Phase compositions and saturated densities for the binary system of carbon dioxide with 2-ethoxyethanol

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Abstract

The compositions and densities of the liquid and vapor phases at equilibrium of the binary system CO$_2$ + 2-ethoxyethanol were measured in a high-pressure VLE apparatus at 313.2, 320.2 and 328.2 K and for pressures ranging from ambient up to ca. 10 MPa. These measurements are ideally suited for testing equation-of-state models. The recently developed non-random hydrogen-bonding (NRHB) model was used for correlating the experimental data by taking the intramolecular hydrogen bonding in account. A satisfactory agreement was obtained between experimental and calculated phase compositions and saturated densities.

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1. Introduction

The thermodynamic properties of highly non-ideal mixtures of associated or hydrogen-bonded fluids and their correlation/analysis in terms of molecular thermodynamic models are not only of academic interest but also of importance for the rational design of industrial chemical processes involving such systems. Systematic experimental measurements of these properties over an extended range of external conditions are of key interest in the development and testing of statistical thermodynamic models capable of correlating the macroscopic properties of the fluid systems, especially those involving supercritical fluids, with their molecular structure.

The most widely used supercritical solvent is carbon dioxide, while 2-ethoxyethanol (widely known by its trade name, cellosolve) is a common solvent in laboratory practice and in the chemical industry. Their combination is attracting particular interest not only for the increased polarity of the modified supercritical solvent but also for the study of the hydrogen bonding itself of the alkoxyalcohol at supercritical conditions, especially, since 2-ethoxyethanol is able to form two types of hydrogen bonds, inter- and intra-molecular ones.

In our previous work [1], we provided new experimental spectroscopic data on two alkoxyethanol + n-alkane systems in very dilute mixtures and discussed the extent of the two competing types of hydrogen bonds as well as the validity of the lattice-fluid-hydrogen-bonding [2] statistical thermodynamic approach. A systematic study of other thermodynamic properties (excess enthalpy and volume, dielectric properties) has also been done [3]. The present work falls in the same line with the previous work [1,3] on systems of alkoxyethanol + inert solvent and extends it with phase equilibrium and density measurements at high pressures.

High pressure vapor–liquid equilibrium (VLE) of the binary mixture of CO$_2$ + 2-ethoxyethanol at two temperatures has been published by Holscher et al. [4], and at four temperatures by Joung et al. [5] but we have not found in the open literature experimental data on phase compositions and simultaneous data on the saturated densities of the phases at equilibrium. In fact, this type of data are not very abundant, in spite their importance in designing processes involving supercritical fluids.

Recently, we have described and tested a new recirculation type (analytical method) apparatus, equipped with two U-tube vibration densitometers for the measurement of saturated densities and with a gas chromatograph for the determination of phase compositions [6]. In the present work, we have used this experimental setup and measured the vapor–liquid equilibrium compositions and the saturated densities for the system of
2. Experimental

2.1. Materials

CO₂ + 2-ethoxyethanol at three temperatures (313.2, 320.2 and 328.2 K) and at pressures up to 10 MPa. The new experimental data have been correlated with the recently developed equation-of-state model non-random hydrogen-bonding (NRHB) [7] by properly modifying it in order to account for, both, inter- and intra-molecular hydrogen bonding.

2.2. Apparatus and experimental procedure

The schematic diagram of the experimental apparatus is shown in Fig. 1. The main parts of the apparatus are an equilibrium cell (A), two vibrating density meters (B and C), two Milton Roy circulation pumps (E and F), a gas chromatograph (D), two sampling valves (G and H), a gas chromatograph (D), and a gas chromatograph (D). The detailed experimental procedure was presented in our previous work [6], where the reliability and accuracy of the measurements was confirmed by critical comparison with previously published data in the literature. The mole fraction of the CO₂ in the mixture of pure compounds through calibrated syringes and sampling valves. The obtained data were correlated with a linear equation. The calibration of the thermal conductivity detector for CO₂ was made through the sampling valves. The CO₂ mass (moles), at various pressures, was calculated with PVT data taken from reference [10]. The obtained data were correlated with a quadratic polynomial equation. The uncertainty of the equilibrium composition is ±0.0005 mol fraction.

3. Experimental results

As already mentioned, the vapor (√) and liquid (√) phase compositions at equilibrium and the corresponding saturated densities of the studied CO₂(1) + 2-ethoxyethanol(2) system, were measured at three temperatures: 313.2, 320.2 and 328.2 K, and at pressures up to 10 MPa. The obtained experimental data are summarised in Table 1. The mole fraction of the CO₂ in the mixture of pure compounds through calibrated syringes and sampling valves. The obtained data were correlated with a quadratic polynomial equation. The uncertainty of the equilibrium composition is ±0.0005 mol fraction.

