties, such as polarizability, density and viscosity, as well as the number of phases. This has allowed CXLs to find niche uses as reaction medium for the synthesis of specialized materials, homogenous and heterogeneous catalysis and for the analytical separations and extraction [1,3–8]. The use of moderate conditions of temperature and pressure have advantages such as being benign for thermolabile compounds and lower cost of the instruments. Moreover, the use of CXLs allows its application to more polar and moderate polar compounds due to the presence of relatively large proportions of organic solvent (≥50%) in comparison with supercritical CO₂ or without a small volume fraction (5–20%) of co-solvent. Ethanol is still one of the most commonly used moderately polar green solvents in CXLs [3,9–12]. Other options of green solvents used in CXLs are methanol [12], alkyl acetates [12], acetone [13], 2-methyltetrahydrofuran [13], ethyl lactate [14], glycerol [14], acetic acid + water [15], among others [16]. Solvents with higher polarity have been increasingly used recently due to the need of suitable solvents for more polar molecules, such as peptides and polar pharmaceutical drugs [17–20].

It is well-known that the information of polarity, acidity and basicity of the solvent are important information for different applications using supercritical and subcritical fluids, such as in chromatography [21,22] and in extraction [23,24]. One way to measure polarity, or rather the dielectric properties of the solvent, is by determining the relative static permittivity (εr). Different methods can be seen in the literature for the measurement of εr of supercritical fluids [25–27]. For CXLs, experimental data of εr can be found in the literature for solvent mixtures of CO₂-expanded acetone, ethanol, and methanol, respectively [28]. However, no experimental data of εr are found in the literature so far for CXLs of highly polar co-solvent mixtures, including water or glycerol.

Another way to obtain information about solvent dielectric properties is by using the Kamlet-Taft solvatochromic parameters [29]. For CXLs systems, Kamlet-Taft parameters (polarizability π*, acidity α and basicity β) of various solvents are reported. Among which, the π* parameter can be found in the literature for CO₂-expanded acetone, ethanol, and methanol, respectively, at 25 °C [28]. Kamlet-Taft π* and α parameters have been reported for CO₂-expanded ethyl lactate at 40 °C and pressure lower than 6 MPa [30]. Kamlet-Taft parameters for CO₂-expanded methanol [31,32] and CO₂-expanded acetone mixtures [31] were obtained previously in literature. However, once again no experimental data of any of the Kamlet-Taft parameters are observed in the literature so far for highly polar CXL mixtures containing water and/or glycerol.

In this study, the relative static permittivity (εr) and the Kamlet-Taft parameters (π*, α and β) were measured for one-phase binary and ternary CXLs systems, consisted of pressurized CO₂ mixed with highly polar and moderate polar green solvent mixtures (ethanol, ethyl lactate, water, glycerol). For the measurements of εr, an in-line microchip consisting of a flow channel between two capacitor plates was used. The construction and validation of this microfluidic platform is described with more details in Anderson et al. [33]. It presents the advantages of high accuracy in the in-line measurements and considerable low volume. The conditions of pressure and temperature chosen in this work (8 MPa and 35 °C) aim for having a one single phase (L) for all the studied mixtures, i.e. avoiding the two-phase regime (V + L), but still operating at mild conditions of temperature and pressure. Ethanol and ethyl lactate were chosen for presenting moderate polarity, while water and glycerol were chosen for being highly polar green solvents. The high viscosity of glycerol has limited its potential to be used for extraction and other analytical applications [34]. This limitation was addressed in this work by combining glycerol with ethanol or ethyl lactate and water with ethyl lactate before adding compressed liquid CO₂ to the solvent mixtures to form one-phase CXL mixtures.

