

1 **Determination of density, viscosity and vapor pressures of**  
2 **mixtures of dimethyl sulfoxide + 1-allyl-3-methylimidazolium**  
3 **chloride at atmospheric pressure**

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12 **Abstract**

13 In this work, densities, viscosities and vapor pressures of dimethyl sulfoxide (DMSO) + 1-allyl-  
14 3-methylimidazolium chloride (AmimCl) mixtures have been experimentally determined.  
15 Densities and viscosities were measured at temperatures  $T = [293.15, 373.15]$  K and molar  
16 fractions of dimethyl sulfoxide  $x_{\text{DMSO}} = 0, 0.05, 0.1, 0.15, 0.25, 0.5, 0.75, 0.9$  and 1 at atmospheric  
17 pressure with a Stabinger densimeter-viscosimeter. Viscosities and densities were found to  
18 decrease with increasing temperature and DMSO concentrations. Correlation of viscosity was  
19 made as a function of temperature and concentration with two modifications of the Seddon and  
20 Grunberg-Nissan equation, one with an average relative deviation of 6.8% and the second one of  
21 16.3%. Vapor pressures of the mixtures were measured at  $T = [353.1, 433.1]$  K. and were  
22 correlated with Non-Random-Two-Liquid (NRTL) model, obtaining ARD% between 5 and 12%.

23 **Keywords:** ionic liquid, viscosity, vapor pressure, correlation.

24

25

## 26 **List of symbols**

|    |               |  |
|----|---------------|--|
| 27 | %ARD          | Average relative deviation   |
| 28 | %Max          | Maximum deviation  |
| 29 | $k$           | coverage factor  |
| 30 | $n$           | number of experimental data  |
| 31 | $P$           | pressure [=] bar   |
| 32 | $T$           | temperature [=] K  |
| 33 | $V_m$         | molar volume [=] $\text{cm}^3 \cdot \text{mol}^{-1}$                       |
| 34 | $u(z)$        | uncertainty of the measurement $z$   |
| 35 | $x_i$         | molar fraction of the component $i$ [=] $\text{mol} \cdot \text{mol}^{-1}$ |
| 36 | Greek symbols |  |
| 37 | $\alpha_{ij}$ | NRTL non-randomness parameter between substances $i$ and $j$               |
| 38 | $\gamma_i$    | activity coefficient of the substance $i$                                  |
| 39 | $\mu$         | viscosity [=] $\text{mPa} \cdot \text{s}$                                  |
| 40 | $\rho$        | density [=] $\text{g} \cdot \text{cm}^{-3}$                                |
| 41 | $\tau_{ij}$   | NRTL binary interaction parameter between substances $i$ and $j$           |

42

## 43 **1 Introduction:**

44 Ionic liquids (ILs) are ionic substances liquids at room or near-room temperature. They have a  
45 practically negligible vapor pressure. They also present high solvation power for different kinds  
46 of substances and it is possible to adjust their properties by choosing the ions and its substituents  
47 [1]. Due to their low vapor pressure they are considered as “green” solvents and they have been  
48 proposed as replacement of the conventional organic solvents with high volatility [2]. In the last  
49 years they have attracted a lot of attention as no derivatizing solvents for cellulose [3]. In special,  
50 the ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl) has attracted a lot of attention in  
51 the last years due to its ability to dissolve cellulose and its relatively low viscosity and melting  
52 point [4,5].

53 The most important disadvantage of using ILs as solvents of cellulose is their high viscosity. In  
54 addition, the viscosity of the ILs increase dramatically when cellulose is added [3,6]. Therefore,  
55 ionic liquids for cellulose processing are frequently used in combination with co-solvents [7,8],  
56 as it is well known that molecular solvents are able to decrease the viscosity of ionic liquids [9].  
57 Some solvents as dimethyl sulfoxide (DMSO) are frequently used in applications of cellulose  
58 processing with ILs because it is a swelling agent of the cellulose [4], it decreases the friction  
59 between monomers [10] and it does not reduce cellulose solubility [11]. Andanson et al. [8]  
60 studied the effect of DMSO in the mixtures of DMSO + IL and concluded that the DMSO does  
61 not affect the ionic liquid – glucose interactions.

62 Some fundamental physical properties of mixtures of imidazolium chloride based ionic liquids  
63 with co-solvents have been measured by different authors in recent years. Density, viscosity,  
64 refractive index and conductivity of mixtures H<sub>2</sub>O + AmimCl at 298.15 K were measured by Wu  
65 et al. [12]. Sescousse et al. [13] measured the viscosity of mixtures cellulose + 1-butyl-3-  
66 methylimidazolium chloride (BmimCl) at different temperatures. Calvar et al. [14] measured  
67 densities, refractive indices, speeds of sound and isentropic compressibility of the ternary mixture  
68 ethanol + water + BmimCl. In addition, for binary mixtures of BmimCl with ethanol or water, the  
69 said properties were also determined at 298.15 K and atmospheric pressure. Lopes et al. [15]  
70 studied the reduction in the viscosity of the ionic liquid AmimCl caused by dissolution of CO<sub>2</sub>.  
71 Jiménez et al. [16] measured densities and viscosities of aqueous mixtures of AmimCl and they  
72 found negative excess molar volumes of the mixtures and correlated the viscosities of the  
73 mixtures. However, to the best of our knowledge there are no experimental data of viscosities or  
74 vapor pressures of mixtures DMSO + AmimCl.

75 Some authors have studied the influence of the ionic liquids in the vapor pressure of organic  
76 compounds and water. It has been found that in general ionic liquids reduce the vapor pressure of  
77 mixtures IL + organic compounds and IL + water, presenting a negative deviation from the  
78 Raoult's law that is attributed to the interactions and affinity between the molecules [17,18]. This  
79 has been observed among others by Zhao et al. [17], who measured and adjusted vapor pressures

80 of a variety of alkylimidazolium dialkylphosphates based ionic liquids, Jiang et al. [18] measured  
81 vapor pressures of systems containing water, alcohols + 1-ethyl-3-ethylimidazolium  
82 diethylphosphate (Et<sub>2</sub>imEt<sub>2</sub>PO<sub>4</sub>). Han et al. [19] studied the vapor pressure of mixtures containing  
83 1-ethyl-3-methylimidazolium tetrafluoroborate (EmimBF<sub>4</sub>) using benzene, thiophene, toluene and  
84 water as solutes. However, some authors reported positive deviations of the Raoult's Law, such  
85 as in the systems containing bis(trifluoromethyl-sulfonyl) imide (TF<sub>2</sub>N), PF<sub>6</sub> and BF<sub>4</sub> anions [20–  
86 22].

87 In this work viscosity and densities of mixtures of DMSO + AmimCl were measured at  
88 atmospheric pressure at various conditions of temperature and concentration and correlated.  
89 Vapor pressures of the mixtures were also experimentally determined and correlated with the  
90 Non-Random Two Liquids (NRTL) Model.

## 91 **2 Experimental**

### 92 **2.1 Materials**

93 The DMSO used in the experiments was provided by Sigma– Aldrich and has a purity of 98%  
94 with a humidity of 200 ppm. The ionic liquid 1-allyl-3-methylimidazolium chloride was  
95 purchased from Iolitec (assay (NMR) = 98%; 1-Allyl-3-methylimidazolium (IC) = 99.9%;  
96 Chloride (IC) = 99.9%; 1-Methylimidazole (IC) < 1% and Water (KF) = 0.2467% in mass  
97 fraction). The ionic liquid was further dried by applying a high level of vacuum while using a  
98 magnet stirring at temperature of 86°C for two days, and the final humidity was below 0.14% in  
99 mass fraction, determined by a Karl - Fischer Coulometric titration using Mettler Toledo C20 KF.  
100 The compound data are summarized in the sample table in Table 1.

101 Table 1: Materials and purification methods.

| Chemical name                        | Source  | Initial mass fraction purity | Purification method | Final mass fraction purity | Analysis method |
|--------------------------------------|---------|------------------------------|---------------------|----------------------------|-----------------|
| 1-allyl-3-methylimidazolium chloride | Iolitec | 0.98                         | Vacuum treatment    | 0.9986 <sup>a</sup>        | KF <sup>a</sup> |

|                    |       |                   |   |                   |   |
|--------------------|-------|-------------------|---|-------------------|---|
| dimethyl sulfoxide | Sigma | 0.98 (mole basis) | - | 0.98 (mole basis) | - |
|--------------------|-------|-------------------|---|-------------------|---|

102 a: Based on water impurity only  
 103 b: Karl - Fischer Coulometric titration  
 104

105 2.2 Measurements with Stabinger viscometer

106 The mixtures were prepared gravimetrically by using a high precision balance (Sartorius Basic  
 107 BA 310P, precision = 0.001 g) inside an inert gas chamber. The water concentration of the  
 108 mixtures was determined with Karl - Fischer Coulometric titration using Mettler Toledo C20 KF  
 109 before the experiments, and immediately equipment was charged. Thus a proper handling was  
 110 used to avoid as much as possible the absorption of water of the mixtures, as both IL and DMSO  
 111 are hygroscopic compounds, some water was effectively absorbed being the final concentration  
 112 of the samples those shown in table 2. Molar fractions are defined by the amount of the component  
 113 in mol divided by the total amount in mol of all components in the mixture. For the composition  
 114 shown in this table water was the only impurity taken into account.

115 Table 2: Composition of the mixtures DMSO + AmimCl measured in this work

| $x_{\text{DMSO}} / \text{mol/mol}$ | $x_{\text{water}} / \text{mol/mol}$ |
|------------------------------------|-------------------------------------|
| 0                                  | 0.059                               |
| 0.048                              | 0.042                               |
| 0.091                              | 0.047                               |
| 0.14                               | 0.048                               |
| 0.241                              | 0.049                               |
| 0.482                              | 0.031                               |
| 0.729                              | 0.023                               |
| 0.893                              | 0.008                               |
| 0.999                              | 0.001                               |

116 Uncertainty (k = 2) of the molar fraction is 0.001 mol/mol

117 To determine densities and viscosities at atmospheric pressure, a Stabinger viscometer (SVM  
 118 3000 model) was used. The Stabinger viscometer consists of two rotating concentric tubes. It  
 119 works based on the principle of Couette that states that the viscosity is proportional to the torque

120 difference between the rotating cylinders. The Stabinger viscometer can simultaneously measure  
 121 the density because it has a vibrating tube densimeter integrated into its structure. Both density  
 122 and viscosity cells are filled in one cycle, and the measurements are carried out simultaneously.  
 123 With this apparatus the measurements can be done from 233.15 to 373.15 K in a viscosity range  
 124 from 0.2 mPa·s to 20,000 mPa·s and in a density range from 0.65 g·cm<sup>-3</sup> to 2 g·cm<sup>-3</sup>. The  
 125 uncertainty of the temperature is 0.22 K (k = 2, level of confidence 95.45%) from (278.15 to  
 126 343.15) K. Apparatus performs five measurements automatically with a relative uncertainty of  
 127 the viscosity 2.0 % (k = 2), and the expanded uncertainty of the density is 0.00052 g·cm<sup>-3</sup> (k = 2,  
 128 level of confidence 95.45%).

