On the Selection of Proper Thermodynamic Conditions for the Gas Antisolvent Process (GAS) at Nearcritical and Supercritical Conditions

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Abstract
In this work the volume expansion for the binary systems of ethanol and toluene, as industrial organic solvents, in the presence of nearcritical and supercritical carbon dioxide, CO₂, at a temperature range of 293 to 333 K has been meticulously measured. The effect of the temperature and pressure of binary systems on volume expansion for organic solvents have also been investigated. It can be observed that by increasing the pressure of the system at a constant temperature, the volume of the liquid phase increases smoothly, while at higher pressures a sudden volume expansion can occur. The range of pressure that can lead to a sudden increase in the volume expansion of the liquid phase in each specified temperature can be reported as a proper condition in producing micro and nanoparticles. The experimental data for the volume expansion of organic solvents were modeled using the conventional cubic Peng Robinson equation of state. The Average Absolute Relative Deviation percent (AARD%) for the binary systems of ethanol + CO₂ and toluene + CO₂ were reported as 14.9% and 15.1%. As inferred, it is vital to develop a thermodynamic model with greater accuracy in order to correlate the volume expansion of the systems studied in this work at various conditions.

Keywords: nanopowders, GAS process, supercritical fluids, equation of state

Introduction
Nowadays, utilizing supercritical technology in producing micro and nanoparticles has significantly increased. Using this technology, particles with a controlled size distribution can be produced and this fact has remarkably directed studies towards this field [1-3]. The various methods of the industrial production of micro and nanoparticles are very important in many chemical and pharmaceutical industries. For instance, the production of some materials such as colors, polymers, salts, medicines and pharmaceuticals containing proteins can be mentioned [4-6].

In the previous methods of decreasing particle size, the mechanical methods such as grinding, shattering, recrystallization of materials with other solvents and also spray drying were given more heed. All of these methods have disadvantages such as degraded quality of materials because of thermal and chemical effects, or the problems in removing solvent from the produced crystal, especially in producing medicines [1-2]. Therefore, new methods for producing
micro and nanoparticles with controlled size distribution and a higher quality of crystals with respect to their purity, is needed. This supercritical technology provides various preparations for achieving the mentioned goals [3-5]. Carbon dioxide is a commonly used fluid in the supercritical technology process [6]. Having a critical pressure of 73.8 bar and a critical temperature of 31.1ºC, CO₂ is suitable for different processes. Moreover, carbon dioxide is nontoxic, nonflammable and an inexpensive fluid [7-9].

The Supercritical Antisolvent System (SAS), Gas Antisolvent system (GAS) and Precipitation with compressed Antisolvent (PCA) are three important methods in producing micro and nanoparticles using an organic solvent [1-3]. In these methods, a high pressure gas or a supercritical fluid acts as an antisolvent for recrystallization or precipitation of a solid which is dissolved in an organic solvent [4-6]. The antisolvent gas, which is highly soluble in the liquid solvent, causes a volume expansion of the liquid solvent and thus reduces the solvation power of the organic solvent. As a result, the precipitation of a dissolved solute occurs and fine particles with a narrow size distribution can be obtained. Schemes of the SAS, PCA and the GAS processes are shown in figures 1 and 2 [7-9]. In the GAS process, while an organic solvent is usually used as an industrial solvent to a solid solute, a supercritical fluid such as supercritical carbon dioxide is used as an antisolvent. Therefore, volumetric properties such as the VE for the binary mixtures containing an organic solvent and supercritical fluid play a fundamental role in a good designing of the GAS process [10]. This research work is useful for designing the GAS process.

As mentioned earlier, determining the range of pressure in which the sudden volume expansion occurs is of central importance in supercritical processes as it controls the proper condition in producing micro and nanoparticles.

In this work the volume expansion for toluene and ethanol, which are significant solvents in producing microparticles and nanoparticles in various applications, have been measured in the presence of nearcritical and supercritical CO₂. The measurements have been performed within a wide temperature range. Notably, this temperature range can be regularly used in GAS processes. The PR equation of state has been used to correlate the experimental data of the volume expansion obtained from this experimental work. The results showed that the PR equation of state can correlate the experimental data with less accuracy.

**Volume expansion**

Volume expansion is one of the most important parameters in producing micro and
nano powders. By determining this parameter in various pressures and temperatures, the proper operational condition in producing small particles can be found. Volume expansion is a function of temperature, pressure, solvent and antisolvent. The size and the size distribution of particles are also dependent on this parameter. The volume expansion of the solvent can be defined by the following relation [11, 12]:

\[ \frac{\Delta V}{V_0} = \frac{V(T, P) - V_0(T, P_0)}{V_0(T, P_0)} \times 100 \]  

(1)

Where, \( P_0 \) and \( V \) are atmospheric pressure and volume of the liquid mixture at the measured temperature and pressure respectively, also \( V_0 \) represents the volume of the pure solvent at the measured temperature and atmospheric pressure.