4. Correlation with the NRHB model

4.1. The NRHB formalism

The NRHB model is particularly suited for treating our experimental data since it is a model applicable to the liquid as well as to the vapor and to supercritical state and, in addition, it can handle hydrogen bonding. The presentation in this paragraph will heavily be based on our previous work [6,7], where the details of the original non-random hydrogen-bonding model are presented. According to NRHB model, each fluid of type $i$ in our system is characterised by three scaling constants and one geometric or surface-to-volume-ratio factor. The three scaling constants are:

\[
\alpha_i = \frac{\rho_i^0 \sigma_i}{\rho_i^\text{crit} \sigma_i^\text{crit}}
\]

\[
\beta_i = \frac{\sigma_i^\text{crit}}{\sigma_i}
\]

\[
\gamma_i = \frac{\rho_i^\text{crit}}{\rho_i^0}
\]

where $\rho_i^0$ and $\sigma_i$ are the saturated density and surface tension of pure component $i$, respectively. The NRHB model is particularly suited for treating our experimental data since it is a model applicable to the liquid as well as to the vapor and to supercritical state and, in addition, it can handle hydrogen bonding. The presentation in this paragraph will heavily be based on our previous work [6,7], where the details of the original non-random hydrogen-bonding model are presented. According to NRHB model, each fluid of type $i$ in our system is characterised by three scaling constants and one geometric or surface-to-volume-ratio factor. The three scaling constants are:

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\]

\[
\beta_i = \frac{\sigma_i^\text{crit}}{\sigma_i}
\]

\[
\gamma_i = \frac{\rho_i^\text{crit}}{\rho_i^0}
\]
the mean interaction energy per segment, $e^s_i$, the hard-core volume per segment, $v^s_i$, and the hard-core density, $\rho^s_i = 1/v^s_i$, for interactions between segments. The models are assumed to be arranged on a quasi-lattice of $N_i$ sites, where empty sites, $N_0$, are assumed to be equal to 10 in this work. Each molecule is divided into $r_i$ segments and has $q_i = 6/r_i$ external intermolecular contacts, where $s_i$ is its geometric factor. Similar scaling constants, indicated without subscript, are defined for the mixture through the following combining and mixing rules.

The average segmental volume, $v^s$, for a binary mixture is given by

$$v^s = P^s v^s = RT^s = \theta_1 v^s_1 + \theta_2 v^s_2 + 2\theta_1 \theta_2 v^s_12$$

(1)

where a Berthelot-type combining rule is adopted for the cross term

$$v^s_{12} = (1 - k_{12}) \sqrt{v^s_1 v^s_2}$$

(2)

The average segmental volume, $v^s$, is given by

$$\bar{v}^s = \frac{\phi_1 v^s_1 + 2\phi_1 \phi_2 v^s_{12} + \phi_2 v^s_2}{\phi_1 + \phi_2}$$

(3)

The adjustable parameters $k_{12}$ and $\lambda_{12}$ are determined by fitting the experimental data through a Simplex least-squares minimisation procedure. As described previously [6], the equation of state of our mixture has the following form:

$$\tilde{P} + T \left( \ln(1 - \tilde{\theta}) - \tilde{\theta} \left( \sum_j \Phi_j \frac{L_j}{r_j} - \ln \frac{\tilde{\theta}L}{r} \right) - \frac{2}{\tilde{\theta}} \ln (1 - \tilde{\theta} + \frac{2}{\tilde{\theta}}) \right)$$

$$+ \frac{\tilde{\theta}}{2} \ln \Gamma_0 = 0$$

(4)

while the chemical potential for the component 1 is given by:

$$\mu_1 = \ln \frac{\Phi_1}{\alpha_1 r_1} - r_1 \sum_j \Phi_j \frac{L_j}{r_j} + \ln \tilde{\theta} - \tilde{\theta} (\tilde{\theta} - 1) \ln(1 - \tilde{\theta})$$

$$- \frac{\tilde{\theta}}{2} r_1 \left[ \ln(1 - \tilde{\theta}) - \tilde{\theta} \ln \frac{\tilde{\theta}L}{r} \right] - \frac{\tilde{\theta}}{2} \ln \Gamma_0$$

$$+ \frac{\tilde{\theta}}{\phi_1} (\tilde{\theta} - 1) \ln \Gamma_0 - \frac{\tilde{\theta}}{\phi_1} \frac{L_1}{L} + \frac{\tilde{\theta}}{L} \frac{P_0}{P} + \frac{\tilde{\theta} \phi_1 v^s_1 + \phi_2 v^s_{12} - v^s}{v^s} + \frac{\mu_1}{RT}$$

