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# Binary mixtures of supercritical carbon dioxide with methanol. A molecular dynamics simulation study

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## Abstract

Molecular dynamics simulations were performed on supercritical mixtures of MeOH in CO<sub>2</sub> with MeOH mole fractions in the range 0.0939–0.1173 at 323.15 K and pressure from 9.952 to 16.96 MPa. It is found that the EPM2 model of CO<sub>2</sub> with the J2 model of MeOH predicts the experimental  $p/T$  relationship of the fluid in this region quite good. Furthermore, the structural and hydrogen-bonding data obtained reveal the existence of MeOH type aggregates in the mixed fluid. The latter finding was found to be in agreement with conclusions from previous experimental studies on this system.

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## 1. Introduction

It is well known that the properties of supercritical fluids (SCFs) depend sensitively on pressure and temperature. This makes SCFs attractive as solvents for a variety of chemical, analytical and material processes such as fluid extraction, chromatography, as well as synthesis and analysis. The efficiency, for instance, of some SCFs for replacing toxic industrial solvents is one of the most important reasons for the current scientific interest in such substances. Note that many experimental and theoretical studies have been attempted so far to improve our knowledge concerning the behavior of SCFs [1].

Among several types of solvents, SC CO<sub>2</sub> appears to be an extremely interesting molecular system, because it satisfies a significant number of requirements for the above-mentioned applications [2–6]. For this reason CO<sub>2</sub> find a wide range of use as a solvent in the liquid and SC state for chemical technologies.

As it becomes apparent from earlier studies, the solubility of organic compounds in SC CO<sub>2</sub> decreases dramatically when their polarity increases [7]. On the other hand, experimental studies have revealed [8] that a relatively small amount (less than 10%) of a polar co-solvent can lead to an enhancement of the solubility of these compounds in SC CO<sub>2</sub>. It is worthwhile to note here, that among many polar organic compounds used widely for this purpose are certainly methanol (MeOH), ethanol (EtOH) and 2-propanol. Therefore, it is understandable why investigating the

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properties of pure SC CO<sub>2</sub> and its binary mixtures with the aforementioned alcohols, becomes a very interesting and useful task. As far as we know, however, apart from the substantial research effort on the pure SC CO<sub>2</sub>, thorough investigations of the properties of these cosolvents in SC CO<sub>2</sub> are still needed. Note that only a few experimental papers regarding mainly the thermodynamics of these SC mixed solvents have been published so far. In addition, computer simulation (CS) studies of these mixed fluids are not available except for only one, namely, that of MeOH in SC CO<sub>2</sub> reported very recently as a MD proceeding paper [9]. In that paper the densities used to simulate the mixed fluid were set equal to the experimental values of pure CO<sub>2</sub> at the pressures of interest. Furthermore, the authors in that study pointed out that no attempt was made to approximate the experimental  $pVT$  data of the system at the SC state points under investigation.

In this Letter, we demonstrate the first part of our results obtained from a series of molecular dynamics (MD) simulation studies of SC mixtures of MeOH in CO<sub>2</sub>. Our first objective has been to provide information regarding the accuracy of the proposed potentials for CO<sub>2</sub> and MeOH to describe the properties of MeOH/CO<sub>2</sub> mixed solvent especially at SC conditions. Note, however, that our main purpose has been to investigate the density or pressure dependence of the bulk thermodynamic, structural and some dynamic properties of the system.

## 2. Computational details

Following the literature we can notice that a considerable number of potentials have been developed so far to model the molecular interactions in pure CO<sub>2</sub>. According to their origin, all these CO<sub>2</sub> potentials can be divided into two groups. The first group contains two-body empirical models based on experimental data, usually the properties of liquid and solid CO<sub>2</sub>. The second group of potentials for CO<sub>2</sub> is based on ab initio dimmer quantum mechanical calculations. The detailed description of all these models can be found in previous studies [10–20]. Note that re-

garding the behavior of pure SC CO<sub>2</sub> and its binary solutions with H<sub>2</sub>O or alcohols (MeOH, EtOH, 2-propanol), the properties of the available CO<sub>2</sub> models have not been thoroughly examined so far when employed to describe the CO<sub>2</sub>–CO<sub>2</sub> interactions in the aforementioned molecular systems. Therefore, it makes sense to reassess the properties of these SC CO<sub>2</sub> solutions for the most accurate models of CO<sub>2</sub> in combination with available models for the aforementioned cosolvents.

