Development of a New Vibrating Tube Densimeter for PVT Measurements at High Temperatures

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ABSTRACT
We have developed a new vibrating tube densimeter by employing the laser doppler technique without using any permanent magnets that cannot avoid the weakening of the magnetic flux density at higher temperatures. Vibration stimulus was applied to the tube with a function generator via a piezoelectric actuator. A He-Ne laser vibrometer is used to detect the vibrating frequency of the tube, and FFT (Fast Fourier Transform) analyzer provides vibration frequency. This setup allowed for us to measure densities with a fairly good accuracy even at high temperatures and high pressures.

With the developed equipment, we have conducted the density measurement of methanol-water mixture at 673 K and 40 MPa with an accuracy of 0.009 g/cm³. The density data was analyzed to clarify the features of PVT behavior of this mixture and the solution structure of this mixture was discussed via molecular dynamics simulation results.

KEYWORDS:
PVT, Density, Vibrating tube, methanol-water, supercritical fluid, high temperature

INTRODUCTION
P-V-T relation is an important thermodynamic property for liquids/gases and especially for supercritical fluids studies that can vary their solvent properties in terms of density change by a slight change of temperature or pressure. For example, supercritical water has been used for hydrolysis of biomass, hydrothermal synthesis of metal oxides, and hydrogen production (Tylor et al., 2003). To tune the solvent properties, the precise densities has to be required, especially densities of mixtures at high temperatures and high pressure.

Vibrating tube densimeters are widely used for the P-V-T measurements because it is capable of continuous experiment and controlling the residence time of fluids in the tube. Various commercial vibrating tube densimeters based on the idea of Wood et al. (1984, 1989) have been available for precise density measurements, most of which adopt the permanent magnet to generate and detect the vibration frequency of the tube. However, it has been pointed out that the permanent magnet decreases its magnetic flux with increasing temperature and many researchers have tried to develop the vibrating tube densimeter. Majer et al. (1991) have developed a vibrating tube densimeter which used two permanent magnets to increase the magnetic flux at high temperatures. Chang et al. (1996) developed a vibrating densimeter which requires no additional attachment.
by alternating current and the densimeter didn’t require attachment of appendages to
the oscillating tube. Seitz et al. (1996, 1999) developed a custom made vibrating tube
densimeter capable of 500 C with magnetic coupling technique. Hynek and Cibulka et
al.(1996,2001) have built a new flow vibrating-tube densimeter with a photoelectric
pick-up system and a new concept of an electromagnetic drive system for high
temperature and pressure conditions. Even if using these apparatus mentioned above, it
can be said that it has been difficult to perform accurate measurements at high
temperatures and pressures.

In this work, we developed a new vibrating tube densimeter without using any
permanent magnets that is able to measure at high temperatures and high pressures.
The vibration was generated by a function generator and its stimulus was transferred to
a tube that was originally designed to enhance the intrinsic vibration via a
piezoelectric actuator. The vibration frequency was detected by a He-Ne laser doppler
vibrometer with FFT analyzing technique. For high temperature measurements, some
ideas were worked out to minimize the temperature profile in a thermostat and to
detect the vibration frequencies stably. The capability of this apparatus at high
temperature was demonstrated for density measurement of methanol-water mixtures at
high temperature and high pressure were measured by using developed vibrating tube
densimeter.

EXPERIMENTAL

Basic principle of vibrating tube
densimeter

A vibration frequency of an oscillator
depends on the weight of the oscillator. On a
vibrating tube densimeter, the relationship
between the frequency and the weight is
applied to determine the density. Thus, the
fluid density ($\rho$) in a tube can be determined
from the frequency of the tube ($f$) using the
following equation (Eq. 1):

$$\rho - \rho_0 = K(T,P) \left( \frac{1}{f^2} - \frac{1}{f_0^2} \right)$$  \hspace{1cm} (1)

where $\rho_0$ is the density of a reference fluid, $f_0$ is the vibration frequency of the tube
when a reference fluid is in the tube and $K(T,P)$ is an apparatus constant, which is a
function of temperature and pressure. The $K(T,P)$ is decided from the frequencies of
two reference fluids of which densities at the temperature and the pressure is known.

Apparatus

The vibrating tube is shown in Figure 1. The tube was Inconel 600 (or SUS316L)
and the size was 3.2mm o.d. and 0.8mm i.d. The vibrating tube was consisted of a
measurement part (U shape part) and a spring part (S shape) as shown in Figure 1.

Figure 2 shows the schematic diagram of the apparatus of densimeter. The apparatus
was mainly consisted of two syringe pumps (ISCO: 100 DX), preheating unit (2m
length), measurement unit, cooling unit, vibration generation unit and frequency
detection unit. Vibration generation unit was made up of a piezoelectric actuator
(NEC TOKIN Corp.: ASB170C801NP0) and a function generator (Hewlett Packard:
33120A). Frequency detection unit had a laser doppler vibrometer (ONO SOKKI
Corp.: LV1300) and a FFT analyzer (ONO SOKKI Corp.: CF5120). The frequency was evaluated from the doppler shift of laser measured. The laser used in this study was He-Ne laser (wavelength: 632.8 nm). For high precision measurement at high temperatures, a quartz light-guide was attached on the laser light path to reduce the scattering due to air convection. The temperatures of the units were monitored using K-type thermocouples (Suigawa Electric Industry Corp.), and controlled separately to minimize the temperature difference of the two thermocouples by PID controller. The inlet ($T_1$) and outlet ($T_2$) temperature of U-tube were measured and also controlled to minimize these temperature differences. The measurement temperature of the density was adopted as a mean value of $T_1$ and $T_2$.