129 The uncertainty of the Stabinger viscometer was calculated following the *law of propagation of*  
 130 *uncertainty* described in JCGM 100: 2008 [23]. The results are summarized in Table 3 and Table  
 131 4.

132 Table 3: Uncertainty budget of density for Stabinger Viscometer. Values calculated for  $x_{\text{DMSO}} = 0.091$ , 313.15 K and  $\rho$   
 133 = 1.1378 g·cm<sup>-3</sup>

| Uncertainty |               | Units                                   | Estimate | Divisor | u(x)   |
|-------------|---------------|---|----------|---------|--------|
| u(T)        | Calibration   |   | 0.020    | 1       |        |
|             | Resolution    | K                                       | 0.001    | 2√3     | 0.1    |
|             | Repeatability |   | 0.005    | 1       |        |
| u(ρ)        | Calibration   |   | 0.0005   | 2       |        |
|             | Resolution    | g·cm <sup>-3</sup>                      | 0.0001   | 2√3     | 3 E-04 |
|             | Repeatability |   | 0.0001   | 2       |        |
| U(ρ)        |               | g·cm <sup>-3</sup>                      |          | k = 2   | 5 E-04 |
| U(ρ)        |               | g·cm <sup>-3</sup> / g·cm <sup>-3</sup> |          | k = 2   | 5 E-04 |

134

135 Table 4: Uncertainty budget of viscosity for the Stabinger viscometer. Values calculated for  $x_{\text{DMSO}} = 0.091$ , 323.15 K  
 136 and  $\mu = 130$  mPa·s

| Uncertainty | Units | Estimate | Divisor | u(x) |
|-------------|-------|----------|---------|------|
|-------------|-------|----------|---------|------|

|      |               |               |        |       |        |
|------|---------------|---------------|--------|-------|--------|
| u(T) | Calibration   |               | 0.020  | 1     |        |
|      | Resolution    | K             | 0.001  | 2√3   | 0.1    |
|      | Repeatability |               | 0.005  | 1     |        |
| u(μ) | Calibration   |               | 1.3    | 1     |        |
|      | Resolution    | mPa·s         | 0.0001 | 2√3   | 1      |
|      | Repeatability |               | 0.13   | 1     |        |
| U(μ) |               | mPa·s         |        | k = 2 | 3      |
| U(μ) |               | mPa·s / mPa·s |        | k = 2 | 2 E-02 |

137 Mixtures were carefully introduced in the viscometer in order to avoid bubbles. The viscosity and  
 138 the density were measured from 293.15 K to 373.15 K with a temperature step of 10 K. After the  
 139 measurement of each mixture the viscometer was first cleaned with water, then with hexane and  
 140 finally with air. To ensure that the Stabinger was clean after this process, the properties of pure  
 141 water were measured after the cleaning step and if the obtained values were close to the theoretical  
 142 values obtained from Refprop [24], it was considered that the equipment was clean.

### 143 2.3 Equipment and procedure for vapor pressure measurements

144 The equipment used for the measurements of the vapor pressure consisted of a stainless steel cell  
 145 of 20 mL of internal volume homogenized by magnetic stirrer. The inner pressure of the cell was  
 146 determined by an absolute pressure gauge GE DPI 104, with an expanded uncertainty of 0.1 % (k  
 147 = 2), the final uncertainty was calculated taking into account the repeatability, the pressure gauge  
 148 uncertainty and other error sources, the final expanded uncertainty of the vapor pressure  
 149 measurements is 9 % (k = 2). The temperature inside of the cell was determined by a Pt100 with  
 150 an uncertainty of ± 0.1 K for T < 433.15 K, and a thermocouple with an uncertainty of ± 2 K for  
 151 T > 433.15 K. The temperature inside the cell was fixed by a clamp electric heater controlled by  
 152 a PID regulator connected to the temperature sensor. The cell was also connected to a vacuum  
 153 pump through a valve.

154 The experimental procedure consists of the following steps:

1551) The cell was loaded with an approximate volume of 10 mL of mixture. The ionic liquid previously  
156 dried as explained in section 2.1 (5.9 % mol water) was stored in a flask inside of a desiccator  
157 under vacuum. Then it was loaded in the cell and mixed with DMSO of a nitrogen chamber,  
158 closed and all the connections were checked.

159 With a vacuum pump, vacuum was made until the pressure was lower than 0.01 bar. The electric  
160 resistance was connected and the temperature was raised to 333.15 K. After a period of at least  
161 60 min at 333.15 K, (the vapor pressure of DMSO at 333.15 K is 0.007 bar) vacuum was made  
162 again until a pressure lower than 0.01 bar. The purpose of this step was to remove absorbed air or  
163 volatiles components that may be present in the IL and could distort the measurements. It was  
164 considered that the composition of the sample was not influenced by this step due to the low vapor  
165 pressure of DMSO at this temperature that causes a negligible loss of DMSO by evaporation. As  
166 the cell was not opened again in this point the final water content until this last step could not be  
167 experimentally determined, but it can be estimated from the initial water concentration of DMSO  
168 and IL

1692) The temperature was fixed for the first vapor pressure measurement. Once the equilibrium was  
170 reached, that is, when pressure and temperature were constant, the value of these properties was  
171 registered, and then the temperature was increased until the next value.

172

### 173 **3 Experimental results**

#### 174 3.1 Densities of DMSO + AmimCl

175 Densities are presented in table 5. In literature several melting temperatures were reports for the  
176 AmimCl [5,25,26] . In a previous work of the group it was determined to be 324.95 K by DSC  
177 (Differential Scanning Calorimetry) using AmimCl of the same supplier and nominal purity [26].  
178 Below this temperature the AmimCl is presented as a liquid, as happens frequently with most



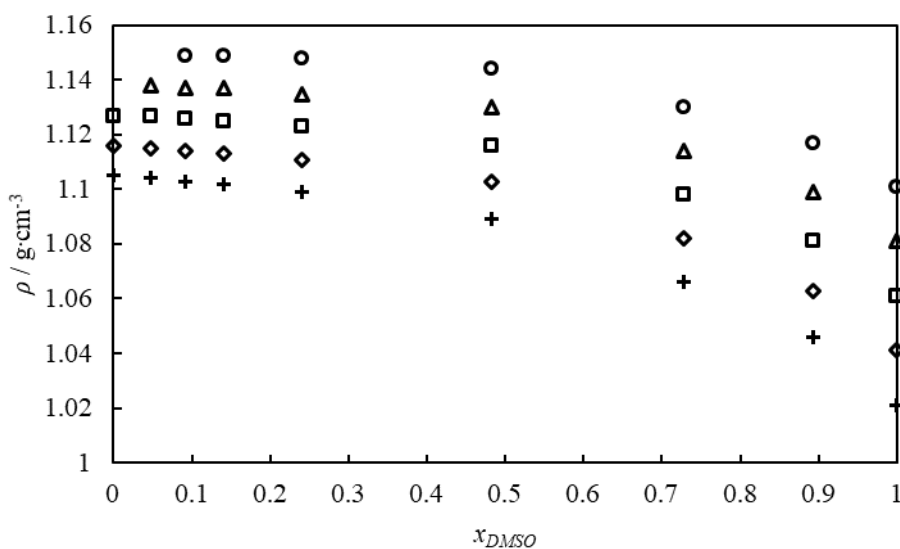
179 ionic liquids that can be liquid at temperatures much below the melting point [27]. Data at higher  
 180 concentrations of IL and at lower temperatures were not measured to prevent blockage of the  
 181 equipment due to possible solidification of the IL.

182 Table 5: Densities of the binary mixture DMSO + AmimCl.

| Atmospheric<br>pressure /<br>bar | 0.934                                | 0.931  | 0.928  | 0.928  | 0.929  | 0.931  | 0.930  | 0.935  | 0.934  |
|----------------------------------|--------------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| $x_{\text{H}_2\text{O}}$         | 0.059                                | 0.042  | 0.047  | 0.048  | 0.049  | 0.031  | 0.023  | 0.008  | 0.001  |
| $x_{\text{DMSO}}$                | 0.000                                | 0.048  | 0.091  | 0.140  | 0.241  | 0.482  | 0.728  | 0.893  | 0.999  |
| $T / \text{K}$                   | $\rho / \text{g}\cdot\text{cm}^{-3}$ |        |        |        |        |        |        |        |        |
| 293.15                           |                                      |        | 1.1500 | 1.1496 | 1.1482 | 1.1436 | 1.1302 | 1.1169 | 1.1012 |
| 303.15                           |                                      |        | 1.1439 | 1.1434 | 1.1420 | 1.1367 | 1.1223 | 1.1080 | 1.0912 |
| 313.15                           |                                      | 1.1382 | 1.1378 | 1.1373 | 1.1357 | 1.1297 | 1.1143 | 1.0990 | 1.0811 |
| 323.15                           | 1.1327                               | 1.1324 | 1.1319 | 1.1313 | 1.1292 | 1.1229 | 1.1062 | 1.0900 | 1.0711 |
| 333.15                           | 1.1271                               | 1.1267 | 1.1261 | 1.1254 | 1.1231 | 1.1161 | 1.0981 | 1.0810 | 1.0612 |
| 343.15                           | 1.1215                               | 1.1210 | 1.1203 | 1.1195 | 1.1172 | 1.1093 | 1.0901 | 1.0720 | 1.0513 |
| 353.15                           | 1.1160                               | 1.1154 | 1.1146 | 1.1136 | 1.1112 | 1.1026 | 1.0824 | 1.0631 | 1.0411 |
| 363.15                           | 1.1105                               | 1.1099 | 1.1089 | 1.1079 | 1.1052 | 1.0960 | 1.0745 | 1.0543 | 1.0313 |
| 373.15                           | 1.1052                               | 1.1045 | 1.1034 | 1.1024 | 1.0993 | 1.0894 | 1.0668 | 1.0455 | 1.0214 |

183 The expanded uncertainty ( $k = 2$ ) of the density is  $5.2 \cdot 10^{-4} \text{ g}\cdot\text{cm}^{-3}$ . Expanded uncertainty in the temperature is 0.22 K.  
 184 Expanded uncertainty of the molar fraction is 0.001 mol/mol. Expanded uncertainty of the atmospheric pressure is  
 185 0.001 bar.