In the case of MeOH in SC CO<sub>2</sub>, our approach has utilized site–site pair wise additive potentials for the CO<sub>2</sub>–CO<sub>2</sub> and MeOH–MeOH interactions. Note that, the well-known condensed-phase polarization effects are implicitly included in the parameters of the models used in an average sense. Concerning the simulation methodology applied to study the fluid, all the MD simulations have been performed under the same way described hereinafter. For this purpose, we have carried out trial MD runs by using the most popular intermolecular potentials for CO<sub>2</sub> in combination with MeOH OPLS models. Specifically, we found that among the potentials used here to model the fluid, the elementary physical model EPM2 [16] with the OPLS model J2 for MeOH [21], provide the most accurate results at the investigated SC conditions of the fluid. Note that here we demonstrate only the results based upon the EPM2/J2 models while the concluding remarks concerning the impact of the rest CO<sub>2</sub>/MeOH combined models employed to simulate the fluid will be summarized elsewhere.

A complete description of the EPM2 and J2 potentials is given in Table 1. Note that in each case the Lorentz–Berthelot combining rules were used to obtain the Lennard-Jones (LJ) parameters for the cross interactions. All the MD runs were performed in the canonical ensemble (NVT) with systems of 500 molecules in a cubic box with periodic boundary conditions. The equations of motion were integrated with use of a leapfrog algorithm and with a time step of 1 fs. The length of each equilibrated run was 50 ps. Note also that in order to achieve accurate statistics, the production runs were extended to about 300 ps. In each simulation, a cut off radius at half the length of the simulation box was applied to all interaction sites

Table 1

Parameter values for the potential models for CO<sub>2</sub> and MeOH used in the present study to simulate their mixtures at SC conditions

CH <sub>3</sub> OH–CH <sub>3</sub> OH J2 model [21]		CO <sub>2</sub> –CO <sub>2</sub> EPM2 model [16]	
$r_{\text{O-H}}$ (Å)	0.945	$r_{\text{C-O}}$ (Å)	1.149
$r_{\text{Me-O}}$ (Å)	1.430	$\sigma_{\text{O-O}}$ (Å)	3.033
$\angle \text{HOMe}$ (deg)	108.5	$\varepsilon_{\text{O-O}}/k_{\text{B}}$ (K)	80.507
$\sigma_{\text{O-O}}$ (Å)	3.071	$\sigma_{\text{C-C}}$ (Å)	2.757
$\varepsilon_{\text{O-O}}/k_{\text{B}}$ (K)	85.59	$\varepsilon_{\text{C-C}}/k_{\text{B}}$ (K)	28.129
$\sigma_{\text{Me-Me}}$ (Å)	3.775	$q_{\text{O}}$ (e)	–0.3256
$\varepsilon_{\text{Me-Me}}/k_{\text{B}}$ (K)	104.21	$q_{\text{Me/C}}$ (e)	0.6512
$q_{\text{O}}$ (e)	–0.700		
$q_{\text{H}}$ (e)	0.435		
$q_{\text{Me}}$ (e)	0.265		
$\mu$ (D)	1.9338		

among the molecules of the fluid. Long-range corrections to the LJ potential arising from the truncations of the site–site interactions were calculated according to the well-known statistical mechanical formulas [22]. Finally, Ewald sums have been employed to account for the corrections of the long-range electrostatic interactions.