(5)

where $\tilde{T} = T/T^*$, $\tilde{P} = P/P^*$ and $\tilde{\theta} = 1 - \theta = \rho^2/\rho$ are the reduced temperature, pressure and specific volume, respectively. Furthermore, $L_1$ and $\phi_i$ are characteristic quantities for each fluid. The parameters $\Gamma_0$, and $\Gamma_i$, are factors for the non-random distribution of empty sites around an empty site and for the distribution of molecular segments around a central molecular segment, respectively. Details for the equa-

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**Table 1**

<table>
<thead>
<tr>
<th>$P$ (MPa)</th>
<th>$x_1$</th>
<th>$\rho_i^s$ (g cm$^{-3}$)</th>
<th>$\rho^s_1$ (g cm$^{-3}$)</th>
<th>$P$ (MPa)</th>
<th>$x_1$</th>
<th>$\rho_i^s$ (g cm$^{-3}$)</th>
<th>$\rho^s_1$ (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.10</td>
<td>0.140</td>
<td>0.0315</td>
<td>0.0142</td>
<td>6.26</td>
<td>0.180</td>
<td>0.0499</td>
<td>0.0151</td>
</tr>
<tr>
<td>3.27</td>
<td>0.142</td>
<td>0.0340</td>
<td>0.0151</td>
<td>6.35</td>
<td>0.181</td>
<td>0.0481</td>
<td>0.0154</td>
</tr>
<tr>
<td>3.45</td>
<td>0.144</td>
<td>0.0370</td>
<td>0.0151</td>
<td>6.44</td>
<td>0.182</td>
<td>0.0471</td>
<td>0.0154</td>
</tr>
<tr>
<td>3.65</td>
<td>0.146</td>
<td>0.0390</td>
<td>0.0151</td>
<td>6.54</td>
<td>0.184</td>
<td>0.0473</td>
<td>0.0154</td>
</tr>
</tbody>
</table>

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**Model**

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predictions that define all these parameters can be found elsewhere [6, 7].

Three types of hydrogen bonds occur in the CO2 + 2-ethoxyethanol system, through the self-association of 2-ethoxyethanol, namely intermolecular OH−OH and OH−O− and intramolecular OH−O− hydrogen bonds. In this case, the average per segment number of intermolecular hydrogen bonds is given by:

\[ \frac{N_{11}}{rN} = \frac{N_{11} + N_{12}}{rN} \] (6)

where \( N_{11} \) and \( N_{12} \) are the number of intermolecular hydrogen bonds OH−OH and OH−O−, respectively. For the number of intramolecular hydrogen bonds, we will follow our previous approach [1, 11]. In the general case of alkoxyalkans, if \( x \) is the number of ether oxygen acceptor sites, the number of proton donors and acceptors of type 1 (−OH) is \( N_1 \), and of proton acceptors of type 2 (−O−) is \( xN_1 \). As previously [1, 11], \( x \) is assumed to be equal to 2. As a consequence, the total number of free proton donors is:

\[ N_{10} = N_1 - N_{11} - N_{12} - B \] (7)

where \( B \) is the number of intramolecular bonds OH−O− in the system. Applying the rationale of the LFHB approach [1, 11], the number of the three types of hydrogen bonds can be obtained from the following coupled equations:

\[ \frac{B(N_1 - N_{11} - N_{12} - B)}{(N_1 - N_{11} - N_{12} - B)} = \rho \exp\left(-\frac{G_1^0}{RT}\right) = K_B \] (8)

\[ \frac{N_{11}}{(N_1 - N_{11} - N_{12} - B)} = \frac{\rho}{rN} \exp\left(-\frac{G_{11}^0}{RT}\right) = K_{11} \] (9)

\[ \frac{N_{12}}{(N_1 - N_{11} - N_{12} - B)} = \frac{\rho}{rN} \exp\left(-\frac{G_{12}^0}{RT}\right) = K_{12} \] (10)

where \( G_1^0 \) and \( G_{ij}^0 \) are the free energy changes upon formation of the intermolecular hydrogen bonds of types 1−1 and 1−2, respectively, and \( G_{0}^0 \) is the corresponding free energy change for the formation of the intramolecular hydrogen bonds. The free energy change for the \( i-j \) bond can be resolved as following:

\[ G_{ij}^0 = G_j^0 + PV_j^0 - TS_j^0 \] (11)

\( E_j^0, V_j^0 \) and \( S_j^0 \) are the energy, volume, and entropy change, respectively, upon formation of the same hydrogen bond.

