High Pressure Vibrating Tube Densimeter의 보정과 Dimethyl ether의 밀도 측정에 관한 연구

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Calibration of the High Pressure Vibrating Tube Densimeter and Measurements of Compressed Liquid Densities of Dimethyl Ether

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1. Introduction

Reliable knowledge of the P-ρ-T behavior of pure compounds and mixtures is great important in many fields of research as well as in industrial practice. The densities of fluids as a function of temperature and pressure are particularly important for the design of industrial plants, pipelines and pumps.

Dimethyl ether (DME) is of used for various substances like an aerosol propellant, assistant solvent, fuel additive, and liquefied petroleum gas substitute. Especially, recent investigations of clean alternative fuels have shown that DME and its mixtures have excellent properties as diesel fuels and have a promising future as a replacement for fuels obtained from fossil reserves. The thermophysical properties of DME, however, are insufficient

for these applications, besides the density of DME in high pressure is not yet reported. So we measured the density of compressed liquid DME using Anton Paar DMA 512P vibrating tube densimeter at temperatures from 313.15 to 353.15 K and pressures up to 300 bar. The vibrating tube densimeter is calibrated by nitrogen and water as the reference fluids.

2. Theory

The general principle of the vibrating tube densimeter is quite simple. The density of the sample is determined by measuring the period of oscillation of the vibrating tube. The frequency(f) is defined by Eq. (1).

$$f=\frac{1}{2\pi}\sqrt{\frac{C}{M_u+\rho V_u}} \tag{1}$$

The period of the oscillation(λ) is:

$$\lambda=\frac{1}{f}=2\pi\frac{\sqrt{M_u+\rho V_u}}{C} \tag{2}$$

The sample's density ρ can therefore be deduced from the measurement of λ:

$$\rho(T,P)=A(T,P)\,\lambda^2+B(T,P) \tag{3}$$

with

$$A(T,P)=\frac{C(T,P)}{4\pi V_u(T,P)},\quad B(T,P)=\frac{M_u}{V_u(T,P)} \tag{4}$$

Where M_u is the mass of tube, V_u is an internal volume of tube for a given temperature−pressure set and C is elasticity constant.

It needs the reference fluids which are comparatively high dense substance and low dense substance to calibrate the densimeter among the density of substance well known. Water and nitrogen are used generally.

The following relationship between periods of oscillation and density is valid.

$$\rho(T,P) = \rho_w(T,P) + \frac{1}{A(T,P)}[\lambda^2(T,P) - \lambda_w^2(T,P)] \quad (5)$$

$$\frac{1}{A(T,P)} = \frac{\rho_w(T,P) - \rho_N(T,P)}{\lambda_w^2(T,P) - \lambda_N^2(T,P)}$$

Where ρ and λ are the density and the oscillating periods of sample, respectively[1,2].

3. Experiment

Materials. Water (HPLC grade) was purchased from J.T.Baker Inc. and degassed before use. Carbon dioxide (min. 99.99%) and nitrogen (min. 99.999%) were purchased from Korea industrial gases. Water and nitrogen were used as calibrating fluids for the density measurement. DME (min. 99.999%) was provided by LG Chem..

Experimental Method. Fig. 1 shows a schematic diagram of the experimental cell that is a special type for density measurement under high pressure (up to 700 bar) and temperature (up to 420 K) and its peripheral equipment.

The periods of oscillation of samples were studied with following experimental procedures. The cell and U-shaped tube were initially made of vacuum condition to remove air and filled with samples using a hand pump (High pressure Equipment Co., model 62-6-10). The densimeter set up of the experimental condition (pressure and temperature) and then measured oscillating periods at equilibrium.

4. Results and discussion

Calibration. For calibration of the our apparatus, water and nitrogen were measured along five isotherms between 313.15 and 353.15 K at

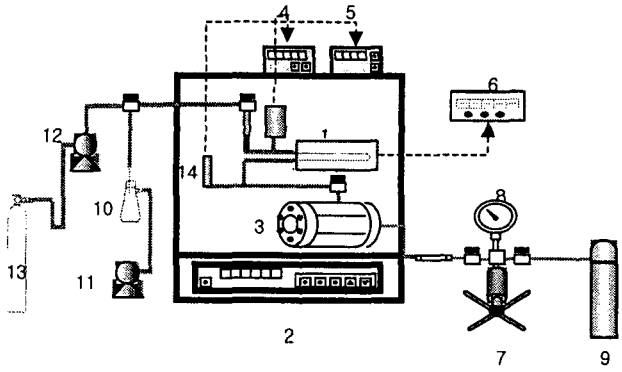

Figure 1. Schematic diagram of the experimental apparatus: (1) U-tube; (2) Air bath; (3) View cell; (4) Digital pressure transducer; (5) Digital thermometer; (6) U-tube indicator; (7) Hand pump; (8) Pressure gauge; (9) Water or Nitrogen bomb; (10) Trap; (11) Vacuum pump; (12) Gas booster; (13) CO_2 bomb; (14) fast response PRT.