The fluid was simulated at SC conditions for which experimental volumetric data are available [23]. Generally, volumetric data of this fluid mixture in the CO<sub>2</sub>-rich region ( $X_{\text{MeOH}} < 0.11614$ ) are scarce. Concretely, we carried out MD-NVT simulations at four different SC state points ( $P, \rho, T, X_{\text{MeOH}}$ ) of the system at 323.15 K with MeOH mole fractions,  $X_{\text{MeOH}}$ , in the range 0.0939–0.1173 and experimental densities,  $\rho$ , corresponding to pressures,  $P$ , in the range 9.952–16.96 MPa. Note that the above mentioned SC state points of CO<sub>2</sub> with MeOH concentrations in this region are very recently reported in the literature (see Fig. 1 and Table 1 in [23]).

### 3. Results and discussion

Among all the selected CO<sub>2</sub> and MeOH models, only the four CO<sub>2</sub> potentials referred to the parameter sets as MSM [15], Exp-6 [17], EPM and EPM2 [16] and the models J1, J2 [21], H1 and H2 [21,24] for MeOH have been tested in our treatment. We mention here that, the slightly modified LJ version of the EPM2 [16] model of CO<sub>2</sub>, namely the TraPPE force field (transferable potential for phase equilibria) [20] developed recently to predict

the vapor–liquid equilibria (VLE) of *n*-alkanes/CO<sub>2</sub> mixtures, has not been tested in our treatment. The basic argument for this decision has relied on the previous MC predictions concerning the VLE data of pure CO<sub>2</sub> [20]. The results obtained from that treatment have shown that both the EMP2 model for CO<sub>2</sub> and its TraPPE variant yield to a high accuracy VLE data for the pure system. However, the original model EPM2 [16] was found to be somewhat superior to the TraPPE one regarding the aforementioned data very close to the SC point of pure CO<sub>2</sub> (see Fig. 1 in [20]).

The most important thermodynamic properties such as the mean potential energy,  $U^{\text{sim}}$ , and pressure,  $P^{\text{sim}}$ , were obtained and compared with corresponding available data. Thus, the quality of the predicted  $pVT$  diagrams of the system led us to draw conclusions concerning the accuracy of the potentials used. As mentioned in the introduction, among the models used in this study, the EPM2 model for CO<sub>2</sub> and the MSM to a somewhat lower extent, in combination with model J2 for MeOH provide the most accurate results for the fluid at these conditions. Results from our MD simulations are shown below.

The MD  $pVT$  phase diagrams for the EPM2/J2 models at 323.15 K with concentrations very close to 10 mol% of MeOH and densities or molar volumes corresponding to the pressures in the range 9.9–16.7 MPa are summarized and compared against experimental values in Table 2 and Fig. 1. As can be observed, the calculated pressure shows the expected behavior with density. Further, these results are found to be in quite good agreement

Table 2

Simulated thermodynamic state points of the SC CO<sub>2</sub> with MeOH and the corresponding number of molecules used in the MD-NVT simulations of the fluid

$X_{\text{MeOH}}$	$V_m$ (cm <sup>3</sup> ) $T = 323.15$ K	$P_{\text{exp}}$ [6] (MPa)	$P_{\text{sim}}$ (MPa)	$N_{\text{CO}_2}$	$N_{\text{MeOH}}$
0.1173	68.409	9.952	9.917	441	59
0.1035	60.368	12.27	12.505	448	52
0.0989	57.693	14.05	14.623	451	49
0.0939	54.779	16.96	17.933	453	47