186



187

188 Figure 1: Densities of binary mixtures of DMSO + AnimCl at atmospheric pressure 293.15 K (○); 313.15 K (△);  
 189 333.15 K (□); 353.15 K (◇) and 373.15 K (+).

190 As it is shown in Figure 1, density of the mixtures decreases when increasing the temperature and  
 191 the molar fraction of DMSO, presenting a nonlinear convex trend. Literature data regarding the  
 192 density of imidazolium-based ionic liquid and molecular solvents as water or alcohols presents a  
 193 similar trend [28–30]. The influence of the temperature is slightly bigger at high concentrations  
 194 of DMSO.

195 Table 6 shows that the densities were inconsistent with those determined by Jiménez et al. [16]  
 196 for the “pure” IL ( $x_{\text{water}} = 0.045$  similar to our  $x_{\text{water}} = 0.059$ ). The discrepancy between the  
 197 measures may be caused by different amount of impurities in the ionic liquids. The measurements  
 198 were performed by the same equipment and in both articles the ionic liquid were provided by  
 199 Iolitec.

200 Table 6: Comparison between densities measured in this work and reported by Jiménez et al. [16].

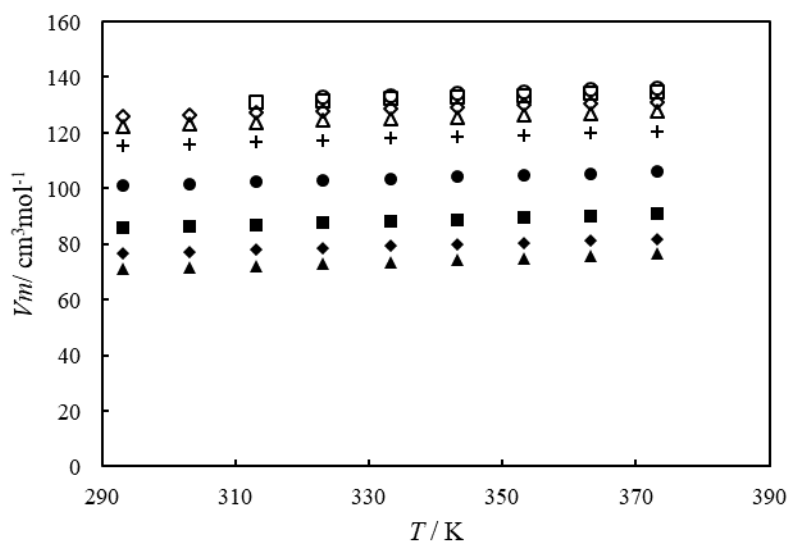
| $T / \text{K}$ | Density, this work<br>$x_{\text{water}} = 0.059$<br>$\text{g cm}^{-3}$ | Density, Jiménez et al. [16]<br>$x_{\text{water}} = 0.045$<br>$\text{g cm}^{-3}$ | $\frac{ \Delta\rho }{\rho} \cdot 100$ <sup>a</sup> |
|----------------|--|--|--|
| 323.15         | 1.1327   | 1.1310   | 0.15   |
| 333.15         | 1.1271   | 1.1254   | 0.15   |

|        |        |        |      |
|--------|--------|--------|------|
| 343.15 | 1.1215 | 1.1199 | 0.14 |
| 353.15 | 1.1160 | 1.1144 | 0.14 |
| 363.15 | 1.1105 | 1.1088 | 0.15 |
| 373.15 | 1.1052 | 1.1036 | 0.15 |

201 a)  $\frac{|\Delta\rho|}{\rho} \cdot 100 = |\rho_{(Jimenez\ et\ al.)} - \rho_{(This\ work)}| / \rho_{(Jimenez\ et\ al.)} \cdot 100$

202

203 The Table 6 compares the relative deviations of density of the ionic liquid at atmospheric pressure  
 204 and different temperatures between our experimental data and Jiménez et al. [16] data. The  
 205 difference can be explained by the imidazolium or chloride impurities in the ionic liquid.



206

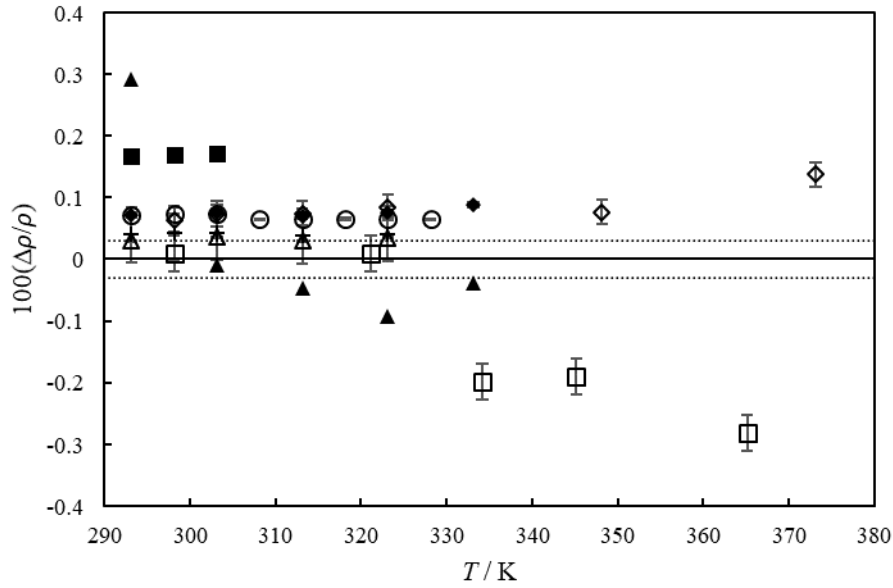
207 Figure 2: Molar volumes of the mixtures at  $x_{DMSO} = 0.000$  (○); 0.048 (□); 0.091 (◇); 0.140(△); 0.241 (+); 0.482  
 208 (●); 0.728 (■); 0.893 (◆); 0.999 (▲).

209

210 In Figure 2 can be seen the linear tendency with the temperature in the molar volume of the  
 211 mixtures at different molar fraction of DMSO.

212 Comparison of the DMSO density with literature data [31–38] is presented in Figure 3. It can be  
 213 observed that our data are consistent with the data reported by others authors. Even though, in  
 214 general there is important dispersion among the data of different authors. Most literature data are

215 presenting deviation lower than 0.1% and in many cases within the experimental uncertainty of  
 216 our data. A few data [31, 36, 38] present higher deviation but in all cases lower than 0.3%.



217

218 Figure 3: Relative deviations for DMSO density against the temperature between the experimental density data of this  
 219 work and those reported by: Campbell [31] (□); Casteel et al. [32] (◇); Wang et al. [33] (△); Ivanov et al. [34] (○);  
 220 Iulian et al. [35] (+); Krakoviak et al. [36] (■); Zarei et al. [37] (◆) and Clever et al. [38] (▲) (uncertainty not  
 221 reported).

### 222 3.2 Viscosity of mixtures DMSO + AmimCl

223 Results of viscosity of mixtures DMSO + AmimCl at atmospheric pressure and different  
 224 temperatures and DMSO concentrations are presented in Table 7.

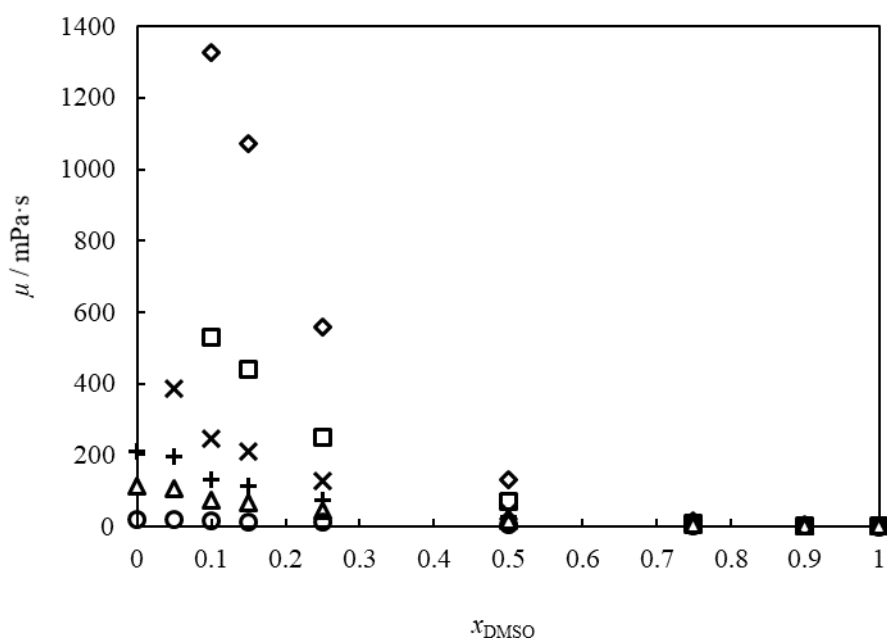
225 Table 7: Viscosities of the binary mixtures DMSO + AmimCl.

| Atmospheric<br>Pressure /<br>bar | 0.934               | 0.931 | 0.928 | 0.928 | 0.929 | 0.931 | 0.930 | 0.935 | 0.934 |
|----------------------------------|---------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| $x_{H_2O}$                       | 0.059               | 0.042 | 0.047 | 0.048 | 0.049 | 0.031 | 0.023 | 0.008 | 0.001 |
| $x_{DMSO}$                       | 0                   | 0.048 | 0.091 | 0.14  | 0.241 | 0.482 | 0.729 | 0.893 | 0.999 |
| $T / K$                          | $\mu / mPa \cdot s$ |       |       |       |       |       |       |       |       |
| 293.15                           |                     |       | 1330  | 1070  | 557   | 133   | 16.3  | 5.33  | 2.26  |
| 303.15                           |                     |       | 529   | 439   | 250   | 70.4  | 11.1  | 4.06  | 1.85  |
| 313.15                           |                     | 388   | 247   | 209   | 128   | 41.7  | 8.04  | 3.21  | 1.56  |

|        |      |      |      |      |      |      |      |      |       |
|--------|------|------|------|------|------|------|------|------|-------|
| 323.15 | 212  | 195  | 130  | 112  | 75.7 | 26.7 | 6.08 | 2.60 | 1.33  |
| 333.15 | 115  | 107  | 75.5 | 66.1 | 46.1 | 18.3 | 4.76 | 2.16 | 1.16  |
| 343.15 | 68.7 | 64.0 | 47.4 | 42.1 | 30.3 | 13.1 | 3.83 | 1.83 | 1.02  |
| 353.15 | 44.0 | 41.3 | 31.6 | 28.4 | 21.0 | 9.85 | 3.16 | 1.57 | 0.905 |
| 363.15 | 30.0 | 28.2 | 22.3 | 20.2 | 15.3 | 7.64 | 2.66 | 1.36 | 0.815 |
| 373.15 | 21.4 | 20.3 | 16.2 | 15.0 | 11.6 | 6.10 | 2.28 | 1.20 | 0.741 |

226 The expanded uncertainty of the viscosity is 2.0%. Expanded uncertainty ( $k = 2$ ) in the temperature is 0.22 K.

227 Uncertainty of the molar fraction is 0.001 mol/mol. Expanded uncertainty of the atmospheric pressure is 0.001 bar.



228

229 Figure 4: Viscosities of binary mixtures DMSO + AmimCl at atmospheric pressure and 293.15 K ( $\diamond$ ); 303.15 K ( $\square$ );

230 313.15 K ( $\times$ ); 323.15 K ( $+$ ); 333.15 K ( $\triangle$ ) and 373.15 K ( $\circ$ ).