10 K intervals and pressures up to 300 bar at 50 bar intervals. Fig.2 is experimental results for water and nitrogen. As shown in Fig. 2 oscillating periods are plotted against pressure. In the case of water, the plots give straight lines.

Density of CO_2 To test the validity of our new apparatus and this

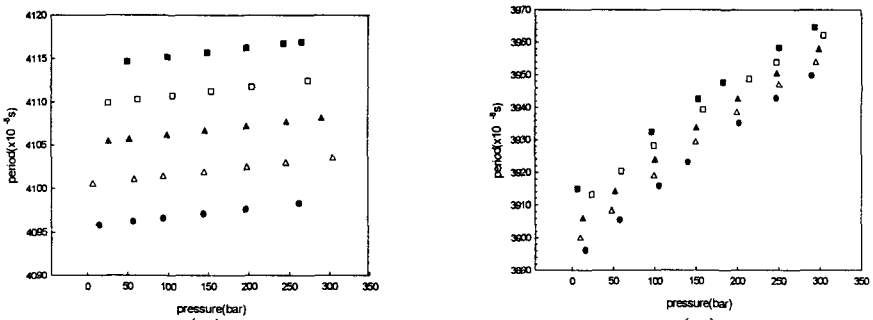

Figure 2. Experimental oscillating period of (a)water and (b)nitrogen; •, 313.25 K; △, 323.15 K; ▲, 333.15 K; □, 343.15 K; ■, 353.15K.

calibration method we compared the values obtained by measuring density of carbon dioxide with those given by the National Institute of Standards and Technology(NIST).

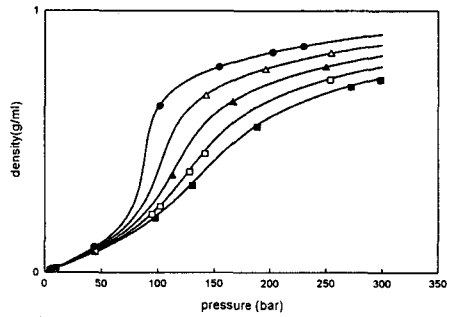

Figure 3. The density of carbon dioxide; •, 313.25 K; △, 323.15 K; ▲, 333.15 K; □, 343.15 K; ■, 353.15K.

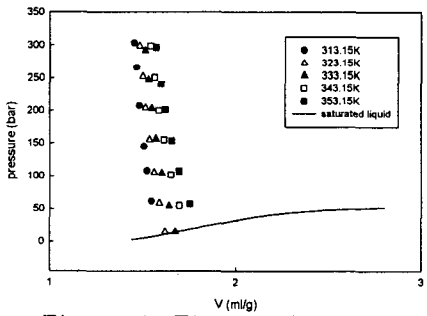

Figure 4. The density of DME.

The results are represented in Fig. 3. The symbols correspond to the values that we measured using equation (5) and the solid lines to the values given in the NIST. The results show good agreement.

Density of DME The oscillating periods of DME were measured a total of 30 points at 5 isotherms in the range between 313.15 and 353.15 K, for 6 pressures per isotherm ranging up to 300 bar in compressed liquid phase. The densities of DME were determined by equation (5). Fig. 4 represents this results. The range of densities is from 0.572 to

0.689 g/mL. Saturated liquid points are reported by Jiangtao Wu et al [3].

5. Conclusions

From this study we calibrated vibrating tube densimeter by nitrogen and water as the reference fluids and verified our new apparatus and calibration method as we measured the densities of CO_2 and showed the differences between the our experimental results and the ones reported by NIST. And then we measured the densities of DME at temperatures from 313.15 to 353.15 K and pressures up to 300 bar.

6. References

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3. Jiangtao Wu et al., "Measurement of the critical parameters and the saturation densities of dimethyl ether", *Journal of Chemical Engineering Data*, 49, 704-708, (2004)