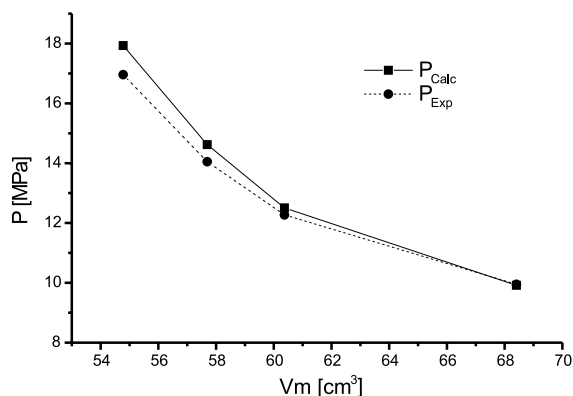


Fig. 1. The experimental  $pVT$  phase diagram of the binary mixtures of MeOH in SC CO<sub>2</sub> and that predicted in this MD study by using the EPM2/J2 models at 323.15 K with MeOH mole fractions very close to 0.1 and densities or molar volumes corresponding to the pressures in the range 9.95–16.96 MPa.

with experiment. It is also interesting to notice that the largest deviation between simulated and experimental pressure observed is about 6%. Such deviation has been obtained at the corresponding state point with the highest simulated density. Note that the aforementioned SC state point is very close to the critical one.

The calculation of the self-diffusion coefficients of both species has also been included in the framework of our study. All the calculations concerning this transport property were based on the mean square displacement method. As can be observed from the data depicted in Fig. 2, the self-diffusion coefficients of both species change considerably with pressure, as expected. Concretely, they show the following behavior:

- (a) the diffusivities of both species decrease with increasing pressure,

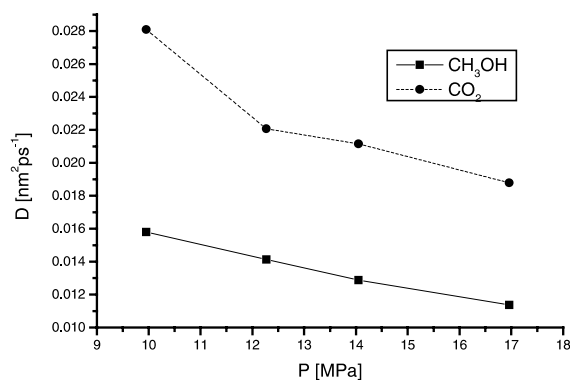


Fig. 2. The pressure dependence of the simulated self-diffusion coefficients for MeOH and CO<sub>2</sub> molecules from EPM2/J2 mixture model predicted in this MD study.

- (b) The mobility of CO<sub>2</sub> decreases more rapidly with pressure than that of MeOH in the mixed fluid, and,

- (c) the diffusion coefficients for MeOH are significantly smaller compared to those obtained for CO<sub>2</sub>. This result may be characterized as an unexpected one due to the fact that the molar mass of MeOH is smaller than that of CO<sub>2</sub>.

Unfortunately, the latter finding cannot be tested against experiment since experimental self-diffusion coefficients for this fluid are not available. Note, however, that similar experimental self-diffusion data for other diluted solutes in SC and liquid solvents have been reported in the literature [25]. It is of interest to mention here our previous MD study of carbonyl sulfide (OCS) diluted in krypton (Kr) [26] at different densities, where we found that the self-diffusion of Kr is greater than that of OCS. On the other hand, for an acceptable interpretation of this behavior one needs to explore a number of factors and possible

mechanisms, which could affect the molecular motion in the fluid. A possible explanation of this behavior might be the existence of some kind of strong correlation among the MeOH molecules in the sample. A kind of hydrogen-bonding network or local aggregation, for instance, formed between the MeOH molecules could affect dramatically the mobility of the solute molecules in this fluid. The existence of such MeOH aggregation in similar fluids has been supported in previous experimental spectroscopic studies of MeOH in organic liquid and SC solvents [27,28].

The local structure in the system was investigated in terms of the appropriate center of mass-center of mass (COM) and site-site radial distribution functions (RDFs). The calculated COM RDFs with pressure are depicted in Fig. 3.