2. Experimental

2.1. Materials

CO₂ (purity ≥99.9993%) was purchased from AGA (Växjö, Sweden). Ethanol (purity ≥99.7%) was purchased from Solveco (Rosersberg, Sweden). Methanol (purity 99.8%) was purchased from VWR chemicals (Pennsylvania). 2- Propanol (purity 99.8%) and acetoni trile (purity 99.9% LC-MS grade) were purchased from Scharlau (Sentmenat, Spain). Glycerol (purity 99.5%) was purchased from Merck (KGaA, Darmstadt, Germany). Ethyl lactate (99%) was purchased from Alfa Aesar (Karlsruhe, Germany). Cyclohexane (purity 99.5%) was purchased from Honeywell (Riedel-de Haen, Germany). n-Octanol (purity 99%, anhydrous grade), 4-nitroanisole (purity 97%), N, N-dimethylcyclohexane (purity 97%) and 4- nitrophenol (purity 97%) were purchased from Sigma Aldrich (St Louis, MO, USA). Milli-Q water with a resistance of 18.2 MΩ was produced using Millipore Milli-Q Plus system (Model Milli-Q Gradient A10, Merck).

2.2. Relative static permittivity

The equipment setup previously reported by Cunico et al. [14] was modified by adding an in-line microchip having integrated capacitor plates connected to a vector network analyzer - VNA (Agilent Technologies N9923A Field Fox Handheld RF) (see Fig. 1). This set up was used to measure the capacitance, making it possible to calculate εr for the dielectric liquid. CXL mixtures with different compositions and molar ratios were produced by mixing certain amounts of each compound. All liquid solvents were kept at room temperature, and were added volumetrically to the view cell, except for glycerol which was added gravimetrically. Liquid CO₂ was kept at 4 °C and was added volumetrically to the view cell. In order to keep the total masses constant for all mixtures, a generalized reduced gradient optimization was used to calculate the necessary amounts of each component for the different compositions and molar ratios. The density data needed for these calculations were acquired from the NIST Chemistry Webbook, SRD 69 [35].

A K-type thermocouple connected to a thermometer was used to measure the temperature throughout each experiment (uncertainty of ca. ±1.0 °C). A Swagelok pressure gauge of model C 400 bar (EN 837-1) was also connected to the view cell giving an uncertainty of ca. ±0.6 MPa. The CXLs mixtures inserted in the view cell were then pressurized to near the target pressure by using CO₂ to push the piston from the outside, and magnetic stirring was provided using a magnetic stir bar during heating. This was done to obtain faster heating and homogenization of the sample. When the target temperature was reached, the pressure was increased to the target pressure, and the recirculation line was opened. The system was allowed to re-equilibrate at the target temperature during re-circulation, until the CO₂-pump flow rate, recirculation line pressure, and VNA response was stable. A MATLAB script was used to record the capacitance as measured by the VNA at 800 points over 400 s, and the average of these points was taken to minimize the effect of instrument noise on the result. After each measurement, the system was vented into a waste container.

The basis for the calibration design is the linear relationship between the measured capacitance (C) and relative static permittivity εr, Eq. (1):

\[ \varepsilon_r = \frac{(C - a)}{b} \]  

(1)

where a and b are constants [33]. To find the values of a and b, the method of least squares was used for compounds having known εr.
The effect of temperature on the $a$ constant within the 25–35 °C range was considered negligible. It has been postulated that the $\varepsilon_r$ of an ideal mixture is additive, and therefore the empirical Eq. (2) (the additive model) has been popular for decades (especially in chemical pharmacology) for approximating the $\varepsilon_r$ of solvent mixtures [36]. Other, non-linear models are available for non-ideal systems [37], but they are not practical for applications such as chromatography and extractions as they require several fitting points. In comparison, the additive model only requires knowledge of the $\varepsilon_r$ of the components. In this work, the linearity of the binary and ternary mixtures and their fit to the additive model were analyzed.

$$\varepsilon_{r(\text{mix})} = \sum_{i=1}^{n} x_i \varepsilon_{r(i)}$$

(2)