231 From Figure 4 it can be observed that the viscosity decreases with the temperature and with

232 DMSO concentration. It has an exponential behavior in all temperatures. At lower temperatures

233 the influence of the DMSO concentration increases considerably.

234 Comparing the viscosities of pure AmimCl measured by Jiménez et al. [16] with our data in the

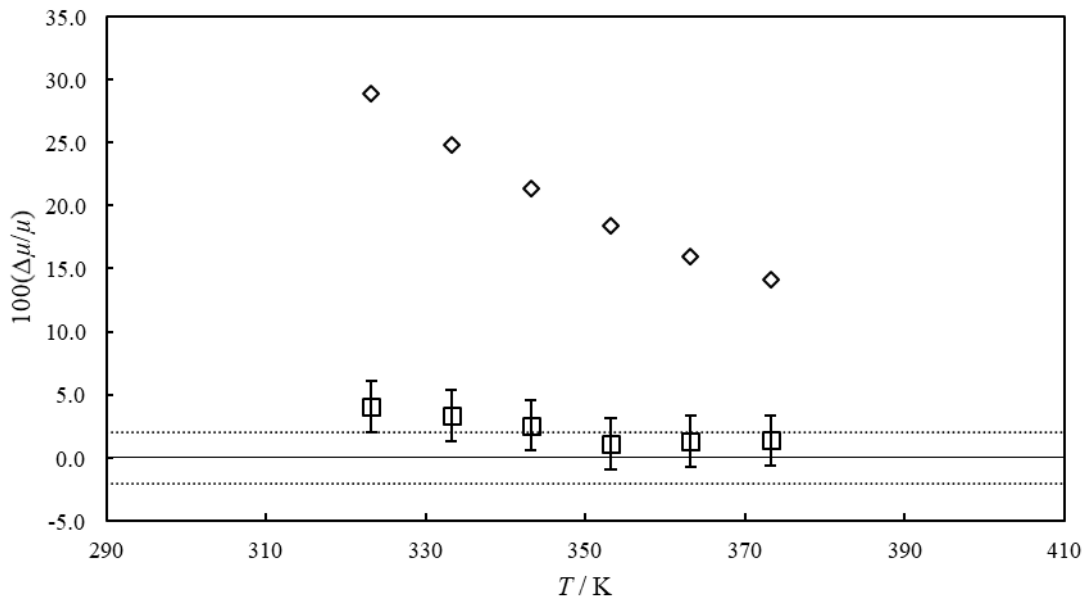
235 Table 8, the results of Jiménez et al. are slightly lower, with a maximum difference of 8.6 % at

236 323 K and a minimum difference of 3.6 % at 373 K. This can be explained by the lower water  
 237 content of water in the samples prepared in the work of Jiménez et al, and the strong influence of  
 238 the co-solvent concentration in viscosity [16].

239 Table 8: Comparison between viscosities measured in this work and results reported by Jiménez et al. [16] corrected  
 240 for  $x_{\text{water}} = 0.059$ . The water concentration in this work was  $x_{\text{water}} = 0.059$ .

| $T / \text{K}$ | Viscosity, this work | Corrected viscosity, Jiménez et al. | $\frac{ \Delta\mu }{\mu} \cdot 100$ <sup>b</sup> |
|----------------|----------------------|-------------------------------------|--|
|                | mPa s                | mPa s                               |  |
| 323.15         | 212                  | 221                                 | 4.07   |
| 333.15         | 115                  | 119                                 | 3.36   |
| 343.15         | 68.7                 | 70.5                                | 2.55   |
| 353.15         | 44.4                 | 44.9                                | 1.11   |
| 363.15         | 30.0                 | 30.4                                | 1.32   |
| 373.15         | 21.4                 | 21.7                                | 1.38   |

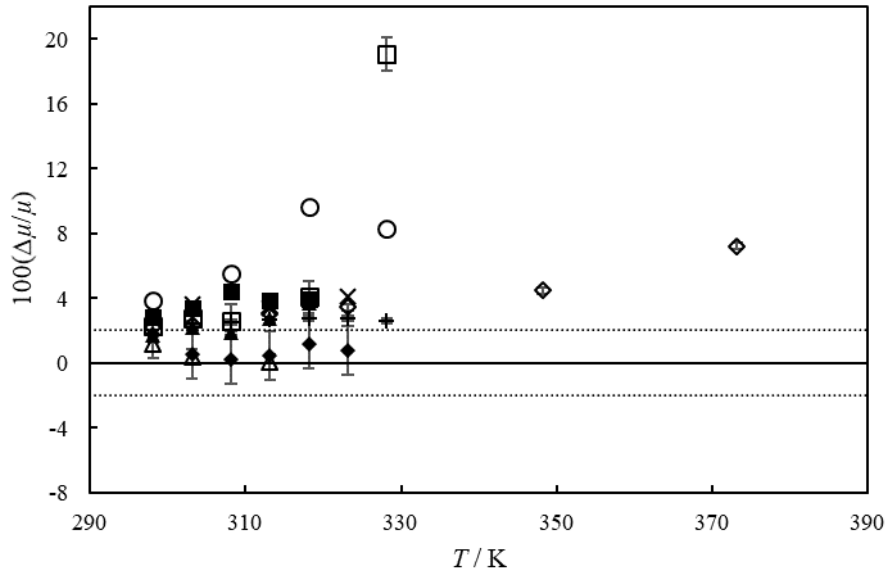
241 b)  $\frac{|\Delta\mu|}{\mu} \cdot 100 = |\mu_{\text{(Jimenez et al.)}} - \mu_{\text{(This work)}}| / \mu_{\text{(Jimenez et al.)}} \cdot 100$



242  
 243 Figure 5: Relative deviations for viscosity of pure AmimCl against the temperature between the experimental viscosity  
 244 data of this work and those reported by Jiménez et al. [16] (□) and Hiraga et al. [39] (◇) (estimated  $x_{\text{H}_2\text{O}} = 0.01$ ).  
 245 Dotted lines represent uncertainty of our data.

246 Figure 5 shows the relative deviations of viscosity of AmimCl at atmospheric pressure and  
 247 different temperatures between our data and other data from literature [16,39]. Important

248 differences with the data of Hiraga et al. [39] can be observed, but differences can be explained  
249 due to the impurities (1-Methylimidazole) present in the ionic liquid and / or presence of water in  
250 our samples.



251

252 Figure 6: Relative deviation for viscosity of pure DMSO against the temperature between the experimental viscosity  
253 data of this work and those reported by: Casteel et al. [32] (◇); Ciocirlan et al. [40] (△); Yang et al. [41] (×)  
254 (uncertainty not reported); Govinda et al. [42] (□); Gokavl et al. [43] (○) (uncertainty not reported); Saleh et al. [44]  
255 (+); Ali et al. [45] (■) (uncertainty not reported); Zhao et al. [46] (◆) and Kapadi et al. [47] (▲).

256 Figure 6 shows the relative deviations of viscosity of DMSO at atmospheric pressure and different  
257 temperatures between our data and other data from literature [32,40–47]. In general, some  
258 scattering is found between our data and literature data, with data within or slightly outside the  
259 uncertainty limit. Only a few literature data present important deviation at temperatures above  
260 320 K. Reported data by Kapadi et al. [47] shows a good agreement with this work. Discrepancies  
261 can be due to different content of impurities in the samples. DMSO is hygroscopic, so the water  
262 content can be different between the authors. In the literature, only Govinda et al. [43] measured  
263 the water content in their samples, which was kept below 70 ppm.

264

### 3.3 Viscosity correlation

265 The viscosity was correlated as a function of temperature and concentration with two viscosity  
 266 correlations previously used by our research group to describe viscosities of mixtures of  
 267 imidazolium ionic liquids with molecular solvents [15,16].

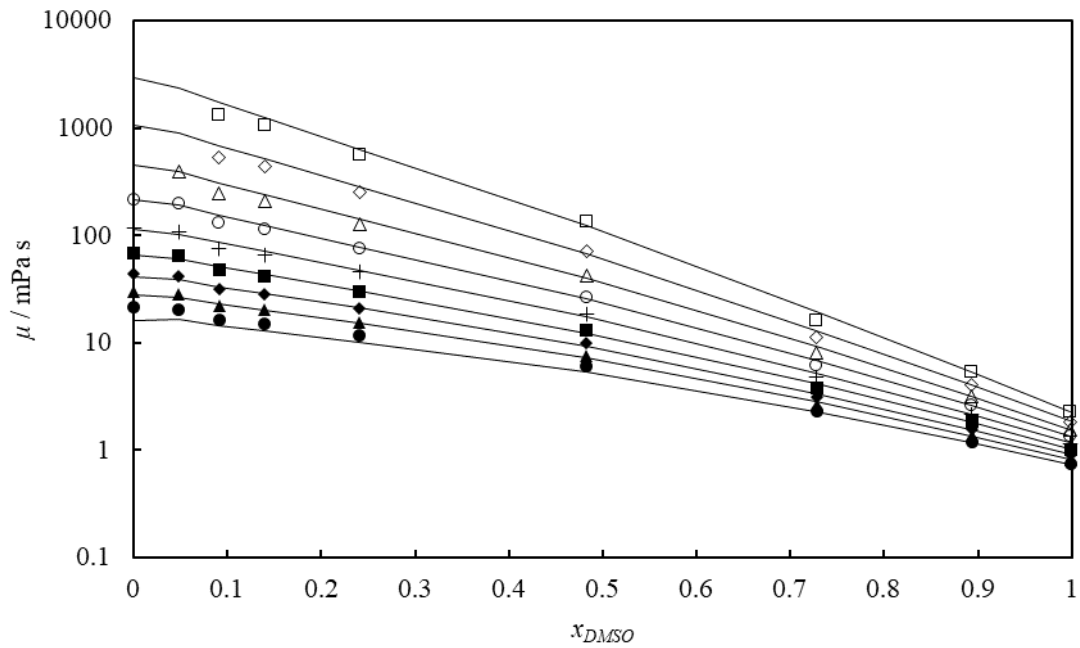
268 Equation ( 1 ) modified from the correlation of Grunberg and Nissan, was used to correlate data  
 269 with DMSO molar fractions in all the concentration range as a function of temperature. Due to  
 270 the big influence of water in viscosity, the concentration of water of each sample was also  
 271 considered in the correlation. The parameters for the pure IL, E, A and B, were taken from the  
 272 original work of Jiménez et al. with the same IL [16]. Parameters F, D and C used for describing  
 273 the interaction water-AmimCl water were also taken from the work of Jimenez et al. [16]. The  
 274 parameters G, H and I, corresponding to the interactions with DMSO, were adjusted in this work  
 275 by minimization of the average relative deviation (ARD %) defined in eq.( 2 ). An ARD of 6.8%  
 276 was obtained with a maximum deviation of 30.7% at 373.15 K and  $x_{DMSO} = 0$ , which represents a  
 277 good description of the system. The parameters obtained are reported in Table 9. Experimental  
 278 data is compared with predictions from the correlation (Eq. 1) in Figure 7, in logarithmic scale.  
 279 A good correlation of the data is observed.