![Figure 2 The schematic of the experimental apparatus](image)

**Procedures**

A pump delivered fluids to the vibrating tube with a constant flow rate. Simultaneously another pump received the fluids by withdrawing the syringe to keep a constant pressure. These two pumps were systematically controlled. H$_2$O, CH$_3$OH and these mixtures were degassed before delivering to the vibrating tube through degassing units (GL Sciences Inc.: DG660-3).

The sine-wave from low to high frequencies was generated by the function generator and transmitted to the piezoelectric actuator. The electric signal was converted into the mechanical signal (vibration stimulus) by the piezoelectric actuator. The stimulus was conducted to the U-type tube by the piezoelectric actuator through a transmission bar and the free oscillation of the tube was occurred. When the oscillation resonates with the stimulus from the piezoelectric actuator, the amplitude of the tube is strengthened. The He-Ne laser was irradiated to the measurement spot of the vibrating tube from the laser doppler vibrometer. The doppler shift between the irradiation and scatter of the laser was measured. Fast Fourier Transform (FFT) was applied to convert the shift to the velocity signal, and the proper vibration frequency of the tube was provided as spectra (shown in Figure 3).

The density resolutions were defined by using Eq. (2).

\[
\text{Measurement Resolution} = \left( \frac{\Delta \rho}{\Delta f} \right) \times f_{\text{FFT}}
\]  

(2)

where $\Delta \rho$ is the density difference of two reference fluids, $\Delta f$ is the difference of two
detected frequencies of the reference fluids and $f_{\text{FFT}}$ is the frequency resolution on a FFT analyzer. Since the spectra were expressed from 800 dots on display at any frequency range, the value of $f_{\text{FFT}}$ was determined by the following equation (Eq. 3).

In this work, the frequency range of the FFT analyzer was 20 Hz, and the value of $f_{\text{FFT}}$ was calculated to 0.025 Hz.

$$f_{\text{FFT}} = \frac{\text{scanning frequency range}}{800 \text{ channels}} \quad (3)$$

The temperatures ($T_1$ and $T_2$) and the pressure were monitored by using a data acquisition unit (Hewlett Packard: 34970A) on a GP-IB Instrument. Temperature, pressure, and the frequency of the tube were scanned continuously by a personal computer at 45 seconds interval.

HPLC grade water (H$_2$O) and methanol (CH$_3$OH: purity > 99.7%) were obtained from Wako Pure Chemical Corp. and used without further purification. High purity N$_2$ (purity > 99.99%) and CO$_2$ (purity > 99.9%) were used as reference fluid. CH$_3$OH-H$_2$O mixtures were prepared by weighing technique and the molar fraction of CH$_3$OH ($X_M$) was confirmed by TCD Gas Chromatograph (HITACHI Ltd.: HITACHI 163). Measurement temperature was ~ 673 K and measurement pressure was ~ 40 MPa.

**MOLECULAR DYNAMICS SIMULATIONS**

The potentials used in this work were 3-sites flexible models for both methanol (Honma et al., 2003) and H$_2$O (Liew et al., 1998). The 3-sites for methanol are oxygen (O), hydrogen (H) and methyl (-CH$_3$). Both flexible models can be represented as a sum of intra- and inter-molecular potentials. The intra-molecular potential used the angular form of Toukan-Rahman (TR) potential (Toukan and Rahman, 1985). The inter-molecular potentials were a Lennard-Jones (LJ) 12-6 potential and a Coulombic potential.

All simulations were performed for the NVT-ensembles of 500 molecules at 50°C and 11 MPa for several methanol mole fractions.

To explore the solution structure of methanol-water system at higher temperatures in terms of intermolecular interaction, the potential mean forces (PMF) about a methanol and a water molecule have been evaluated.

**RESULTS AND DISCUSSION**

Table 1 shows the densities of CH$_3$OH and CH$_3$OH-H$_2$O mixture measured in this work and those of literature values. Measurement temperature was 423 K and pressure was 7 MPa and 10 MPa. It could be noted that each of the measured densities in this work agreed with the literature data well. The error was estimated to be 0.004 ~ 0.008 g/cm$^3$. 

![detected frequency spectrum](image-url)
Figure 4 shows the time profiles of the temperatures ($T_1$ and $T_2$) and the pressure of H$_2$O at 40 MPa and 673 K. It could be noted that both temperatures, $T_1$ and $T_2$, were controlled within ±0.5 K by using the divided air bath and pressure was controlled within ±0.05 MPa by using two syringe pumps. In addition, the detected vibration frequencies of H$_2$O at 40 MPa and 673 K in the total measurement time were shown in Figure 5 as histogram. It could be noted that the vibration frequencies were detected stably at high temperatures by attaching the quartz light-guide.

