

## Phase behavior of Carbon dioxide/Trimethoxy(methyl)silane and Methylsilicate 51 system

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### ABSTRACT

The phase behaviors of carbon dioxide (CO<sub>2</sub>)/trimethoxy(methyl)silane (MTMS) and CO<sub>2</sub>/Methylsilicate 51 (MS-51: methylsilicate tetramer) binary systems were determined. The experiments were performed using a synthetic method by observing the bubble point. The phase boundaries were determined at temperatures of 313.2 K–393.2 K and CO<sub>2</sub> molar fractions of 0.2–0.9. The experimentally obtained bubble points of the CO<sub>2</sub>/MTMS binary system were correlated using the Peng-Robinson equation of state (PR EoS), and the molecular interaction parameters  $k_{ij}$  and  $l_{ij}$  were determined. The results of the CO<sub>2</sub>/MS-51 binary system were correlated using the PR EoS and the Sanchez-Lacombe equation of state (SL EoS). In the SL EoS, two types of mixing rules, originally proposed by Sanchez et al. which uses  $k_{ij}$  as a fitting parameter and modified by McHugh et al. which uses two fitting parameters  $k_{ij}$  and  $l_{ij}$ , were used. For this system, the experimental results were correlated better using the SL EoS than using the PR EoS, and the latter mixing rule was more suitable than the former.

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### 1. Introduction

Supercritical carbon dioxide (scCO<sub>2</sub>) has many advantages, such as low cost, non-toxicity, non-flammability, and chemical inertness; moreover, its supercritical conditions can easily be accessed and its physicochemical properties can be tuned by pressure and/or temperature variation [1]. Thus, it is considered as an alternative to organic solvents for extraction [2], drying [3], particle formation [4], chromatography [5], etc. In addition, it is a useful blowing reagent for polymer foams [6]. In particular, scCO<sub>2</sub> is used as a foaming reagent for polymers instead of chlorofluorocarbons, which deplete the ozone layer, and chemical blowing agents, which remain as residue in the products [7].

Energy consumption in Japan nearly doubled from 1973 to 2007. Although the energy consumption of the industrial sector did not change significantly, that of the transportation sector doubled while that of the public sector increased by approximately 2.5 times. More than half of the energy consumption of the public sector is attributed to air conditioning, heating, and hot water supply. Thus, there is a critical need for high-performance insulating materials to ensure efficient use of energy.

One of the most popular insulating materials is plastic foam, which contains gas bubbles inside a solid matrix of polymers. The heat transfer mechanisms of polymer foams are conduction through polymeric materials, and radiation and convection inside the gas bubbles. Recently, to prevent heat transfer by the above-mentioned radiation and convection mechanisms, polymeric foams filled with silica aerogel [8,9] have been developed. Mass production of this composite material is achieved by CO<sub>2</sub>-assisted extrusion of a polymer and the tetraalkoxysilane as the raw materials of the silica aerogel [10]. At the exit of the extruder,

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nucleation and growth of CO<sub>2</sub> bubbles occur from the thermodynamically stable ternary mixture of CO<sub>2</sub>/tetraalkoxysilane/polymer owing to a decrease in pressure. The bubbles thus formed are slowly filled by tetraalkoxysilane-rich liquid bleeding from the bubble walls, which are gelled via subsequent hydrolysis by the humidity in the air and/or a catalyst. The structure of the composite material is mainly determined by the initial separation of CO<sub>2</sub> from the mixture, which depends on the phase behaviors of the systems. Therefore, to design the new process, the phase behaviors of the CO<sub>2</sub>/tetraalkoxysilane binary system and the CO<sub>2</sub>/tetraalkoxysilane/polymer ternary system are crucial. For the CO<sub>2</sub>/tetraalkoxysilane binary systems, data for CO<sub>2</sub>/tetraethoxysilane (TEOS) binary system [11–13] and CO<sub>2</sub>/tetramethoxysilane (TMOS) system [13] have already been reported. Unfortunately, TMOS has designated as a poison in Japan, and trimethoxy(methyl)silane (MTMS), silane compound in which one of four methoxy groups is replaced by a methyl group, is supposed to be the replacement of the TMOS. Further, many other silane compounds also have a possibility to be designated as poisons. In that case, methylsilicate 51 (MS-51), methylsilicate tetramer (average) (Fig. 1), is the other candidate for silane compound. In addition, in the present state of the development, there is a fair possibility of many suitable combinations for polymers and silane compounds. Therefore, data of various types of silicon alkoxide are required.

In this study, the phase behaviors of the MTMS and the MS-51 are investigated with the objective of increasing the number of silane compounds. Experimental results of the CO<sub>2</sub>/MTMS binary system were correlated with the Peng-Robinson equation of state (PR EoS) [14] using the van der Waals one-fluid mixing rule, and the molecular interaction parameters  $k_{ij}$  and  $l_{ij}$  for CO<sub>2</sub>/MTMS were determined. The results of the CO<sub>2</sub>/MS-51 binary system were correlated using three methods, i.e., with the PR EoS and the Sanchez-Lacombe equation of state (SL EoS) having two types of mixing rules originally proposed by Sanchez et al. and modified by McHugh et al. [14–17]. The most suitable thermodynamics model is discussed.