$$\ln \mu = x_{IL} \left( \frac{E}{T^2} + \frac{A}{T} + B \right) + x_{DMSO} \ln \mu_{DMSO} + x_{H_2O} \ln \mu_{H_2O} + \frac{x_{IL} x_{H_2O}}{x_{IL} + F} (C + DT) \quad (1)$$

$$+ \frac{x_{IL} x_{DMSO}}{x_{IL} + G} (H + IT)$$

$$ARD\% = \frac{\sum \left( \frac{|\mu_{exp} - \mu_{calc}|}{\mu_{exp}} \right)}{n} \cdot 100 \quad (2)$$





280

281 Figure 7: Correlation of experimental viscosity for the binary mixtures DMSO + AmimCl at 293.15 K (□); 303.15 K  
 282 (◇); 313.15 K (△); 323.15 K (○); 333.15 K (+); 343.15 K (■); 353.15 K (◆); 363.15 K (▲) and 373.15 K (●). The  
 283 points represent the experimental data, and lines represent the data calculated with equation ( 1 )

284 Table 9: Fitted parameters for the correlation of viscosity of the mixtures DMSO + AmimCl with equation ( 1 ) for all  
 285 concentration range.

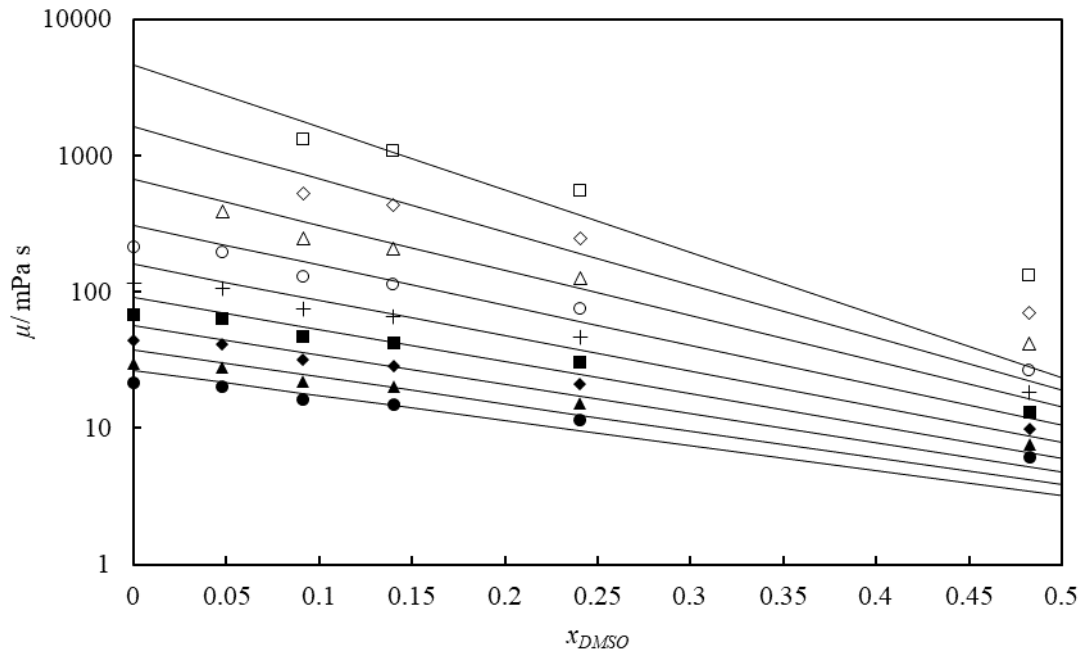
|      |           |
|------|-----------|
| A    | -1.51E+04 |
| B    | 1.76E+01  |
| C    | -8.72+05  |
| D    | -4.25E+07 |
| E    | 3.64E+06  |
| F    | 5.02E+07  |
| G    | 9.01E+07  |
| H    | 3.00E+05  |
| I    | -8.49E+06 |
| %ARD | 6.8 %     |
| %Max | 30.7%     |

286 The equation ( 3 ) is also a modification of Grunberg and Nissan correlation, it is used to correlate  
 287 the viscosity with DMSO molar fractions lower than 0.25, where the viscosity presents a liner  
 288 behavior with the impurity molar fraction. Parameters F, C and D were adjusted for the DMSO

289 by minimization of the average relative deviation (ARD %) in the same way defined in eq.( 2 ).  
 290 An ARD% of 16.3% was obtained with a maximum deviation of 45.2% at 293.15 K and  $x_{DMSO} =$   
 291 0.091, which represent a good description of the system. Parameters E, A and B were taken from  
 292 Jiménez et al. [16], C and D parameters are adjusted and shown in Table 10. Correlation prediction  
 293 and experimental data are compared in Figure 6. It can be observed how the predictions are not  
 294 valid for concentrations higher than  $x_{DMSO} = 0.15$ , as shown in Figure 8.

$$\mu = \exp\left(\frac{E}{T^2} + \frac{A}{T} + B\right) \cdot \exp\left(\frac{x_{H_2O}}{C + DT}\right) \cdot \exp\left(\frac{x_{DMSO}}{F + GT}\right) \quad (3)$$

295



296

297 Figure 8: Correlation of experimental viscosity for the binary mixtures DMSO + AmimCl at 293.15 K (□); 303.15 K  
 298 (◇); 313.15 K (△); 323.15 K (○); 333.15 K (+); 343.15 K (■); 353.15 K (◆); 363.15 K (▲) and 373.15 K (●). The  
 299 points represent the experimental data, and straight lines represent the data calculated with equation ( 3 )

300 Table 10: Fitted parameters for the correlation of viscosity of the mixtures DMSO + AmimCl with equation ( 3 ). Valid  
 301 for co-solvent concentration lower than 0.15.

|          |           |
|----------|-----------|
| <i>A</i> | -1.51E+04 |
| <i>B</i> | 1.76E+01  |

|              |           |
|--------------|-----------|
| <i>C</i>     | -1.51E+05 |
| <i>D</i>     | 4.16E+02  |
| <i>E</i>     | 3.64E+06  |
| <i>F</i>     | 4.30E-01  |
| <i>G</i>     | -1.79E-03 |
| % <i>ARD</i> | 16.3%     |
| % <i>Max</i> | 45.2%     |

302

### 303 3.4 Vapor pressure measurements

304 The experimentally determined vapor pressures of mixtures DMSO + AmimCl are listed in Table

305 11.

306 Table 11: Vapor pressures of mixtures DMSO + AmimCl at various temperatures.

| <i>T</i> / K                        | 353.1   | 363.1 | 373.1 | 383.1 | 393.1 | 403.1 | 413.1 | 423.1 | 433.1 |
|-------------------------------------|---|-------|-------|-------|-------|-------|-------|-------|-------|
| <i>x</i> <sub>DMSO</sub><br>mol/mol | <i>x</i> <sub>H<sub>2</sub>O</sub><br>mol/mol |       |       |       |       |       |       |       |       |
| <i>P</i> / bar                      |   |       |       |       |       |       |       |       |       |
| 1.000                               | 0.020   | 0.032 | 0.050 | 0.076 | 0.112 | 0.160 | 0.227 | 0.316 | 0.432 |
| 0.973                               | 0.018   | 0.028 | 0.045 | 0.068 | 0.100 | 0.147 | 0.210 | 0.296 | 0.411 |
| 0.947                               | 0.017   | 0.026 | 0.041 | 0.065 | 0.096 | 0.142 | 0.205 | 0.292 | 0.408 |
| 0.896                               | 0.015   | 0.024 | 0.039 | 0.063 | 0.092 | 0.138 | 0.201 | 0.288 | 0.405 |
| 0.822                               | 0.013   | 0.021 | 0.035 | 0.051 | 0.085 | 0.128 | 0.190 | 0.276 | 0.394 |
| 0.753                               | 0.012   | 0.019 | 0.032 | 0.051 | 0.080 | 0.122 | 0.182 | 0.266 | 0.383 |
| 0.664                               | 0.011   | 0.018 | 0.029 | 0.047 | 0.074 | 0.113 | 0.169 | 0.248 | 0.358 |
| 0.580                               | 0.011   | 0.017 | 0.027 | 0.045 | 0.072 | 0.110 | 0.164 | 0.242 | 0.350 |
| 0.452                               | 0.010   | 0.015 | 0.026 | 0.041 | 0.066 | 0.100 | 0.151 | 0.222 | 0.322 |
| 0.357                               | 0.008   | 0.013 | 0.022 | 0.035 | 0.055 | 0.084 | 0.126 | 0.185 | 0.268 |
| 0.344                               | 0.008   | 0.013 | 0.021 | 0.035 | 0.054 | 0.082 | 0.122 | 0.180 | 0.259 |
| 0.194                               | 0.007   | 0.012 | 0.019 | 0.030 | 0.046 | 0.069 | 0.102 | 0.147 | 0.210 |
| 0.167                               | 0.006   | 0.010 | 0.016 | 0.026 | 0.042 | 0.065 | 0.098 | 0.145 | 0.211 |
| 0.150                               | 0.005   | 0.009 | 0.015 | 0.024 | 0.038 | 0.059 | 0.090 | 0.133 | 0.195 |
| 0.088                               | 0.011*  | 0.005 | 0.008 | 0.013 | 0.020 | 0.033 | 0.051 | 0.076 | 0.113 |

