

Measurement and correlation of PVT for organic-inorganic hybrid nanoparticles

Taiki Homma¹, Masaki Ota^{*1,2}, Yoshiyuki Sato³ and Hiroshi Inomata¹

¹ Research Center of Supercritical Fluid Technology, Department of Chemical Engineering,
Graduate School of Engineering, Tohoku University
6-6-11-403, Aoba, Aramaki, Aoba-ku, Sendai, 980-8579, Japan

² Department of Frontier Science for Advanced Environment, Graduate School of
Environmental Studies, Tohoku University
6-6-11-403, Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan

³ Department of Applied Chemistry and Environment, Tohoku Institute of Technology
35-1 Yagiyama Kasumicho, Taihaku, Sendai, Miyagi, 982-8577, Japan

* To whom correspondence should be addressed.

E-mail : masaki.ota.a5@tohoku.ac.jp Tel & FAX : +81-(0)22-795-7282

Abstract

PVT behaviors of decane and decanoic acid-modified ceria (C10CeO₂) nanoparticle were measured with a bellows type apparatus at temperatures ranging from room temperature to 473 K and pressures ranging from 10 to 200 MPa. The obtained PVT data were correlated by the Tait equation to calculate volumetric and derivative properties; isobaric thermal expansivity and isothermal compressibility. The derivative properties of C10CeO₂ were found to show smaller values, compared with those of decane. The PVT data for the C10CeO₂ nanoparticles were also used to determine the parameters of Sanchez-Lacombe equation of state (EoS). These parameters allow us to apply Sanchez-Lacombe EoS for the C10CeO₂ nanoparticle as a pseudomolecule.

Keywords

Organic-inorganic hybrid nanoparticles, PVT, Equation of state

1. Introduction

Organic-inorganic hybrid nanoparticles (HNPs), which are composed of both inorganic nanoparticle core and organic modifier shell, have been expected for utilization as fillers in polymer functional materials. HNPs are usually single-nanometer in size and their

physical behaviors in the polymer materials have been occasionally recognized as those of molecules. Assuming such a small HNP as a pseudomolecule, molecular thermodynamics can be applied to evaluate its thermodynamic properties. Since the features of inorganic core and modifier shell are quite different, it is important to quantitatively characterize their effects on the properties of the HNP, which may be a key factor in thermodynamic modelling of pseudomolecule. However, it should be noted that it is very difficult to find an effective approach of such characterization considering two different features in a HNP pseudomolecule. An possible method for such effective evaluation of HNP is PVT measurement and successive correlation of PVT data with an equations of state (EoS) for determining EoS parameters, which can allow thermodynamic discussion for HNPs.

This work adopted decanoic acid-modified ceria (C10CeO₂) nanoparticle as a model HNP, and measured the PVT with the bellows type apparatus originally developed by Sato *et al* [1]. The validity of the experimental apparatus and procedure were firstly demonstrated by measuring the PVT of decane by comparing with the NIST data. The obtained experimental PVT data were correlated with the Tait equation [2] to evaluate the volumetric and derivative properties of HNPs. The PVT data were also used to determine the parameters of the Sanchez-Lacombe equation of state (SL-EoS) [3], which are widely applied to thermodynamic property calculations of polymer systems.

2. Experimental

2.1. Materials

The C10CeO₂ nanoparticles (ITEC Co. Ltd.) were synthesized by supercritical hydrothermal method, using decanoic acid as modifying agent [4-6]. The C10CeO₂ sample was used for experiments after fractionation by solvent. The average core diameters for sample nanoparticles measured by TEM were 5.8 nm [7]. Decane (>99%) was obtained from FUJIFILM Wako Pure Chemical Corporation. The reason for using decane is that the number of carbon atoms is equivalent to the the modifier chain of nanoparticles.

2.2. Thermogravimetric analysis

The C10CeO₂ nanoparticles were analyzed the stability of modifier chain of HNP by thermogravimetry (TGA-51, Shimadzu Corp.). The temperature program included a heating from room temperature to 120°C (10 °C/min), isothermal holding at 120°C for 10 min, and then a second heating from 120°C to 900°C (10 °C/min) due to the minimization of the effect of adsorbed water evaporation. A N₂-gas effluent 50 cm³/min was used to purge desorbed species.