**Materials**

For accomplishing the experiments, high purity carbon dioxide (99.99%) has been purchased from the Raham Gas Company, and toluene and ethanol with a purity of 99% have been obtained from Merck Company. All materials were used as they were purchased without further purification. The pure component data are presented in Table 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>( T_c ) (K)</th>
<th>( P_c ) (bar)</th>
<th>( \omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 )</td>
<td>304.1</td>
<td>73.8</td>
<td>0.239</td>
</tr>
<tr>
<td>Ethanol</td>
<td>513.9</td>
<td>61.4</td>
<td>0.644</td>
</tr>
<tr>
<td>Toluene</td>
<td>591.8</td>
<td>41.0</td>
<td>0.263</td>
</tr>
</tbody>
</table>

**Apparatus**

The PVT apparatus was used for experimental studies in this work. The schematic diagram of the PVT apparatus is presented in figure 3. This apparatus consists of a high accurate temperature controlled airbath with accuracy of ±0.1°C. The PVT cell has a high-pressure variable view cell equipped with a magnetic mixer and a low volume sampling port. The pressure of the system has been measured with a digital pressure indicator (Heise model 901 A) with an accuracy of ±0.5 bar. The temperature of the airbath unit and the PVT cell is measured with two platinum 100 ohm resistance thermocouples with an accuracy of ±0.3°C. The volume of the liquid phase in the PVT cell is measured using a CCD camera with an accuracy of ±0.01 ml. Pressurization of the PVT cell is achieved via a computer controlled high-pressure positive displacement pump with a volume resolution of 0.01 ml. The apparatus also contains a high-pressure densitometer rated to 700 bar and 150°C and an in-line viscometer rated up to 1400 bar and 190°C with a viscosity range of 0.1 to 10,000 cp.

**Experimental Procedures**

Before starting the experiments, the PVT cell is cleansed with an organic solvent and vacuum dried, and then airbath temperature is set to a desired value. After reaching the desired temperature, all transmission lines ended at the PVT cell are vacuumed via the corresponding valves as shown in figure 1 using a vacuum pump. A specified amount of solvent (3 to 5 ml) is then injected into the evacuated view cell via the sampling cell by the positive displacement pump. It should be pointed out that the precise injected volume is monitored by the CCD camera. A known amount of carbon dioxide is also injected into the view cell using the high-pressure positive displacement pump. The changes in the volume expansion of the liquid phase have been monitored with increasing
the pressure up to the bubble pressure of the binary systems studied in this work. In order to reach the equilibrium condition as quickly as possible, a magnetic stirrer was used in the view cell during the experiments. In order to study the effect of temperature on the volume expansion of the solvents, a number of experiments have been conducted at different temperatures.

**Modeling**

For determining the volume expansion of organic solvents, the conventional equations of state can be used. One of the most common equations of state is the Peng Robinson EOS which can be shown according to the following relation [13]:

\[
P = \frac{RT}{\nu - b} - \frac{a(T)}{\nu(\nu + b) + b(\nu - b)}
\]

(2)

The parameters of the PR EOS can be obtained using the following quadratic mixing rules:

\[
a = \sum_i \sum_j x_i x_j a_{ij}
\]

(3)

\[
a_{ij} = (a_i a_j)^{0.5} (1 - k_{ij})
\]

(4)

\[
b = \sum_i x_i b_i
\]

(5)

\[
a_i = 0.45724 \frac{R^2 T_i^2}{P_{c_i}}
\]

(6)

\[
b_i = 0.077796 \frac{RT_i}{P_{c_i}}
\]

(7)

The binary interaction parameters \(k_{ij}\) were obtained by fitting PR EOS to the experimental data and for two binary systems, can be written as a function of temperature (°C) [14]:

\[
k_{\text{CO}_2-\text{Toluene}} = -1.6101 \times 10^{-6} T^3 + 2.1748 \times 10^{-4} T^2 - 1.001 \times 10^{-2} T + 0.2291
\]

(8)
\[ k_{\text{CO}_2-\text{Ethanol}} = 2.0667 \times 10^{-7}T^3 - 2.52596 \times 10^{-5}T^2 + 6.58076 \times 10^{-4}T + 0.103063 \]  

(9)

Using these relations leads to more accurate results for the PR equation of state.

**Results and discussion**

The volume expansion of toluene and ethanol expanded by carbon dioxide was measured in various temperatures and pressures, and the PR EOS was used in predicting the volumetric behavior of our binary systems. The experimental and theoretical results for the volume expansion of the systems studied in this work are presented in figures 4 and 5.

Results show that in each specific temperature, the solubility of carbon dioxide in organic solvents increases with increasing the pressure. This fact causes the increase in the volume expansion of the organic solvents. As seen from figures 4 and 5, the volumetric behavior stipulates the fact that in all temperatures, the increase in volume expansion with pressure displays the same behavior in both binary systems, and volume expansion increases gradually with pressure in lower pressures until the systems reach a specific range of pressure in which the volume expansion shows a sudden increase. As it is obvious in both figures, these specific ranges of pressure shift to higher pressures with the increase in temperature.

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**Figure 4.** Variation of the volume expansion for the binary system of toluene + carbon dioxide at various temperatures as a function of pressure.

**Figure 5.** Variation of the volume expansion for the binary system of ethanol + carbon dioxide at various temperatures as a function of pressure.
Conclusions
In this work, the volume expansion of two organic solvents, ethanol and toluene, was measured in the presence of supercritical carbon dioxide at a temperature range of 293 to 333 K. It can be found that by increasing the pressure of the system at a constant temperature, the volume of the liquid phase increases smoothly, while at higher pressures a sudden volume expansion occurs. Such phase behavior would be of central importance in producing microparticles, nanoparticles and nanopowders. The experimental data for the volume expansion of organic solvents collected in this work were modeled using the Peng Robinson equation of state. The Average Absolute Relative Deviation percent (AARD%) for the binary systems of ethanol + CO2 and toluene + CO2 were reported as 14.9% and 15.1%. Inferior results obtained from the PR equation of state confirm that it is necessary to develop a thermodynamic model with greater accuracy in order to correlate the volume expansion of the systems studied here at various conditions.

References