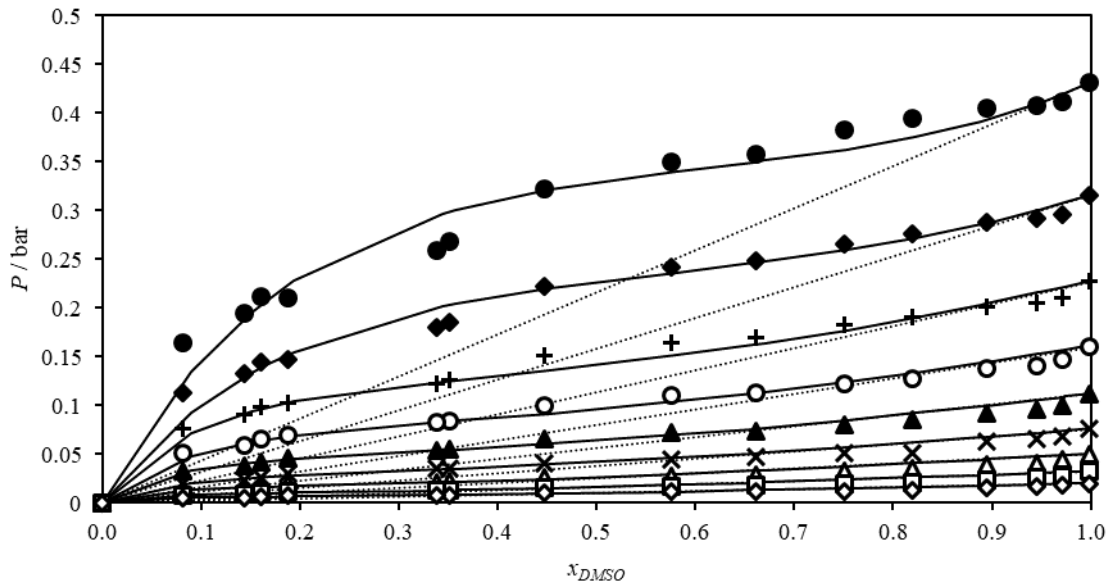
307 Expanded uncertainty of the DMSO molar fraction is 0.001 (*k* = 2). The expanded uncertainty of the pressure is 9 %

308 (*k* = 2). The uncertainty of the temperature is ± 0.1 K for *T* < 433.15 K (*k* = 2) The uncertainty of the temperature is ±

309 2 K for *T* ≥ 433.15 K (*k* = 2).

310 \* In this point the estimated contribution of the water to the vapor pressure is higher than the uncertainty of the pressure,  
311 so the expanded uncertainty at this point is increased to 13%. Composition was estimated from the water content of the  
312 pure DMSO and IL.

313 Vapor pressure data of the mixture DMSO +AmimCl at different temperatures are presented in  
314 Figure 9.



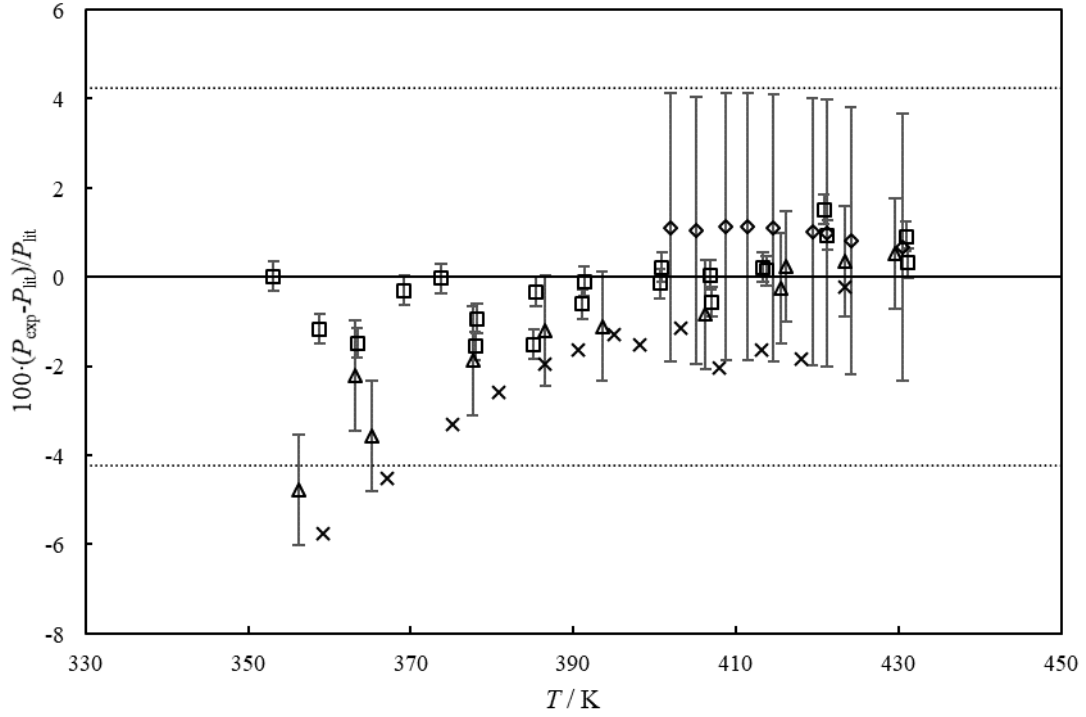
315

316 Figure 9: Experimental vapor pressures of mixtures of DMSO + AmimCl at 433.15 K (●); 423.15 K (◆); 413.15 K  
317 (+); 403.15 K (○); 393.15 K (▲); 383.15 (×); 373.15 K (Δ); 363.15 K (□); 353.15 K (◇). Symbols represent the  
318 experimental data, solid lines represent NRTL calculations and dotted lines represent Raoult's Law prediction.

319 It is observed that the uncertainties achieved in the pressure are higher than the uncertainties  
320 achieved by other authors [48] ( $\pm 10^{-4}$  bar) and [18,49] ( $\pm 4 \cdot 10^{-4}$  kPa). The vapor pressure present  
321 positive deviations from the Raoult's Law at low concentrations of DMSO and thus, high  
322 concentrations of ionic liquid, while at low concentrations of ionic liquid the data presents a very  
323 slight negative deviation of the Raoult law, presenting a good approximation to it as expected.  
324 This behavior suggests unfavorable interactions between the DMSO and the ionic liquid. A  
325 positive deviation from the Raoult's Law was also observed by Nebig et al. [50] and Kato et al.  
326 [51] that measured vapor pressure of a variety of alkyl imidazolium  
327 bis(trifluoromethylsulfonyl)imide IL with some alkanes, alkenes, aromatics and alcohols. Zhao

328 et al. [52] measure the vapor pressures of binary systems containing water, methanol or propanol  
329 plus some imidazolium dialkylphosphate family ionic liquids. The authors found a negative  
330 deviation of the Raoult's law, but with different extends depending on the different affinity  
331 between the different solvents. Similar results were found by Huo et al. [22], they studied the  
332 vapor pressure of imidazolium [BF<sub>4</sub>-] and [PF<sub>6</sub>-] with organic solvents, and found a that the vapor  
333 pressure of the solvents reduces when these ionic liquids are added until below the Raoult's Law  
334 due to the complex interactions between the aromatic compounds and the ionic liquids. Carvalho  
335 et al. [53] studied the system composed by 1-alky-3-methylimidazolium chloride family of ionic  
336 liquids plus water or ethanol. They found negative deviations of the Raoult's law that suggest  
337 favorable interactions between these components and the ionic liquid.

338 In order to test our measurements the vapor pressures of the pure DMSO were compared to that  
339 of literature [54–57]. Results are reported in Figure 10 showing some scattering between the data  
340 reported by different authors in the literature. Despite the scattering, data reported in this work is  
341 in agreement with the authors due to the high uncertainty of our data. Some of the discrepancies  
342 can be explained due to the possible presence of impurities as water, only Tochigi et al. [56] and  
343 Zhang et al. [57] report purities in the DMSO, being 99.9 % mass fraction for both authors.



344

345 Figure 10: Relative deviation (%) of the experimental data of DMSO vapor pressure from the literature as a function  
 346 of the temperature: Jakli et al. [54] (□); Nishimura et al. [55] (×) (data uncertainty not reported); Tochigi et al. [56] (△)  
 347 and Zhang et al. [57] (◇). Interpolation of our data was used in order to calculate the relative deviation of the  
 348 literature data.

349 The data were correlated with the Non-Random-Two-Liquids (NRTL) Model. This model  
 350 correlates the activity coefficients  $\gamma_i$  with  $x_i$ .

351 The equations for a binary mixture are:

$$\begin{cases} \ln \gamma_1 = x_2^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \\ \ln \gamma_2 = x_1^2 \left[ \tau_{12} \left( \frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \end{cases} \quad (4)$$

$$\begin{cases} \ln G_{12} = -\alpha_{12} \tau_{12} \\ \ln G_{21} = -\alpha_{21} \tau_{21} \end{cases} \quad (5)$$

352 Correlated parameters are presented in Table 12.

353 Table 12: Correlated parameters of the NRTL Model for the vapor pressure of DMSO+IL mixtures

| $T / K$                     | 353.1 | 363.1 | 373.1 | 383.1 | 393.1 | 403.1 | 413.1 | 423.1 | 433.1 |
|-----------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $\alpha_{12} = \alpha_{21}$ | 0.30  | 0.30  | 0.30  | 0.30  | 0.30  | 0.30  | 0.30  | 0.30  | 0.30  |
| $\tau_{12}$                 | 3.12  | 3.04  | 2.82  | 2.41  | 2.36  | 2.07  | 1.85  | 0.85  | 0.71  |
| $\tau_{21}$                 | -0.92 | -0.89 | -0.78 | -0.58 | -0.45 | -0.26 | -0.07 | 0.83  | 1.20  |
| ARD%                        | 11.82 | 11.93 | 9.87  | 7.16  | 5.67  | 4.05  | 3.69  | 4.03  | 4.75  |

354 The vapor pressures calculated with the NRTL model are represented in Figure 9. Symbols  
 355 represent the experimental data and the solid line represents the NRTL values. The ARD%  
 356 reduces when the temperature rises, however, at 433.15 K, the uncertainty of the temperature  
 357 increases therefore the ARD% increases as well.