### 2.3. Kamlet-Taft Parameters

The equipment setup used for the Kamlet-Taft parameters is shown in Fig. 2. In this setup, CO$_2$ was also delivered to the view cell by using a piston pump connected to a cooling bath (F12-ED, Julabo, Germany). The main differences between the two equipment setups (Figs. 1 and 2) is that for the Kamlet-Taft parameters the temperature of the view cell was controlled through a heating jacket that was connected to a heating controller to facilitate the visualization of the chromophore dissolution, and it contained a flow cell (Knauer, Germany) with a path length of 1 cm connected to an in-line spectrophotometer (AvaSpec-ULS2048L, Avantes-Netherlands). Stirring was provided inside the view cell using a magnetic stir bar in order to accelerate the dissolution of the chromophore in the CXLs and the temperature equilibration.
Originally, five to seven chromophores were selected in the probing of Kamlet-Taft parameters, and the results for each parameter were based on averaging the measurement of each chromophore [38–40]. However, recent publications have shown several options of chromophores, such as 4-nitroanisole or N,N-dimethyl-4-nitroaniline for polarizability ($\pi^*$), N,N-dimethylbenzamide or 4-carbo-methoxy-1-ethylpyridinium iodide for acidity ($\alpha$), and 4-nitroaniline or 4-nitrophenol for basicity ($\beta$) in conventional solvents, ionic liquids or CXLs [29,41].

Briefly, the Kamlet-Taft parameters were calculated from the wavelength at maximum absorbance of the selected indicators. The chromophore was dissolved in the solvent to be characterized, as well as in a reference solvent, which is normally cyclohexane. The shift in the maximum absorption wavelength of the chromophore when dissolved as in a reference solvent, which is normally cyclohexane. The shift in the maximum absorption wavelength of the chromophore when dissolved in the targeted solvents as compared to in the reference solvent was measured experimentally. The calculation of $\pi^*$ is as shown in Eq. (3).

In this work, 4-nitroanisole, a common chromophore used for $\pi^*$ determination, was considered together with the following equation for the calibration [38]:

$$\pi^* = \frac{\nu - \nu_0}{s} + a \alpha + b \beta$$  

(3)

where $\nu = 10,000/\lambda_{\text{max}}$ and $\lambda_{\text{max}}$ is the maximum absorption wavelength of the CXLs mixtures. $\nu_0$ is the maximum absorption wavelength of reference solvent (cyclohexane), and $s$ is the susceptibility coefficient obtained from standardization in which the value is set to zero (0) for cyclohexane and one (1) for dimethyl sulfoxide.

For the acidity ($\alpha$) measurements, phenol blue (N, N-dimethyl-lindoaniline) was selected due to its response to hydrogen bond donor solvents and due to the fact that there is no evidence of the interaction between the hydrogen donor and the dye [42,43]. The following equation was considered for the calibration [40]:

$$XYZ = XYZ_0 + s \pi^* + a \alpha$$  

(4)

Where $XYZ$ (kcal mol$^{-1}$) = 28,591/$\lambda_{\text{max}}$, $XYZ_0$ is the calculated transition energy for the reference solvent (cyclohexane in this work), and $s$ and $a$ are coefficients obtained from linear regression.

Finally, for the basicity ($\beta$) measurements, 4-nitrophenol was considered, which was previously used in the literature for measurements of CO$_2$ expanded methanol, acetone and some other fluids [29,31]. The following equation was applied for the calibration [39]:

$$XYZ = XYZ_0 + s \pi^* + a \alpha + b \beta$$  

(5)

Where $s$, $a$ and $b$ are obtained from linear regression.

3. Results and discussion

3.1. Relative static permittivity

For the calibration of $\varepsilon_r$, using the equipment setup and methodology previously described in the experimental section, a set of compounds with a wide range of $\varepsilon_r$ values were selected from the literature (CO$_2$, n-octanol, ethanol, acetone, and water, see Table 1) to fit the proportionality constants $a$ and $b$. The average capacitance ($C$, Eq. (1)) was measured in triplicate and the standard deviation ($\sigma_r$) for $\varepsilon_r$ is shown in Table 1.