The apparatus constant, $K(T,P)$, was determined using the frequencies of the reference fluids. Figure 6 shows the plots for determined $K(T,P)$ at 673 K and 40 MPa. Here H$_2$O, N$_2$ and CO$_2$ were used as the reference fluids. The density of H$_2$O was calculated by using Wagner’s equation of state and the densities of N$_2$ and CO$_2$ at the condition were obtained from PROPATH. From the slope of the line in Figure 5, $K(T,P)$ at 673 K and 40 MPa was $1.732 \times 10^6$ [g/(cm$^3 \cdot $s$^2$)]. The density resolution at the condition was 0.089 [g/cm$^3$].

Measured densities of CH$_3$OH-H$_2$O mixtures at 40 MPa and 673 K were shown in Figure 7. The densities shifted from mole fraction average (dashed line) of CH$_3$OH and H$_2$O. This indicated significant non-ideality in the mixing properties of CH$_3$OH-H$_2$O mixtures at high temperatures and high pressures.
Figure 5  Histogram of detected frequencies (H₂O at 40MPa, 673K)

Figure 6  Calibration plots for determining $K(T,P)$

Figure 7  Densities of CH₃OH-H₂O mixtures at 40 MPa and 673 K
The trend of density data in Fig. 7 indicates the large excess volume for this mixture at the condition studied, which means that the methanol-water mixture behaves like a repulsive mixture. It is well known that methanol and water have high affinity each other at ambient temperatures, namely an attractive mixture. However, the results obtained in this work suggested that supercritical condition brings about this attractive mixture to repulsive one. This might result from the balance change between the repulsive force due to high kinetic energy at high temperature and the attractive interactions; mainly hydrogen bonds for methanol-methanol, methanol-water, and water-water pairs. Focusing on the composition dependence of the density data, the whole composition range could be divided into two regions; one is $0<X_m<0.3$, and the other $0.3<X_m<1.0$. The former may correspond to the mixture of methanol molecules as a solute in solvent water, and the latter is that of water molecules as a solute in solvent methanol. To discuss these insights, the solution structures of this mixtures was studied via MD simulation in terms of molecular interaction especially hydrogen bonds.

Figure 8 shows the typical snapshots of the mixtures of $X_m=0.9$ and 0.05. These compositions correspond to water containing small amount of methanol molecules, and methanol containing small amount of water molecules. It can be seen in the snapshots that there are density fluctuations and some cavities exist in the solutions. The detail study indicates that a cavity is found around a solute molecule, leading to the induction of repulsive force by a solute molecule. To elucidate the molecular interactions in the presence of solute molecules, the potential mean force (PMF) was calculated directly for a molecule as a sum of interaction force from the environmental molecules. Figure 9 shows the plots of the calculated PMF against the molecular distance. Although the PMF functions for both methanol and water are negative, namely attractive force, it would be noted that their magnitude for water is larger than that for methanol, indicating stronger interaction for water-water than methanol-methanol. In other words, a water molecule may feel a methanol molecule as a relatively repulsive one in comparison with other water molecules.

![Figure 8 Snapshots of MD simulation for methanol-water mixture at 40 MPa and 673 K.](image)
For considering the total interaction force in the solution at both liquid and supercritical states, we evaluated the average potential force as a composition average of the PMF of methanol and water.

\[
PMF(r)_{\text{mix}} = PMF(r)_{H_2O} \cdot (1 - X_m) + PMF(r)_{CH_3OH} \cdot X_m
\]  

(4)

It was revealed that the PMF\(_{\text{mix}}\) in the liquid state are generally much larger negative than those in the supercritical state, which means the high kinetic energy weakening the intermolecular attractive force in the solution. To quantitatively clarify this discussion, the minima of the PMF\(_{\text{mix}}\) were plotted against the composition in shown Figure 10. The obtained trend for the supercritical solution is found to be similar to that of density in Figure 7 whereas the liquid state exhibited opposite trend. The convex trend means that the mixing is not energetically stable, resulting in the repulsive mixing properties as shown in Figure 7.

Figure 9  Potential Mean Force around a methanol or a water molecules

Figure 10  Plots of PMF minima against the composition, \(X_m\)
CONCLUSION

In this paper, we developed a new vibrating tube densimeter without using any permanent magnets. The vibration in our equipment was generated by the function generator and its stimulus was transferred to the U-type tube that was originally designed to enhance the intrinsic vibration for having highly accurate detection. The vibration frequency was calculated from the He-Ne laser doppler shift via FFT analyzing technique. For high temperature measurements, the air bath was divided into two zones to have stable temperature control and the quartz light-guide was attached on the laser light path to reduce the light scattering due to air convection. The density resolution at 40 MPa and 673 K was determined to 0.0089 [g/cm³] and demonstrated for the methanol-water mixtures. The measured density data for the mixture at 40 MPa and 673 K showed highly non-ideal behavior with large excess volume, which were discussed in terms of molecular interactions by use of molecular dynamics simulations.

REFERENCES

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