358 The parameters  $\tau$  are function of temperature as follows:

$$\tau_{12} = a_{12} + \frac{b_{12}}{T/(K)} \quad (6)$$

$$\tau_{21} = a_{21} + \frac{b_{21}}{T/(K)} \quad (7)$$

359 The parameters were fitted and are presented in Table 13:

360 Table 13: Parameters for equations ( 6 ) and ( 7 ).

|          |         |
|----------|---------|
| $a_{12}$ | -9.7592 |
| $b_{12}$ | 4656.6  |
| $a_{21}$ | 9.5976  |
| $b_{21}$ | -3840.3 |

361

362

## 363 4 Conclusions

364 Density, viscosity, and vapor pressure of DMSO + AmimCl were experimentally determined.  
365 Densities and viscosities were measured at temperatures  $T = [293.15, 373.15]$  K and  $x_{\text{DMSO}} = 0,$   
366 0.05 0.1, 0.15, 0.25, 0.5, 0.75, 0.9 and pure DMSO at atmospheric pressure with a Stabinger  
367 viscosimeter. The mixtures behave as expected in literature.

368 The density and the viscosity decrease with increasing temperature and DMSO concentrations.  
369 Correlation of viscosity was made as a function of temperature and concentration with two  
370 equations. The first one has an average relative deviation (ARD%) = 6.8% and %Max = 30.7%,  
371 The second one has an ARD% = 16.3% and %Max = 45.2%.

372 Vapor pressures of the mixtures were measured at  $T = [353.1, 433.1]$  K. Positive deviations were  
373 observed at low DMSO concentrations while at high concentration the behavior approximates the  
374 Raoult's Law. The measurements were correlated with Non-Random-Two-Liquid (NRTL)  
375 model, obtaining ARD% between 5 and 12%. Therefore, a good fitting for the viscosities and  
376 vapor pressures correlation was achieved.

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382

## 383 **6 References:**

384 [1] K.N. Marsh, J.A. Boxall, R. Lichtenthaler, Room temperature ionic liquids and their  
385 mixtures - A review, Fluid Phase Equilib. 219 (2004) 93–98.  
386 doi:10.1016/j.fluid.2004.02.003.



- 387 [2] J.F. Brennecke, E.J. Maginn, Ionic liquids: Innovative fluids for chemical processing,  
388 *AIChE J.* 47 (2001) 2384–2389. doi:10.1002/aic.690471102.
- 389 [3] J. Vitz, T. Erdmenger, U.S. Schubert, Imidazolium based ionic liquids as solvents, *Cellul.*  
390 *Solvents Anal. Shap. Chem. Modif.* (2010) 299–317. doi:10.102/bk-2010-1033.ch017.
- 391 [4] C. Cuissinat, P. Navard, T. Heinze, Swelling and dissolution of cellulose. Part IV: Free  
392 floating cotton and wood fibres in ionic liquids, *Carbohydr. Polym.* 72 (2008) 590–596.  
393 doi:10.1016/j.carbpol.2007.09.029.
- 394 [5] H. Zhang, J. Wu, J. Zhang, J. He, 1-allyl-3-methylimidazolium chloride room temperature  
395 ionic liquid: A new and powerful nonderivatizing solvent for cellulose, *Macromolecules.*  
396 38 (2005) 8272–8277. doi:10.1021/ma0505676.
- 397 [6] M. Gericke, T. Liebert, O.A. El Seoud, T. Heinze, Tailored media for homogeneous  
398 cellulose chemistry: Ionic liquid/co-solvent mixtures, *Macromol. Mater. Eng.* 296 (2011)  
399 483–493. doi:10.1002/mame.201000330.
- 400 [7] R. Jan, G.M. Rather, M.A. Bhat, Effect of cosolvent on bulk and interfacial characteristics  
401 of imidazolium based room temperature ionic liquids: Impact of cosolvent on  
402 physicochemical characteristics of ionic liquids, *J. Solution Chem.* 43 (2014) 685–695.  
403 doi:10.1007/s10953-014-0165-4.
- 404 [8] J.-M. Andanson, E. Bordes, J. Devémy, F. Leroux, A. a. H. Pádua, M.F.C. Gomes,  
405 Understanding the role of co-solvents in the dissolution of cellulose in ionic liquids, *Green*  
406 *Chem.* 16 (2014) 2528. doi:10.1039/c3gc42244e.
- 407 [9] K.R. Seddon, A. Stark, M.-J.J.M.-J.M.-J.J.M.-J.J. Torres, Influence of chloride,  
408 water, and organic solvents on the physical properties of ionic liquids, *Pure Appl. Chem.*  
409 72 (2000) 2275–2287. doi:10.1351/pac200072122275.
- 410 [10] Y. Lv, J. Wu, J.J. Zhang, Y. Niu, C.Y. Liu, J. He, J.J. Zhang, Rheological properties of  
411 cellulose/ionic liquid/dimethylsulfoxide (DMSO) solutions, *Polymer (Guildf).* 53 (2012)  
412 2524–2531. doi:10.1016/j.polymer.2012.03.037.

- 413 [11] X. Wang, H. Li, Y. Cao, Q. Tang, Cellulose extraction from wood chip in an ionic liquid  
414 1-allyl-3-methylimidazolium chloride (AmimCl), *Bioresour. Technol.* 102 (2011) 7959–  
415 7965. doi:10.1016/j.biortech.2011.05.064.
- 416 [12] D. Wu, B. Wu, Y.M. Zhang, H.P. Wang, Density, Viscosity, Refractive Index and  
417 Conductivity of 1-Allyl-3-methylimidazolium Chloride + Water Mixture †, *J. Chem. {&}*  
418 *Eng. Data.* 55 (2010) 621–624. doi:10.1021/je900545v.
- 419 [13] R. Sescousse, K.A. Le, M.E. Ries, T. Budtova, Viscosity of cellulose-imidazolium-based  
420 ionic liquid solutions, *J. Phys. Chem. B.* 114 (2010) 7222–7228. doi:10.1021/jp1024203.
- 421 [14] N. Calvar, B. González, A. Domínguez, J. Tojo, Physical Properties of the Ternary  
422 Mixture Ethanol+Water+1-Butyl-3-Methylimidazolium Chloride at 298.15K, *J. Solution*  
423 *Chem.* 35 (2006) 1217–1225. doi:10.1007/s10953-006-9073-6.
- 424 [15] J.M. Lopes, S. Kareth, M.D. Bermejo, Á. Martín, E. Weidner, M.J. Cocero, Experimental  
425 determination of viscosities and densities of mixtures carbon dioxide + 1-allyl-3-  
426 methylimidazolium chloride. Viscosity correlation, *J. Supercrit. Fluids.* 111 (2016) 91–  
427 96. doi:10.1016/j.supflu.2015.12.013.
- 428 [16] C. Jiménez de la Parra, J.R. Zambrano, M.D. Bermejo, Á. Martín, J.J. Segovia, M.J.  
429 Cocero, Influence of water concentration in the viscosities and densities of cellulose  
430 dissolving ionic liquids. Correlation of viscosity data, *J. Chem. Thermodyn.* 91 (2015) 8–  
431 16. doi:10.1016/j.jct.2015.07.015.
- 432 [17] J. Zhao, C. Li, Z. Wang, Vapor Pressure Measurement and Prediction for Ethanol +  
433 Methanol and Ethanol + Water Systems Containing Ionic Liquids, *J. Chem. Eng. Data.* 51  
434 (2006) 1755–1760. doi:10.1021/je060163o.
- 435 [18] X. Jiang, J. Wang, C. Li, L. Wang, Z. Wang, Vapour pressure measurement for binary and  
436 ternary systems containing water methanol ethanol and an ionic liquid 1-ethyl-3-  
437 ethylimidazolium diethylphosphate, *J. Chem. Thermodyn.* 39 (2007) 841–846.  
438 doi:10.1016/j.jct.2006.11.013.

- 439 [19] J. Han, Z. Lei, C. Dai, J. Li, Vapor Pressure Measurements for Binary Mixtures Containing  
440 Ionic Liquid and Predictions by the Conductor-like Screening Model for Real Solvents, J.  
441 Chem. Eng. Data. 61 (2016) 1117–1124. doi:10.1021/acs.jced.5b00760.
- 442 [20] R. Kato, J. Gmehling, Systems with ionic liquids: Measurement of VLE and  $\gamma$  data and  
443 prediction of their thermodynamic behavior using original UNIFAC, mod. UNIFAC(Do)  
444 and COSMO-RS(OI), J. Chem. Thermodyn. 37 (2005) 603–619.  
445 doi:10.1016/j.jct.2005.04.010.
- 446 [21] S.P. Verevkin, J. Safarov, E. Bich, E. Hassel, A. Heintz, Thermodynamic properties of  
447 mixtures containing ionic liquids: Vapor pressures and activity coefficients of n-alcohols  
448 and benzene in binary mixtures with 1-methyl-3-butyl-imidazolium bis(trifluoromethyl-  
449 sulfonyl) imide, Fluid Phase Equilib. 236 (2005) 222–228.  
450 doi:10.1016/j.fluid.2005.07.008.
- 451 [22] Y. Huo, S. Xia, S. Yi, P. Ma, Measurement and correlation of vapor pressure of benzene  
452 and thiophene with [BMIM][PF<sub>6</sub>] and [BMIM][BF<sub>4</sub>] ionic liquids, Fluid Phase Equilib.  
453 276 (2009) 46–52. doi:10.1016/j.fluid.2008.09.018.
- 454 [23] Joint Committee for Guides in Metrology, Evaluation of measurement data: Guide to the  
455 expression of uncertainty in measurement, Int. Organ. Stand. (2008).  
456 doi:10.1373/clinchem.2003.030528.
- 457 [24] E.W. Lemmon, R. Span, Short Fundamental Equations of State for 20 Industrial Fluids, J.  
458 Chem. Eng. Data. 51 (2006) 785–850.
- 459 [25] C.I. Melo, A.I. Rodrigues, R. Bogel-Lukasik, E. Bogel-Lukasik, Outlook on the phase  
460 equilibria of the innovative system of “protected glycerol”: 1,4-dioxaspiro[4.5]decane-2-  
461 methanol and alternative solvents, J. Phys. Chem. A. 116 (2012) 1765–1773.  
462 doi:10.1021/jp2107796.
- 463 [26] J.M. Lopes, F.A. Sánchez, S.B.R. Reartes, M.D. Bermejo, Á. Martín, M.J. Cocero,  
464 Melting point depression effect with CO<sub>2</sub> in high melting temperature cellulose dissolving