The validation of the method was then assessed considering $\varepsilon_r$ for mixtures of CO$_2$ and green solvents previously reported in the literature (Table 2). The measured values of low CO$_2$-content mixtures showed small deviation from the available data reported in literature [25,46,48]. For mixtures containing higher amount of CO$_2$, this difference was higher, presumably due to their higher compressibility and hence higher sensitivity towards both temperature and pressure variations (as $\varepsilon_r$ highly depends on density). This is especially true since the final pressure adjustment was performed with cold CO$_2$ after heating and equilibration of the temperature. It is however difficult to draw appropriate conclusions since there are so few published studies with data.

After calibration and validation, $\varepsilon_r$ values were measured for binary mixtures of CXLs and each neat solvent at 35 °C and 8 MPa (Table 3).

The $\varepsilon_r$ values for the binary mixtures of CO$_2$ + ethanol and CO$_2$ + ethyl lactate decreases with the addition of CO$_2$, as expected. This is due to the increment of the concentration of the non-polar compound (CO$_2$) in the mixture. The decrement seems to follow a linear relationship with the changes in CO$_2$ compositions (see Supplementary Material, Fig S1).

For ternary mixtures of CXLs, $\varepsilon_r$ values were also measured at 35 °C and 8 MPa. For the polar solvent glycerol in mixtures with CO$_2$ + ethanol and CO$_2$ + ethyl lactate, the experimental data is shown in Tables 4 and 5, respectively, for different molar ratios of CO$_2$/ethanol and CO$_2$/ethyl lactate. For the highly polar solvent water in mixtures with CO$_2$ + ethyl lactate, the experimental data is shown in Table 6 for different molar ratios of CO$_2$/ethyl lactate. For the ternary mixtures, only the mixtures with highest concentration of glycerol or water were repeated three times and the standard deviations observed were between 0.05 and 1.01, indicating minor variations between each repetition. In order to save time, the rest of the mixtures were measured only once.

A wide range of relatively polar ($\varepsilon_r \geq 15$) one-phase ternary mixtures were identified in this work, containing CO$_2$ molar fractions ranging between 0.01 and 0.5 (mole ratios of 0.1–0.5 for CO$_2$/ethanol and CO$_2$/ethyl lactate). Moreover, this work demonstrates that it is possible to dissolve relatively high molar fractions of a highly polar solvent (glycerol or water) in CO$_2$/ethanol or CO$_2$/ethyl lactate mixtures. These results are graphically demonstrated in Fig. S2.

The solubility limits of glycerol in CO$_2$-expanded ethanol, and glycerol and water in CO$_2$-expanded ethyl lactate, were determined by visual inspection. Nonetheless, the intention is not to report phase equilibria measurements, but rather to verify ranges of miscible compositions for the respective CXLs systems to assure that the measurements were done in one-phase systems. When glycerol was added in large amounts to 1:9 CO$_2$/ethanol, 1:9 CO$_2$/ethyl lactate, and 3:7 CO$_2$/ethyl lactate, viscosity rather than miscibility limited the upper range of the compositions. Despite having a single, homogenous phase, the high viscosity eventually caused low flow rates, line blockages, and local pressure variations. Previously reported vapor-liquid equilibrium (VLE) data for the CO$_2$ + ethanol + glycerol system had glycerol/ethanol molar ratios up to 1:12 [49,50]. In this work, glycerol remained miscible up the molar fraction of 0.60 in 1:9 CO$_2$/ethanol (mole ratio), and molar fraction of 0.28 in 3:7 CO$_2$/ethanol (mole ratio). Glycerol had an even wider miscible and viable compositional range in CO$_2$ + ethyl lactate. A molar fraction of 0.60 of glycerol was successfully added to 3:7 CO$_2$/ethyl lactate (mole ratio), and thus more glycerol could be added to this mixture than to 1:9 CO$_2$/ethyl lactate before reaching a similar viscosity, allowing even higher values of $\varepsilon_r$. Hence, glycerol seems to be a promising polar co-solvent in ternary CXLs as an alternative to water.