The molecular weight of C10CeO₂ nanoparticles was estimated with the following Eqs. (1)-(3). The weight ratio of modifier shell to core particle in Eq. (3) was calculated with

the TG data for C10CeO₂ nanoparticles:

$$M_{\text{HNP}} = m_{\text{HNP}} \times N_A, \quad m_{\text{HNP}} = m_{\text{core}} + m_{\text{modifier}} \quad (1)$$

$$m_{\text{core}} = V_{\text{core}} \times d_{\text{core}} \quad (2)$$

$$m_{\text{modifier}}/m_{\text{core}} = \text{weight loss of modifiers} \quad (3)$$

Here m [g], d_{core} [g/cm³], M [g mol⁻¹] are the loaded C10CeO₂ weight, the density of pure CeO₂ (=7.215 g/cm³) at ambient conditions and the molar mass of pure CeO₂, respectively. In Eq. (2), V_{core} [nm³] (=102.2 nm³) is determined from the average diameter of the core CeO₂ particles obtained from the TEM measurement [7].

2.3. Density at atmospheric pressure

Densities of C10CeO₂ nanoparticles at atmospheric pressure were measured with a gas pycnometer (MICROTRAC MRB, BELPYCNO). A 12 mm ϕ pellet of the sample was molded at 5 MPa for 30 seconds after ground.

2.4. PVT measurements

The PVT behavior of decane and C10CeO₂ HNP were measured with a bellows type apparatus. The apparatus was originally developed by Sato *et al* [1] and consists of a bellows dilatometer, a pressure vessel, multiple temperature control sections, a hand pump, pressure gauges and a section for displacement measurement. In the PVT measurements of C10CeO₂ nanoparticles, the dilatometer was filled with mercury and the measuring cup in which 0.3640 g of sample was pushed into the cup. These operations were carried out under vacuum. For measuring the PVT of decane, the sample was introduced with pure mercury after degassing the inside of the dilatometer. Then, the dilatometer was loaded into the pressure vessel. The change of volume for the sample was obtained from the change of the bellows given by linear variable differential transformer (LVDT). For each sample, the measurements were performed in isothermal series at 40 K intervals with adopting 10 MPa increments up to 200 MPa. The maximum temperature was set to be 473 K above which the modifier shell (chain) decomposes thermally from the observation of preliminary TG experiments.

3. Correlation models

3.1. Tait Equation

The Tait equation, an empirical equation for representing incompressible materials PVT, is expressed as follows:

$$v(P, T) = v(P_0, T) \left[1 - C \ln \left\{ 1 + \frac{P}{B(T)} \right\} \right] \quad (4)$$

where T [K], P [Pa] and $v(P_0, T)$ [$\text{m}^3 \text{kg}^{-1}$] are temperature, pressure and specific volume at atmospheric pressure ($=0.1$ MPa) and temperature at T . The C [-] is a universal parameter given to be 0.08936 for all the hydrocarbons investigated, independent of compound or temperature [8]. For decane, NIST data at an ambient temperature and pressure condition (298.5 K and 101.3 kPa) was used as a standardized data, while the preliminarily-determined density data with the above-mentioned gas pycnometer method was used for the C10CeO₂ HNP. The density data at P_0 were extrapolated from PVT data with a cubic function.

The parameters included in Eq. (4) were expressed by the following exponential relationships, where constants were determined by minimizing the deviation in correlation of the experimental PVT data:

$$v(P_0, T) = a_0 \exp(a_1 T) \quad (5)$$

$$B(T) = b_0 \exp(b_1 T) \quad (6)$$

The objective function for the minimization is given by Eq. (7):

$$ARD[\%] = \frac{100}{N} \sum_{i=1}^N \frac{|v_{\text{calc},i} - v_{\text{exp},i}|}{v_{\text{exp},i}} \quad (7)$$

where ARD is the average relative deviation and N is the number of data.