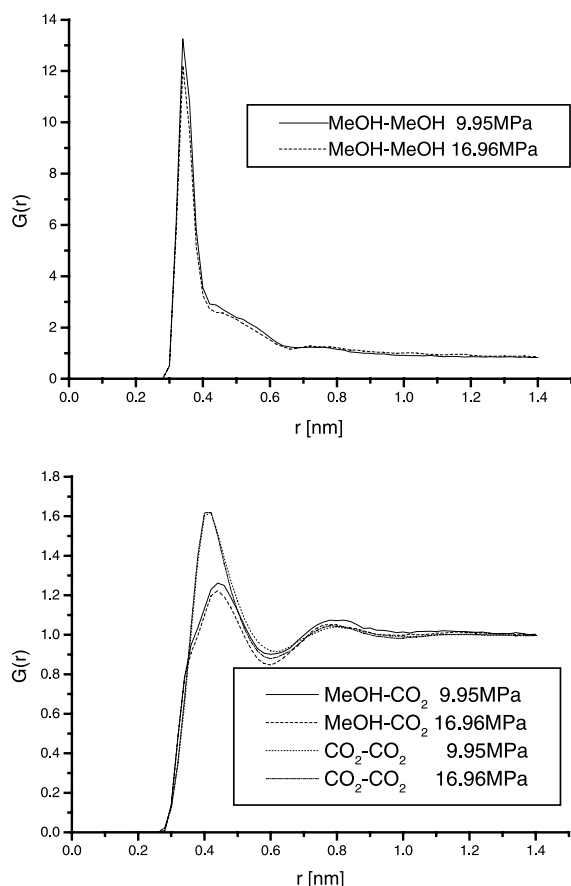


Fig. 3. Center of mass pair distribution functions for the species in the fluid from this MD study.

By inspecting the behavior of these functions, we may easily conclude that there is only a slight variation of them with pressure. Moreover, the short-range part of the COM MeOH–MeOH correlations appears to be very sharp peaked. The amplitude of their first peak ( $\approx 13$ ) appears to be located around 3.1 Å and sufficiently higher compared to the corresponding ones of the CO<sub>2</sub>–CO<sub>2</sub> and MeOH–CO<sub>2</sub> COM RDFs. The first conclusion from these results is that the MeOH molecules in the fluid are highly structured at relatively short intermolecular distances. A deeper insight on the details of the local structure around the MeOH molecules may be gained on the basis of the H–O (MeOH) and H–O (CO<sub>2</sub>) RDFs presented in Fig. 4. The H–O (MeOH) functions provide a very strong sharp-peaked first maximum ( $\approx 25$ ) around 2 Å. This feature indicates the existence of a hydrogen bonded structure among the nearest MeOH molecules in the system. In other words, a kind of MeOH–MeOH aggregation seems to be possible in the sample as discussed above. Contrary to the latter result, the H–O (CO<sub>2</sub>) RDFs do not show a comparable behavior to the H–O (MeOH) functions. Therefore, we may assume that the number of MeOH–CO<sub>2</sub> hydrogen bonds in this fluid should be very restricted at these SC conditions. However, in order to investigate accurately the hydrogen bonding in the system one needs to apply some appropriate analysis of the local structure in the sample.

In this work, the hydrogen bonds (HBs) in the mixed fluid was investigated by using a geometric criterion similar to that used in our previous study of pure SC MeOH [29]. The parameters employed in this criterion are summarized in Table 3. Our calculations are extended to hydrogen-bonds statistics by estimating the percentage distribution  $f_i$  of molecules with  $i$  ( $= 0, 1, 2, \dots$ ) bonds per molecule. The results obtained are depicted in Fig. 5. By inspecting the curves in this figure, we see that the hydrogen bond distributions depend slightly with pressure. Additionally, we see that the hydrogen bonding between MeOH molecules is sufficiently higher compared to MeOH–CO<sub>2</sub> one. Finally the small amount of CO<sub>2</sub> molecules participating in one hydrogen bond, as well as the absence of CO<sub>2</sub> molecules participating in two