For the ternary mixtures, the residuals between the obtained values and the values predicted by the additive model (Eq. (2)) were uniformly distributed around the model estimates for glycerol in CO$_2$/ethanol (1:9 and 3:7), which suggested a good fit across the considered range of compositions. However, the residuals for glycerol in CO$_2$/ethanol (5:5) and for water as well as glycerol in the CO$_2$/ethyl lactate mixtures, all

---

Table 1. Calibration data for $\varepsilon_r$ where $\varepsilon_r$ (exp.) are calculated using (Eq. (1)) with the fitted constants. $\sigma_r$ is the standard deviation for triplicate measurements.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\varepsilon_r$ (exp.)</th>
<th>$\sigma_r$ (litr.)</th>
<th>$\varepsilon_r$ (litr.)</th>
<th>T (°C)</th>
<th>P (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>1.16</td>
<td>0.03</td>
<td>1.13 [44]</td>
<td>25</td>
<td>6.4</td>
</tr>
<tr>
<td>n-Octanol</td>
<td>10.25</td>
<td>0.10</td>
<td>10.19 [45]</td>
<td>25</td>
<td>8.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.44</td>
<td>0.21</td>
<td>24.56 [45]</td>
<td>25</td>
<td>8.0</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>36.26</td>
<td>0.65</td>
<td>36.26 [46]</td>
<td>25</td>
<td>8.0</td>
</tr>
<tr>
<td>Water</td>
<td>77.45</td>
<td>0.14</td>
<td>77.41 [47]</td>
<td>28</td>
<td>7.0</td>
</tr>
</tbody>
</table>
displayed an asymmetrical distribution of the residuals around the zero line, which suggested a poor fit. The residual plots are included in the Supplementary Material (Figs. S3 and S4).

### Table 2
Validation method for $\varepsilon_r$. $x_{CO_2}$ is the molar fraction of CO$_2$ in the binary one-phase mixtures, and $\sigma_r$ is the standard deviation for triplicate measurements.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$x_{CO_2}$</th>
<th>$\varepsilon_r$ (exp.)</th>
<th>$\sigma_r$</th>
<th>$\varepsilon_r$ (litt.)</th>
<th>$T$ (°C)</th>
<th>$P$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.22</td>
<td>27.13</td>
<td>0.18</td>
<td>25.8 [25]</td>
<td>35</td>
<td>7.2</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.73</td>
<td>8.89</td>
<td>1.07</td>
<td>4.9 [25]</td>
<td>35</td>
<td>7.6</td>
</tr>
<tr>
<td>Ethyl lactate</td>
<td>0.79</td>
<td>3.97</td>
<td>1.05</td>
<td>3.2 [48]</td>
<td>31</td>
<td>7.2</td>
</tr>
</tbody>
</table>