The Tait equation was used to estimate derivative properties, the isobaric thermal expansivity α and the isothermal compressibility β from the following relationships:

$$\alpha = \frac{1}{v(P, T)} \left(\frac{\partial v(P, T)}{\partial T} \right) \quad (8)$$

$$\beta = -\frac{1}{v(P, T)} \left(\frac{\partial v(P, T)}{\partial P} \right) \quad (9)$$

3.2. Sanchez-Lacombe equation of state (SL-EoS)

The specific volume of C10CeO₂ nanoparticles was correlated with the Sanchez-Lacombe equation of state (SL EoS) [6, 7] that is expressed as follows:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r} \right) \tilde{\rho} \right] = 0 \quad (10)$$

$$\tilde{T} = \frac{T}{T^*}, \quad \tilde{P} = \frac{P}{P^*}, \quad \tilde{\rho} = \frac{\rho}{\rho^*} \quad (11)$$

$$T^* = \frac{\varepsilon^*}{R}, \quad P^* = \frac{RT^*}{v^*}, \quad r = \frac{MP^*}{RT^* \rho^*} \quad (12)$$

where T^* [K], P^* [MPa] and ρ^* [kg m^{-3}] are characteristic parameters of pure component. The ε^* [J mol^{-1}], r [-], M [kg mol^{-1}] and R [$\text{J mol}^{-1} \text{K}^{-1}$], v^* [$\text{m}^3 \text{mol}^{-1}$] are segment-segment energy, number of segments, molecular weight, universal gas constant and segment volume, respectively.

4. Results and Discussion

4.1. Thermogravimetry analysis (TG)

The weight loss (TG) of C10CeO₂ nanoparticles and its derivative (DTG) are presented in Figs. 1-2. A broad peak appears around 250°C to 600°C, which can be assigned as the thermal desorption (decomposition) of modifier shell (chain). The weight ratio of modifiers to core particles was determined to be 0.2042. From Eqs. (4)-(6), the molecular weights of both C10CeO₂ HNP and modifier shell of C10CeO₂ HNP were estimated to be 534.3 kg/mol and 90.6 kg/mol, respectively.

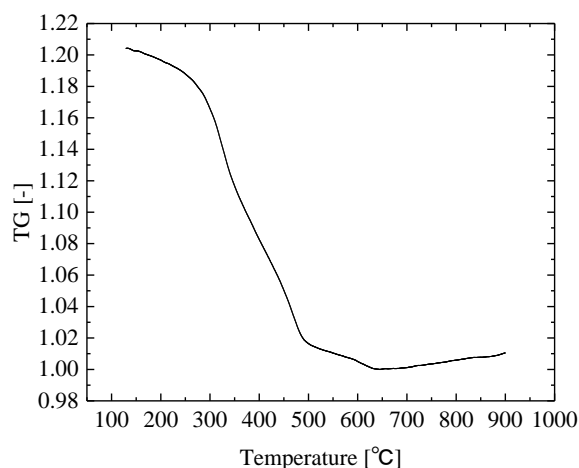


Fig. 1. TGA curves of C10CeO₂ HNP measured under N₂ atmosphere.

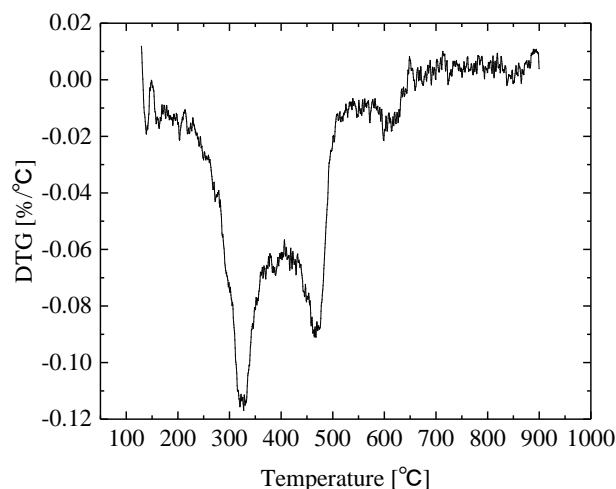


Fig. 2. DTG curves of C10CeO₂ HNP measured under N₂ atmosphere.

4.2. Specific volume of decane and C10CeO₂ HNP

The density of C10CeO₂ HNP at atmospheric pressure was determined as 3.039 g/cm³ from the gas pycnometer analysis. The measured densities of both decane and C10CeO₂ HNP are shown as a function of pressure for six isotherms (298-473 K) in Figs. 3-4. The obtained PVT data of decane was found to coincide with the NIST data (*ARD* = 0.220%). Figs. 3-4 clearly indicate that the specific volume increases with increasing temperature and decreasing pressure. It can be seen that the change rates with temperature/pressure for C10CeO₂ HNP are smaller than those for decane. It may be attributable that one end of the modifier chain in C10CeO₂ HNP was bound to the core particle, leading to the restriction of modifier chain movement on the particle and of the corresponding responses to temperature and pressure.