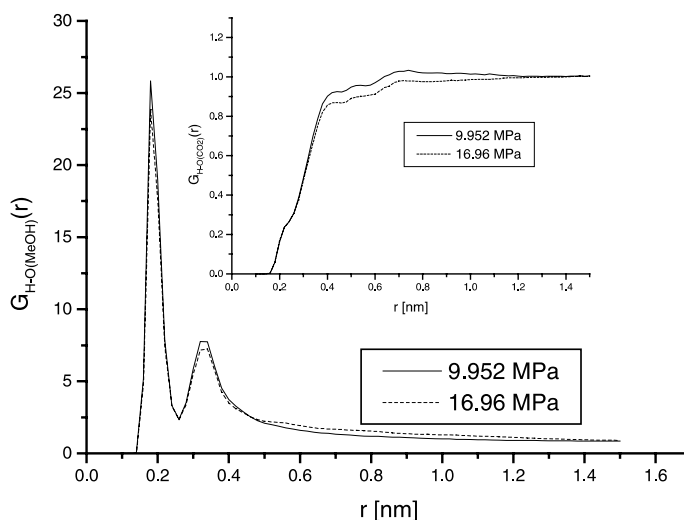


Fig. 4. Hydrogen–oxygen site–site pair distribution functions for the species in the fluid from this MD study. The H–O MeOH–MeOH correlations are depicted in the large scale. The insert curves correspond to the H–O MeOH–CO<sub>2</sub> predicted correlations.

Table 3  
Geometric criterion for hydrogen bonds calculation

	MeOH–MeOH	MeOH–CO <sub>2</sub>
$r_{O-O}$ (Å)	3.60	3.60
$r_{O-H}$ (Å)	2.50	2.60
$\theta_{O-O-H}$ (deg)	30	30

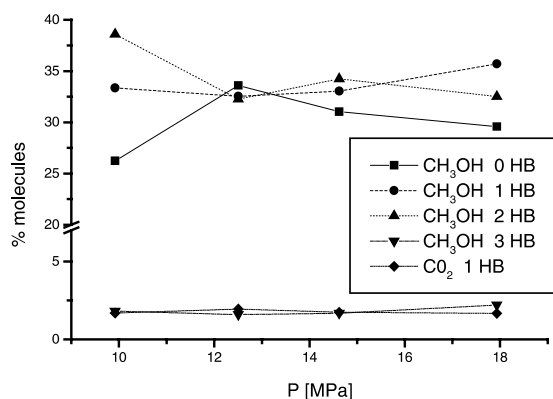


Fig. 5. Hydrogen bonding analysis for the simulated fluid species from this MD study. Depicted are the average percentage  $f_i$  of MeOH in SC CO<sub>2</sub> with  $i$  (0, 1, 2, 3, ...) hydrogen bonds as a function of pressure.

HBs suggest that there is no bridging of the MeOH by CO<sub>2</sub> molecules inside the MeOH rich region in the system.

#### 4. Conclusions

The binary mixtures of MeOH in CO<sub>2</sub> were successfully simulated at SC conditions for which experimental data are available by using the MD–NVT simulation technique. The simulations were carried out for fluids with concentrations of approximately 10 mol% MeOH (the CO<sub>2</sub>-rich region of the mixture) at a temperature of 323.15 K and experimental densities corresponding to the pressures in the range 9.952–16.96 MPa. As a result, we found that the performance of the EPM2 model for CO<sub>2</sub> in combination with the J2 model for MeOH is quite successful in predicting the experimental  $pVT$  data of the system at SC state points of the solution under investigation. The transport properties as well as the local microstructure of both constituents were evaluated. Both properties suggest that this fluid exhibits strong correlation between the MeOH molecules at these conditions. In addition, the hydrogen bonding of the system was studied and its pressure dependence was obtained. According to our results, a molecular network seems to be formed by MeOH molecules at rather low concentrations and the CO<sub>2</sub> molecules were found to participate partially in this.

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