- 465 ionic liquids. Modeling with group contribution equation of state, *J. Supercrit. Fluids*. 107  
466 (2016) 590–604. doi:10.1016/j.supflu.2015.07.021.
- 467 [27] M. Galiński, A. Lewandowski, I. Stępnia, Ionic liquids as electrolytes, *Electrochim.*  
468 *Acta*. 51 (2006) 5567–5580. doi:10.1016/j.electacta.2006.03.016.
- 469 [28] E. Gómez, B. González, a Domínguez, E. Tojo, J. Tojo, Dynamic viscosities of a series  
470 of 1-alkylimidazolium chloride ionic liquids and their binary mixtures with water at  
471 several temperatures, *J. Chem. Eng. Data*. 51 (2006) 696–701.
- 472 [29] W. Qian, Y. Xu, H. Zhu, C. Yu, Properties of pure 1-methylimidazolium acetate ionic  
473 liquid and its binary mixtures with alcohols, *J. Chem. Thermodyn.* 49 (2012) 87–94.  
474 doi:10.1016/j.jct.2012.01.013.
- 475 [30] N. V. Sastry, N.M. Vaghela, P.M. Macwan, Densities, excess molar and partial molar  
476 volumes for water + 1-butyl- or, 1-hexyl- or, 1-octyl-3-methylimidazolium halide room  
477 temperature ionic liquids at  $T = (298.15 \text{ and } 308.15) \text{ K}$ , *J. Mol. Liq.* 180 (2013) 12–18.  
478 doi:10.1016/j.molliq.2012.12.018.
- 479 [31] A.N. Campbell, The density and vapour pressure of dimethylsulfoxide at various  
480 temperatures and the (hypothetical) critical density, *Can. J. Chem.* 57 (1979) 705–707.  
481 doi:10.1139/v79-114.
- 482 [32] J.F. Casteel, P.G. Sears, Dielectric Constants, Viscosities, and Related Physical Properties  
483 of 10 Liquid Sulfoxides and Sulfones at Several Temperatures, *J. Chem. Eng. Data*. 19  
484 (1974) 196–200. doi:10.1021/je60062a001.
- 485 [33] X. Wang, F. Yang, Y. Gao, Z. Liu, Volumetric properties of binary mixtures of dimethyl  
486 sulfoxide with amines from (293.15 to 363.15) K, *J. Chem. Thermodyn.* 57 (2013) 145–  
487 151. doi:10.1016/j.jct.2012.08.021.
- 488 [34] E. V. Ivanov, E.Y. Lebedeva, V.K. Abrosimov, N.G. Ivanova, Densimetric studies of  
489 binary solutions involving H<sub>2</sub>O or D<sub>2</sub>O as a solute in dimethylsulfoxide at temperatures  
490 from (293.15 to 328.15) K and atmospheric pressure, *J. Solution Chem.* 41 (2012) 1311–

- 491 1313. doi:10.1007/s10953-012-9877-5.
- 492 [35] O. Iulian, O. Ciocirlan, Volumetric properties of binary mixtures of two 1-alkyl-3-  
493 methylimidazolium tetrafluoroborate ionic liquids with molecular solvents, *J. Chem. Eng.*  
494 *Data.* 57 (2012) 2640–2646. doi:10.1021/je300316a.
- 495 [36] J. Krakowiak, D. Bobicz, W. Grzybkowski, Partial molar volumes of tetrabutylammonium  
496 perchlorate and tetraphenylborate in N,N-dimethylacetamide, triethylphosphate,  
497 acetonitrile and dimethyl sulphoxide, *J. Mol. Liq.* 88 (2000) 197–207. doi:10.1016/S0167-  
498 7322(00)00154-9.
- 499 [37] H.A. Zarei, S. Shahvarpour, Volumetric Properties of Binary and Ternary Liquid Mixtures  
500 of 1-Propanol ( 1 ) + 2-Propanol ( 2 ) + Water ( 3 ) at Different Temperatures and Ambient  
501 Pressure (81.5 kPa), (2008) 1660–1668.
- 502 [38] H.L. Clever, C.C. Snead, Thermodynamics of Liquid Surfaces: the Surface Tension of  
503 Dimethyl Sulfoxide and Some Dimethyl Sulfoxide—Acetone Mixtures, *J. Phys. Chem.*  
504 67 (1963) 918–920. doi:10.1021/j100798a501.
- 505 [39] Y. Hiraga, A. Kato, Y. Sato, T.M. Aida, M. Watanabe, R.L. Smith, Separation factors for  
506 [amim]Cl–CO<sub>2</sub> biphasic systems from high pressure density and partition coefficient  
507 measurements, *Sep. Purif. Technol.* 155 (2015) 139–148.  
508 doi:10.1016/j.seppur.2015.03.008.
- 509 [40] O. Ciocirlan, O. Iulian, Properties of pure 1-butyl-2,3-dimethylimidazolium  
510 tetrafluoroborate ionic liquid and its binary mixtures with dimethyl sulfoxide and  
511 acetonitrile, *J. Chem. Eng. Data.* 57 (2012) 3142–3148. doi:10.1021/je3007474.
- 512 [41] C. Yang, G. Wei, Y. Li, Densities and Viscosities of N , N -Dimethylformamide + Formic  
513 Acid , and + Acetic Acid in the Temperature Range from (303.15 to 353.15) K, *J. Chem.*  
514 *Eng. Data.* 53 (2008) 1211–1215. doi:10.1021/je700755t.
- 515 [42] V. Govinda, P. Attri, P. Venkatesu, P. Venkateswarlu, Thermophysical properties of  
516 dimethylsulfoxide with ionic liquids at various temperatures, *Fluid Phase Equilib.* 304

- 517 (2011) 35–43. doi:10.1016/j.fluid.2011.02.010.
- 518 [43] G.S. Gokavi, J.R. Raju, T.M. Aminabhavi, R.H. Balundgi, M. V. Muddapur, Viscosities  
519 and Densities of Binary Liquid Mixtures of Dimethyl Sulfoxide with Chlorobenzene,  
520 Pyridine, and Methyl Ethyl Ketone at 25, 35, 45, and 55 °C, *J. Chem. Eng. Data.* 31 (1986)  
521 15–18. doi:10.1021/je00043a004.
- 522 [44] M.A. Saleh, O. Ahmed, M.S. Ahmed, Excess molar volume, viscosity and  
523 thermodynamics of viscous flow of the system dimethylsulfoxide and acetic acid, *J. Mol.*  
524 *Liq.* 115 (2004) 41–47. doi:10.1016/j.molliq.2003.12.021.
- 525 [45] A. Ali, A.K. Nain, D. Chand, R. Ahmad, Viscosities and Refractive Indices of Binary  
526 Mixtures of Dimethylsulphoxide with Some Aromatic Hydrocarbons at Different  
527 Temperatures: An Experimental and Theoretical Study, *J. Chinese Chem. Soc.* (2006)  
528 531–543. doi:10.1002/jccs.200600070.
- 529 [46] T. Zhao, J. Zhang, B. Guo, F. Zhang, F. Sha, X. Xie, X. Wei, Density, viscosity and  
530 spectroscopic studies of the binary system of ethylene glycol + dimethyl sulfoxide at  $T =$   
531  $(298.15 \text{ to } 323.15) \text{ K}$ , *J. Mol. Liq.* 207 (2015) 315–322. doi:10.1016/j.molliq.2015.04.001.
- 532 [47] U.R. Kapadi, S.K. Chavan, O.S. Yemul, Partial Molar Volumes and Viscosity B  
533 Coefficients of Benzyltriethylammonium Chloride in Dimethyl Sulfoxide + Water at  
534 Different Temperatures, *J. Chem. Eng. Data.* 42 (1997) 548–550. doi:10.1021/je960216+.
- 535 [48] N. Calvar, Á. Domínguez, E.A. Macedo, Vapour pressures and osmotic coefficients of  
536 binary mixtures containing alcohol and pyrrolidinium-based ionic liquids, *J. Chem.*  
537 *Thermodyn.* 66 (2013) 137–143. doi:10.1016/j.jct.2013.05.027.
- 538 [49] C. Shen, X.M. Li, Y.Z. Lu, C.X. Li, Effect of ionic liquid 1-methylimidazolium chloride  
539 on the vapour liquid equilibrium of water, methanol, ethanol, and {water + ethanol}  
540 mixture, *J. Chem. Thermodyn.* 43 (2011) 1748–1753. doi:10.1016/j.jct.2011.06.002.
- 541 [50] S. Nebig, R. Bölts, J. Gmehling, Measurement of vapor–liquid equilibria (VLE) and  
542 excess enthalpies (HE) of binary systems with 1-alkyl-3-methylimidazolium

543 bis(trifluoromethylsulfonyl)imide and prediction of these properties and  $\gamma$  using modified  
544 UNIFAC (Dortmund), Fluid Phase Equilib. 258 (2007) 168–178.  
545 doi:10.1016/j.fluid.2007.06.001.

546 [51] R. Kato, M. Krummen, J. Gmehling, Measurement and correlation of vapor-liquid  
547 equilibria and excess enthalpies of binary systems containing ionic liquids and  
548 hydrocarbons, Fluid Phase Equilib. 224 (2004) 47–54. doi:10.1016/j.fluid.2004.05.009.

549 [52] J. Zhao, X.-C. Jiang, C.-X. Li, Z.-H. Wang, Vapor pressure measurement for binary and  
550 ternary systems containing a phosphoric ionic liquid, Fluid Phase Equilib. 247 (2006)  
551 190–198. doi:10.1016/j.fluid.2006.07.007.

552 [53] P.J. Carvalho, I. Khan, A. Morais, J.F.O. Granjo, N.M.C. Oliveira, L.M.N.B.F. Santos,  
553 J.A.P. Coutinho, A new microbulliometer for the measurement of the vapor-liquid  
554 equilibrium of ionic liquid systems, Fluid Phase Equilib. 354 (2013) 156–165.  
555 doi:10.1016/j.fluid.2013.06.015.

556 [54] G. Jakli, W. Alexander Van Hook, The vapor pressures of dimethyl sulfoxide and  
557 hexadeuterodimethyl sulfoxide from about 313 to 453 K, J. Chem. Thermodyn. 4 (1972)  
558 857–864. doi:10.1016/0021-9614(72)90007-9.

559 [55] M. Nishimura, M. Nakayama, T. Yano, Vapor pressure of pure dmsol and vapor-liquid  
560 equilibria in DMSO-H<sub>2</sub>O system under isobaric conditions, (1972) 223–226.

561 [56] K. Tochigi, K. Akimoto, K. Ochi, F. Liu, Y. Kawase, Isothermal vapor-liquid equilibria  
562 for water + 2-aminoethanol dimethyl sulfoxide and its constituent three binary systems, J.  
563 Chem. Eng. Data. 44 (1999) 588–590. doi:10.1021/je980068i.

564 [57] Z. Zhang, M. Lv, D. Huang, P. Jia, D. Sun, W. Li, Isobaric vapor-liquid equilibrium for  
565 the extractive distillation of acetonitrile + water mixtures using dimethyl sulfoxide at 101.3  
566 kPa, J. Chem. Eng. Data. 58 (2013) 3364–3369. doi:10.1021/je400531a.

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