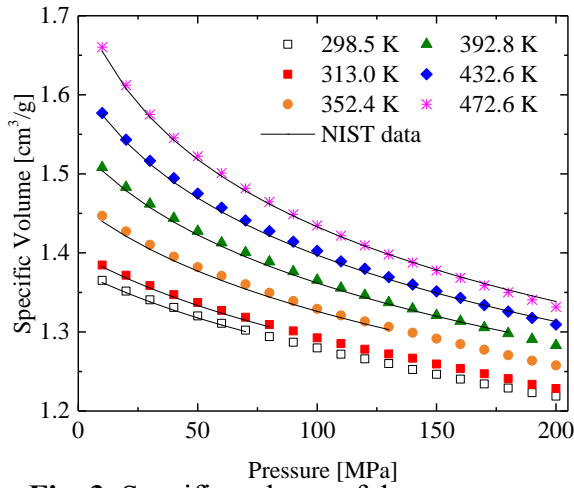


Fig. 3. Specific volume of decane versus pressure at various temperatures.

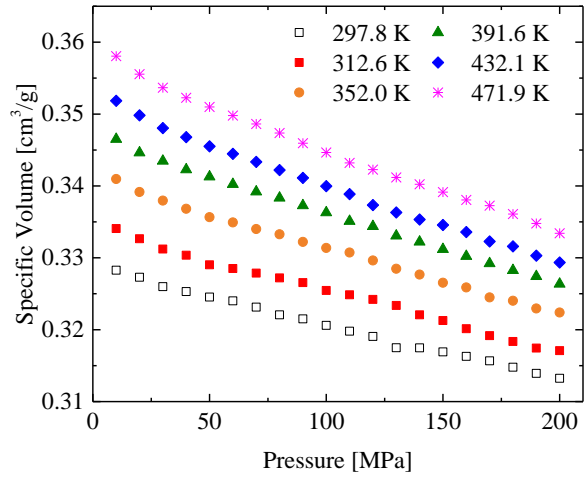


Fig. 4. Specific volume of C10CeO₂ HNP versus pressure at various temperatures.

The correlation results and determined parameters of the Tait equation are shown in Figs. 5-6 and Table 1. The specific volume at 0.1 MPa was extrapolated from the experimental values with the above-mentioned cubic function. The deviations for decane and C10CeO₂ HNP were small while those in the high temperature regions were larger.

Table 1 Tait equation parameters and average deviation (*ARD*) for decane and C10CeO₂ HNP determined by correlation with experimental specific volume at pressures up to 200 MPa.

Samples	$v(P_0, T)$		$B(T)$		ARD
	$a_0 \times 10^{-1}$ cm ³ /g	$a_1 \times 10^{-4}$ K ⁻¹	$b_0 \times 10^2$ MPa	$b_1 \times 10^{-3}$ K ⁻¹	
Decane	9.673	11.76	7.722	-7.470	0.2596
C10CeO ₂	2.873	4.793	6.884	-2.989	0.09358

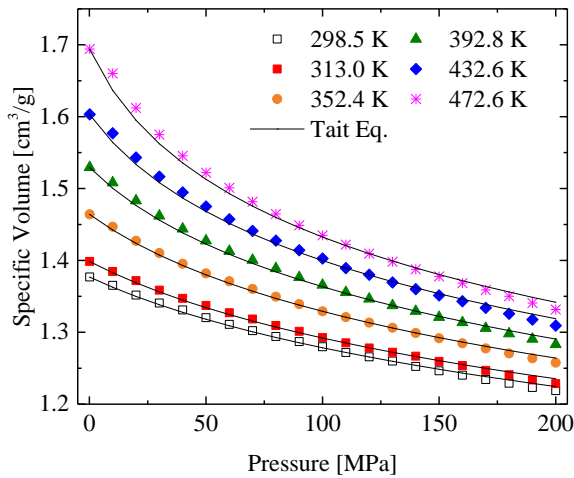


Fig. 5. Correlation with the Tait equation for specific volume of decane.