### Table 3
Measured $\varepsilon_r$ for neat solvents and binary one-phase CXLs at 35 °C and 8 MPa. $x_{CO_2}$ is the molar fraction of CO$_2$ and $\sigma_r$ is the standard deviation ($n = 3$).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$x_{CO_2}$</th>
<th>$\varepsilon_r$</th>
<th>$\sigma_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>1.0</td>
<td>1.42</td>
<td>0.04</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.0</td>
<td>23.86</td>
<td>0.12</td>
</tr>
<tr>
<td>Ethyl lactate</td>
<td>0.0</td>
<td>13.01</td>
<td>0.09</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.0</td>
<td>41.65</td>
<td>0.01</td>
</tr>
<tr>
<td>Water</td>
<td>0.0</td>
<td>81.43</td>
<td>0.78</td>
</tr>
<tr>
<td>Ethanol + CO$_2$</td>
<td>0.1</td>
<td>21.93</td>
<td>0.11</td>
</tr>
<tr>
<td>Ethanol + water</td>
<td>0.1</td>
<td>12.10</td>
<td>0.24</td>
</tr>
<tr>
<td>Ethyl lactate + CO$_2$</td>
<td>0.1</td>
<td>12.10</td>
<td>0.28</td>
</tr>
<tr>
<td>Ethanol + glycerol</td>
<td>0.1</td>
<td>8.82</td>
<td>0.10</td>
</tr>
<tr>
<td>Ethyl lactate + glycerol</td>
<td>0.5</td>
<td>7.71</td>
<td>0.25</td>
</tr>
</tbody>
</table>

### Table 4
Measured $\varepsilon_r$ for CO$_2$ + ethanol + glycerol ternary mixtures at 35 °C and 8 MPa. The molar fraction of glycerol ($x_{glycerol}$) is expressed in relation to the total amount of the ternary mixture. Replicate measurements were done for a selection of experiments ($n = 3$), and $\sigma_r$ is the standard deviation for these.

<table>
<thead>
<tr>
<th>CO$_2$/Ethyl lactate (mole ratio)</th>
<th>$x_{glycerol}$</th>
<th>$\varepsilon_r$</th>
<th>$\sigma_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:9</td>
<td>0.00</td>
<td>21.9</td>
<td></td>
</tr>
<tr>
<td>3:7</td>
<td>0.30</td>
<td>26.3</td>
<td>0.23</td>
</tr>
<tr>
<td>5:5</td>
<td>0.40</td>
<td>29.28</td>
<td>0.23</td>
</tr>
</tbody>
</table>

### Table 5
Measured $\varepsilon_r$ for CO$_2$ + ethyl lactate + glycerol ternary mixtures at 35 °C and 8 MPa. The molar fraction of glycerol ($x_{glycerol}$) is expressed in relation to the total amount of the ternary mixture. Replicate measurements were done for a selection of experiments ($n = 3$), and $\sigma_r$ is the standard deviation for these.

<table>
<thead>
<tr>
<th>CO$_2$/Ethyl lactate (mole ratio)</th>
<th>$x_{glycerol}$</th>
<th>$\varepsilon_r$</th>
<th>$\sigma_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:9</td>
<td>0.00</td>
<td>12.1</td>
<td></td>
</tr>
<tr>
<td>3:7</td>
<td>0.30</td>
<td>14.5</td>
<td></td>
</tr>
<tr>
<td>5:5</td>
<td>0.40</td>
<td>20.70</td>
<td>0.05</td>
</tr>
</tbody>
</table>

### Table 6
Measured $\varepsilon_r$ for CO$_2$ + ethyl lactate + water ternary mixtures at 35 °C and 8 MPa. The molar fraction of water ($x_{water}$) is expressed in relation to the total amount of the ternary mixture. Replicate measurements were done for a selection of experiments ($n = 3$), and $\sigma_r$ is the standard deviation for these.

<table>
<thead>
<tr>
<th>CO$_2$/Ethyl lactate (mole ratio)</th>
<th>$x_{water}$</th>
<th>$\varepsilon_r$</th>
<th>$\sigma_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:9</td>
<td>0.00</td>
<td>12.1</td>
<td></td>
</tr>
<tr>
<td>3:7</td>
<td>0.30</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td>5:5</td>
<td>0.40</td>
<td>15.2</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Aparicio et al. [51] thoroughly characterized neat ethyl lactate, and reported an efficient packing due to its molecular shape, allowing for extensive intermolecular interactions and the formation of hydrogen bonds. In an earlier study by Aparicio et al. [52], mixtures of ethyl lactate and water was shown to have a highly nonlinear compositional dependence of $\varepsilon_r$, primarily through the disruption of water networks by ethyl lactate, and secondarily through the disruption of ethyl lactate clusters by water. This is likely a major part in the explanation of the deviation of the additive model for the CO$_2$ + ethyl lactate + water mixtures studied in this work, as the maximum relative static permittivity of mixing measured by Aparicio et al. [52] was very similar to the maximum residuals in this work.