After some algebra the above three coupled equations lead to the following equation:

\[ N_{12} = \frac{K_{12}}{K_{11}N_1} \delta (N_1 - N_{11} - B) \] (12)

Table 2

<table>
<thead>
<tr>
<th>Fluid</th>
<th>( \varepsilon^* ) (J mol(^{-1}))</th>
<th>( \chi^* (\text{cm}^3 \text{mol}^{-1}) )</th>
<th>( \Delta v^* (\text{cm}^3 \text{mol}^{-1}) )</th>
<th>( \Delta \mu^* (\text{cm}^3 \text{mol}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2 [6]</td>
<td>3.060</td>
<td>5.970</td>
<td>0.707</td>
<td>0.909</td>
</tr>
<tr>
<td>2-Ethoxyethanol</td>
<td>4.873</td>
<td>11.731</td>
<td>1.082</td>
<td>0.938</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Hydrogen bond</th>
<th>( \Delta H ) (J mol(^{-1}))</th>
<th>( \Delta S ) (J K(^{-1}) mol(^{-1}))</th>
<th>( \Delta V ) (cm(^3) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH−OH</td>
<td>−28.100</td>
<td>−26.5</td>
<td>0.0</td>
</tr>
<tr>
<td>OH−O intra-molecular</td>
<td>−10.000</td>
<td>−240</td>
<td>0.0</td>
</tr>
<tr>
<td>OH−O intra-molecular</td>
<td>−10.470</td>
<td>−16.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Table 4: Binary interaction parameters and average absolute deviation (AAD%) between experimental and calculated data

<table>
<thead>
<tr>
<th>System</th>
<th>$k_{12}$</th>
<th>$\lambda_{12}$</th>
<th>AAD (%) in $y^{\text{CO}_2}$</th>
<th>AAD (%) in pressure</th>
<th>AAD (%) in saturated densities</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$–2-ethoxyethanol</td>
<td>-0.0698</td>
<td>-0.0192</td>
<td>&lt;0.02</td>
<td>6.7</td>
<td>12.7</td>
</tr>
</tbody>
</table>

* AAD (%) = $\frac{1}{n} \sum_{i} \frac{|X_{i}^{\text{cal}} - X_{i}^{\text{exp}}|}{X_{i}^{\text{exp}}} \times 100.$

5. Discussion and conclusions

The reported experimental data in this work are simultaneous measurements of compositions and densities of the vapor and liquid phase at equilibrium for mixture of CO$_2$+2-ethoxyethanol over a range of external temperatures and pressures. Although data on phase compositions can be found rather easily in the literature, simultaneous data on the densities of the phases at equilibrium are rather scarce. This kind of experimental measurements are ideally suited for testing equation-of-state models of highly non-ideal systems of fluids.

The additional interest of this particular system is that it exhibits inter- and intra-molecular hydrogen bonding. In terms, then, of data interpretation the question that arises is whether the hydrogen bonding parameters, obtained from systems of the 2-ethoxyethanol with inert solvents at ambient conditions, can be transferred to our system in the studied temperature and pressure range. The results of this work indicate that this can be done with thermodynamically consistent equation-of-state models, such as the LFHB and the NRHB models, since the very same hydrogen bonding parameters, obtained previously from the spectroscopic and heats of mixing measurements [1,3], can be used in correlating rather satisfactorily the present VLE (phase composition and density) data.

It should be pointed out that the contribution to the key thermodynamic properties of intramolecular hydrogen bonding is in no way negligible and, thus, modelling of these systems must take it into consideration.

List of symbols

- $B$: number of intra-molecular hydrogen bonds of types 1–2
- $E$: energy
- $G$: Gibbs energy
- $k$: binary interaction parameter
- $K$: parameter defined by Eqs. (9) and (10)
- $n$: number of experimental points
- $N$: number of molecules
- $N_r$: total number of lattice sites
- $N_{10}$: number of empty lattice sites
- $N_{11}, N_{12}$: number of types 1–1 and 1–2 intermolecular hydrogen bonds
- $N_{10}$: number of free proton donors
- $P$: pressure
- $r$: number of segments per molecule
- $R$: gas constant
- $s$: surface to volume fraction
- $S$: entropy
- $T$: temperature
- $v$: average segmental volume
- $V$: volume
- $x$: mole fraction in liquid phase, number of –O– sites
- $X_i$: physical quantity at point $i$
- $y$: mole fraction in vapor phase
- $\zeta$: lattice coordination number
- $zq$: average number of external contacts per molecule
References