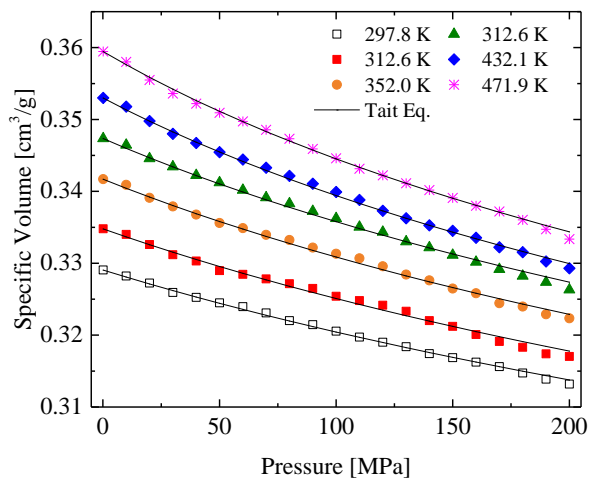


Fig. 6. Correlation with the Tait equation for specific volume of C10CeO₂ HNP

The derivative properties, isobaric expansivity α and isothermal compressibility β , were calculated from the Tait equation with Eqs. (8) and (9) and the fitted parameters in Table 1. Figs. 7 and 8 show the calculated results of α and β for (a) decane and (b) C10CeO₂ HNP. From these figures (Figs. 7 and 8), α decreased with increasing temperature and decreasing pressure, while β increased with increasing temperature and decreasing pressure. Comparing the behaviors of decane and C10CeO₂, it can be recognized that the amount of change for the C10CeO₂ HNP was smaller than that for the decane. This can be attributable to the above mentioned restriction of movement of modifier chain due to bounding its one end to the core particle.

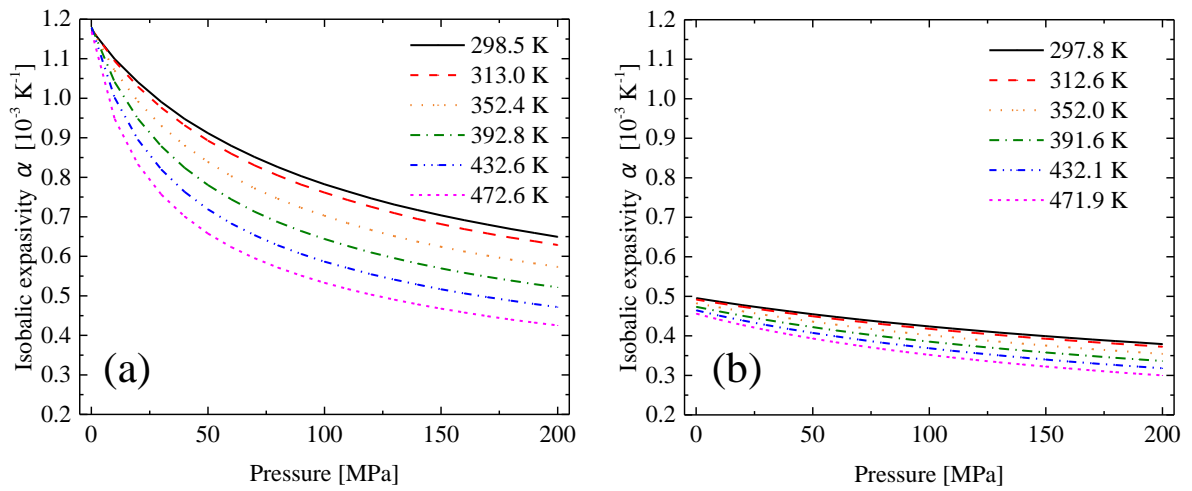


Fig. 7. Isobaric expansivity α of (a) decane and (b) C10CeO₂ HNP.