### 3.2. Kamlet-Taft parameters

For the calibration of the equipment setup with the chosen chromophores, experimental data of Kamlet-Taft, $\pi^*$, $\alpha$, and $\beta$ parameters were used from literature for five different solvents (2-propanol, acetonitrile, water, cyclohexane and ethanol). See Supplementary Material, Table S5, for the experimental data used in the calibration. The obtained coefficients from the calibration can be seen in Eqs. (6)–(8) below:

$$\pi^* = \frac{\lambda_{\text{max}} - 34.028}{-2.214}, \quad \nu = 1000/\lambda_{\text{max}}$$  \hspace{1cm} (6)

$$\sigma = XYZ - 53.389 + 3.367\pi^*, \quad XYZ = 28591/\lambda_{\text{max}}$$ \hspace{1cm} (7)

$$\beta = \frac{\nu - 34.313 + 1.534\pi^* + 0.866\sigma}{-1.007}, \quad \nu = 1000/\lambda_{\text{max}}$$ \hspace{1cm} (8)

Where $\lambda_{\text{max}}$ is the maximum absorption wavelength for the chromophore 4-nitroanisole in Eq. (6), the chromophore phenol blue (N, N-dimethylindoloaniline) in Eq. (7) and the chromophore 4-nitrophenol in Eq. (8). The obtained values for pure compounds after the calibration
showed good agreement with the values reported in literature, as seen in Fig. 3.

The validation of the equipment setup was performed considering the experimental data available for the binary mixture of CO$_2$ + methanol at 35 °C and 8 MPa [31], see Table S6. The experimental values for the $\pi^*$ parameter was similar to the observed values in literature (Fig. 4), although, slightly deviating at CO$_2$ molar fraction over 0.5. The general trend is clear however, in that the $\pi^*$ parameter decreases with CO$_2$ content, and this decrease is more pronounced at higher molar ratio of CO$_2$, which also has been found by others [32]. Obviously, what happens is that hydrogen bonds are weakened with a higher proportion of CO$_2$.

The measured $\alpha$ parameter values decreased with the addition of CO$_2$ in this work, as previously shown by Cui et al., for CO$_2$ + methanol at 25 °C [32]. Similar behavior for the $\beta$ parameter was observed before in literature [31,53]; see for instance Fig. 4 in the cited literature [31].

The information of Kamlet-Taft parameters is scarce in the literature at moderate conditions of pressure and temperature, which makes the use of literature data for validation of methods rather difficult. The measurement of the $\beta$ parameter was performed for pure ethyl lactate...
under ambient conditions to further verify the validation of the equipment setup. The obtained value was 0.55 in comparison with 0.52 from the literature [29].

After the calibration and validation of the equipment setup, measurements to obtain novel data were performed for binary and ternary mixtures of CXLs. The measurement of Kamlet-Taft parameters $\pi^*$, $\alpha$ and $\beta$ for binary mixtures containing CO$_2$ + ethanol and CO$_2$ + ethyl lactate, and ternary mixtures containing CO$_2$ + ethanol + glycerol, CO$_2$ + ethyl lactate + water and CO$_2$ + ethyl lactate + glycerol are shown in Figs. 5, 6, and 7. In the same figures, the values of $\varepsilon_r$ measured in this work are also shown to allow for comparison with the measured values of the Kamlet-Taft parameter $\pi^*$. Note that in these figures, when the molar fraction of water or glycerol is equal to zero, the values of the parameters correspond to the binary mixtures. In order to determine the precision of the measurements, for all three parameters $\pi^*$, $\alpha$ and $\beta$, five repeated measurements were done for one of the ternary mixture (CO$_2$/ethyl lactate, 3:7, with 0.5 molar fraction of water added). The standard deviation obtained from these five measurements for $\pi^*$, $\alpha$ and $\beta$ parameters were ±0.02, ±0.02 and ±0.06, respectively. Due to these relatively small variations, the rest of the compositions were not repeated in order to save time.