## 2. Experimental

### 2.1. Materials

Carbon dioxide (CAS number [124-38-9], purity > 99.99%) was purchased from Showa Yozai Co. Trimethoxy(methyl)silane (MTMS, CAS number [1185-55-3], purity > 98.0% (GC)) was purchased from Tokyo Kasei Co. Methylsilicate 51 (MS-51, Methylsilicate tetramer, Methyl(poly)silicate, CAS number [17988-16-8]) was kindly supplied by Colcoat Co., Ltd. All the reagents used were tabulated in Table 1, and used as received.

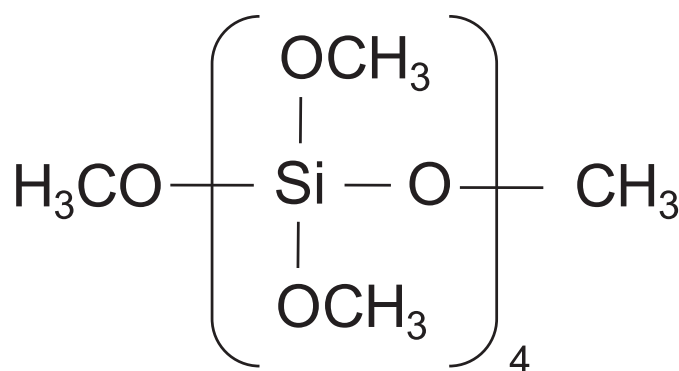


Fig. 1. Methylsilicate 51.

### 2.2. Experimental apparatus and procedure

In this work, the binary system phase diagram was deduced using a synthetic method. The details of this method have been described previously [13].

In summary, appropriate amounts of the silane compound and CO<sub>2</sub> were introduced into the front part of a variable-volume view cell containing a moving piston. The composition in the front part of the cell was calculated from the mass of the materials. The cell was heated to the desired temperature and then pressurized by moving the piston from the back part of the cell until a single phase was achieved. The pressure was then slowly decreased until small vapor bubbles appeared in the cell (bubble point: BP). After the BP was reached, the CO<sub>2</sub>/silane mixture was re-pressurized to obtain the single phase again. These procedures were repeated at least five times until the reproducibility of the BP fell within  $\pm 0.01$  MPa. Finally, the maximum and minimum values were excluded from the data, and the numerical average of the remaining values was determined.

For all the experiments, the maximum uncertainties in temperature and pressure were  $\pm 0.1$  K and  $\pm 0.01$  MPa respectively according to the supplier. Maximum error in CO<sub>2</sub> composition were calculated as  $\pm 2.73 \times 10^{-3}$  for CO<sub>2</sub>/MTMS system and  $\pm 6.75 \times 10^{-3}$  for CO<sub>2</sub>/MS-51 system, respectively (see supplemental information).

### 2.3. Peng-Robinson equation of state (PR EoS)

In this work, the experimental data were correlated with the PR EoS [14]. As the properties of MTMS and MS-51 have not been discussed in the literature, the critical constants,  $T_c$  and  $P_c$ , and normal boiling points ( $T_b$ ) were calculated using a group contribution method reported by Nannoolal et al. [18,19]. Based on the  $T_b$  and  $T_c$  thus determined, acentric factors were estimated using a method proposed by Pitzer et al. [20,21]. The physical properties used in the calculations are listed in Table 2.

### 2.4. Sanchez-Lacombe equation of state (SL EoS)

In this work, the experimental data of the CO<sub>2</sub>/MS-51 binary system were correlated using the Sanchez-Lacombe equation of state (SL EoS) [15,16], which is expressed as

$$\tilde{p}^2 + \tilde{P} + \tilde{T} \{ \ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho} \} = 0 \quad (1)$$

where  $\tilde{P}$ ,  $\tilde{T}$ , and  $\tilde{\rho}$  are the reduced pressure, temperature, and density, respectively, and  $r$  is the size parameter that represents the number of lattice sites occupied by a molecule. The SL EoS was used because it is well known to be suitable for large molecules such as polymers. The reduced parameters for a pure substance are defined as

$$\tilde{T} = T/T^* \quad , \quad \tilde{P} = P/P^* \quad , \quad \tilde{\rho} = \rho/\rho^* = V^*/V \quad (2)$$

$$r = P^*V^*/RT^* \quad (3)$$

where  $P^*$ ,  $T^*$ , and  $\rho^*$  are the SL EoS characteristic parameters and  $M$  is the molecular weight. The characteristic parameters are defined as

$$T^* = \epsilon^*/k \quad , \quad P^* = \epsilon^*/v^* \quad , \quad \rho^* = M/rv^* \quad (4)$$

where  $\epsilon^*$  is the segment interaction energy and  $v^*$  is the segment volume. A pure component can be completely characterized by

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