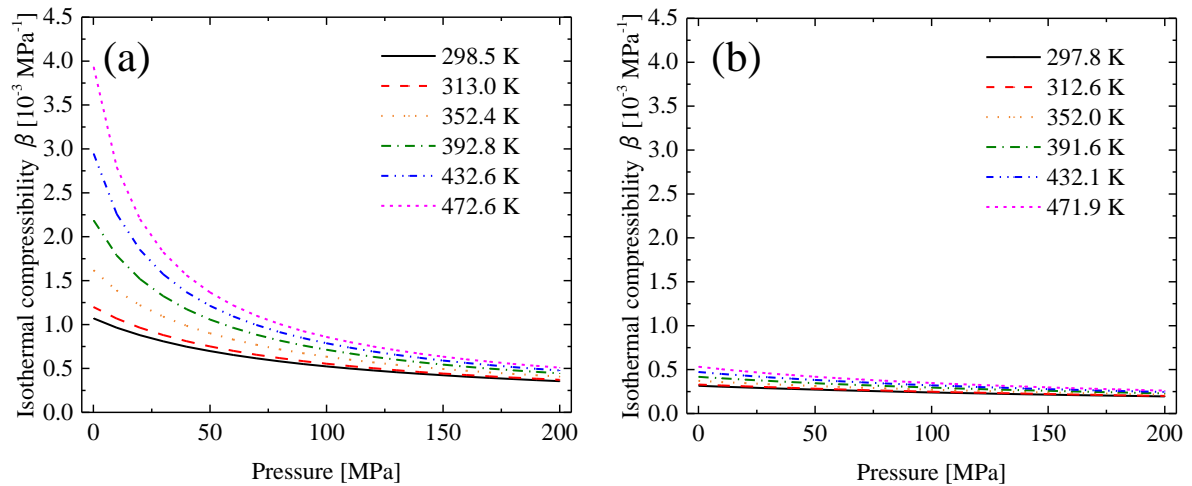


Fig. 8. Isothermal compressibility β of (a) decane and (b) C10CeO₂ HNP.

4.3. Correlation with Sanchez-Lacombe equation of state (SL-EoS)

The parameters in SL-EoS for a pseudomolecule of the C10CeO₂ HNP were determined by fitting to the experimental PVT data at temperatures from 297.8 to 471.9 K and pressures from 10.0 to 200 MPa. Table 2 presents the determined SL-EoS parameters and correlation results were shown in Fig. 9. Here it should be noted that the parameter values are strongly dependent on the number of segment r that was determined from the density data of HNP and core particle. This procedure might be a future research issue in modelling HNP as a pseudomolecule.

Fig. 10 shows the deviation between the experimental and calculated PVT values for the C10CeO₂ HNP. The maximum deviation was found to be within 2.00% in AARD. Although it would be noticed that the deviations are influenced by measurement uncertainty, the general trend can be pointed that the deviation increased with increasing pressure at low temperatures whereas the deviation become smaller at high temperatures.

Table 2 Characteristic parameters of the SL-EoS

T^* [K]	P^* [MPa]	ρ^* [kg/m ³]
698.4	531.2	3181
r	M [kg mol ⁻¹]	ARD [%]
15364	534.3	0.5507

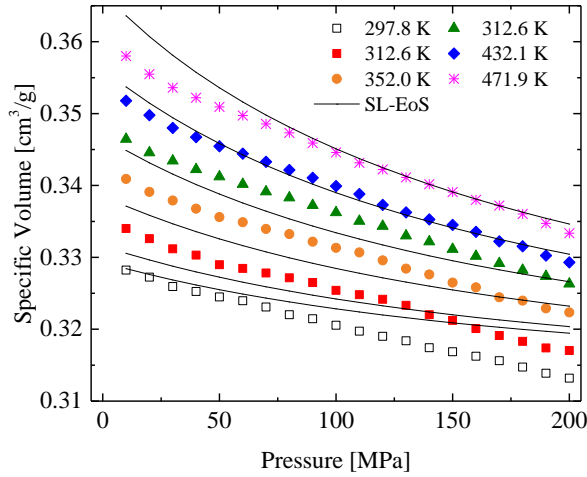


Fig. 9. Correlation of PVT data for C10CeO₂ HNP with the SL-EoS.