In this work we study the effect of adding glycerol or water to CO$_2$/ethyl lactate mixtures and glycerol to CO$_2$/ethanol mixtures in order to tune the solvent properties towards higher polarizability ($\pi^*$) and relative static permittivity ($\varepsilon_r$). CO$_2$ is added as a viscosity-lowering entrainer, which also impacts on the dielectric properties of the solvents.

In Figs. 5–7 it is clear that depending on the mole ratio of CO$_2$ to ethanol respectively ethyl lactate, the starting point in terms of $\pi^*$ and $\varepsilon_r$ differ. The more CO$_2$ that is present from the beginning, the lower the $\pi^*$ and $\varepsilon_r$.

The effect of adding glycerol to either CO$_2$/ethanol (Fig. 5) or CO$_2$/ethyl lactate (Fig. 7), results as hypothesized in an increasing $\pi^*$ and $\varepsilon_r$. The experiments were however only doable at CO$_2$ mole ratios of 0.1 and 0.3. This is because at a CO$_2$ mole ratio of 0.5, the miscibility of glycerol in both CO$_2$/ethanol and CO$_2$/ethyl lactate mixtures was too low. When miscible though, it is obvious from Figs. 5 and 7 that glycerol significantly increases both $\pi^*$ and $\varepsilon_r$ in both types of solvent mixtures.

In terms of water as an additive instead of glycerol, we explore only CO$_2$/ethyl lactate/water mixtures, since the ternary system CO$_2$/ethanol/water is fairly well studied in the literature. As shown in Fig. 6 as compared to in Fig. 7, a larger amount of water can be added to the mixtures, thereby enabling significantly higher $\pi^*$ and $\varepsilon_r$ as compared to when glycerol is used. It is certainly easier to achieve large molar fraction of water, since miscibility is excellent and there is no viscosity limitations.

The effects of glycerol as well as water addition on the overall acidity and basicity of the ternary solvent mixtures are more unclear, and further studies are needed in order to draw any conclusions.
Overall, comparing glycerol and water as potential polarity-increasing additives to CXLs, water has a larger potential, since it has a higher miscibility with CO2/ethyl lactate and also a lower viscosity. However, glycerol is a polar additive that could be interesting to explore further in certain applications.

4. Conclusions

This work shows the potential of using ternary mixtures of nonpolar CO2 + highly polar solvents such as glycerol or water provided that a “bridging” medium polar solvent such as ethanol or ethyl lactate is used. In this study, a large range of relative static permittivity ($\varepsilon_r$ between 7.7 and 75.3), Kamlet-Taft polarizability ($\pi^*$ between 0.36 and 1.07), acidity ($\alpha$ between 0.26 and 0.91) and basicity ($\beta$ between 0.44 and 1.13) have been achieved. $\varepsilon_r$ was well described by the additive model throughout the whole measurement range for all mixtures of the CO2 + ethanol + glycerol system, which was not the case for the CO2 + ethyl lactate + glycerol and CO2 + ethyl lactate + water systems. Our results show that relatively polar one-phase ternary CO2 expanded green solvents can be achieved at the mild condition of 8 MPa and 35 °C, with pertinently low viscosity, and obvious applications in extraction and separation processes targeting polar compounds.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the Swedish Research Council VR (621-2014-4052) and Swedish Research Council FORMAS (222-2014-1924, 2016-00604).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.supflu.2021.105196.

References