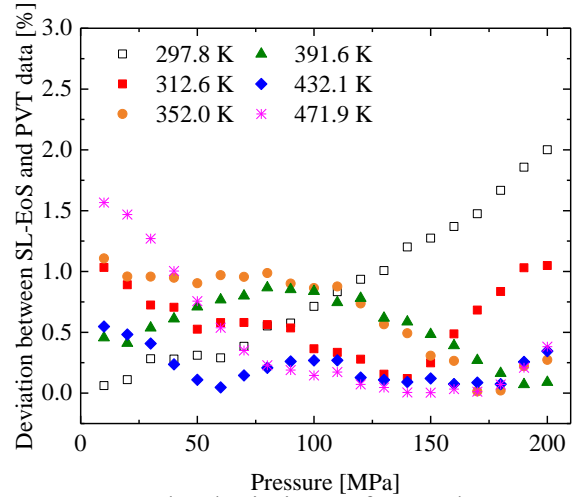


Fig. 10. The deviations of PVT data for the C10CeO₂ HNP.

5. Conclusions

The PVT for C10CeO₂ HNP (organic-inorganic hybrid nanoparticle) was measured with the bellows type apparatus at temperatures ranging from room temperature to 473 K and

pressures ranging from 10.0 MPa to 200 MPa. The obtained experimental PVT data were correlated with the Tait equation and the Sanchez-Lacombe equation of state. The PVT measurement data for the C10 CeO₂ HNP indicated that the specific volume increased with increasing temperature and decreasing pressure. The correlated with the SL-EoS determined the characteristic parameters of SL-EoS by assuming the HNP as a pseudomolecules and the density reflected the contributions of both core particles and surface modifiers.

This investigation suggests the importance of considering how the core particles are involved in surface modifiers. In future, PVT measurements using nanoparticles with different modified chain lengths should be examined to understand the relationship between the modifier shell and core particle to assign the adequate procedure of determining the parameters of the SL-EoS and of applying molecular thermodynamics for HNPs.

Symbols

a_0, a_1, b_0, b_1	constant for Tait equation
d, ρ	density [g cm^{-3}]
M	molecular weight [kg mol^{-1}]
m	weight [g]
N_A	avogadro constant
P	pressure [Pa]
\tilde{P}	reduced pressure
P_0	atmospheric pressure [Pa]
P^*	characteristic pressure for Sanchez-Lacombe EoS [Pa]
R	universal gas constant [$\text{J}/(\text{K} \cdot \text{mol})$]
r	number of segments [-]
T	temperature [K]
\tilde{T}	reduced temperature
T^*	characteristic temperature for Sanchez-Lacombe EoS [K]
V	pressure [$\text{cm}^3 \text{ g}^{-1}$]
v	specific volume [$\text{cm}^3 \text{ g}^{-1}$]
v^*	segment Characteristic volume for Sanchez-Lacombe EoS [$\text{m}^3 \text{ kg}^{-1}$]

Greek letters

α	isobaric thermal expansivity [K^{-1}]
β	isothermal compressibility [MPa^{-1}]
ε^*	segment-segment energy parameter for Sanchez-Lacombe EoS [J mol^{-1}]
$\tilde{\rho}$	reduced density
ρ^*	characteristic density parameter for Sanchez-Lacombe EoS [kg m^{-3}]

Subscripts

core	core particles
modifier	surface modifiers
HNP	organic-inorganic hybrid nanoparticles
<i>i</i>	component <i>i</i>

Reference

- [1] Y. Sato, Y. Yamazaki, S. Takishima, H. Masuoka, *J. Appl. Polym. Sci.*, **66**, 141 (1997)
- [2] J. H. Dymond, R. Malhotra, *Int. J. Thermophys.*, **9**, 941 (1988)
- [3] I. C. Sanchez and R. H. Lacombe, *J. Phys. Chem.*, **80**, 2352 (1976).
- [4] J. Zhang, S. Ohara, M. Umetsu, T. Naka, Y. Hatakeyama, T. Adschiri, *Adv. Mater.*, **19**, 203 (2007)
- [5] A. Yoko, G. Seong, T. Tomai, T. Adschiri, *KONA powder and Part. J.*, **37**, 28 (2020)
- [6] T. Adschiri, A. Yoko, *J. Supercrit. Fluids*, **134**, 167 (2018)
- [7] T. Tomai *et al.*, *J. Colloid Interface Sci.*, **587**, 574 (2021)
- [8] V. S. Nanda, R. Simha, *J. Chem. Phys.*, **41**, 1884 (1964)

Acknowledgement:

This work was supported by Process Science Project of MEXT, Grant Number JPMXP0219192801.