Spinodal Line Measurements of Water

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INTRODUCTION

One of the experimental methods of critical point determination is darkening of scattering light through windows. For a pure substance, it is well known that a critical point satisfies $(\partial P / \partial \rho)_T = 0$ due to density fluctuation. The same mathematical condition should be applied to spinodal lines which are the stability limit of metastable region. At present, we have no information on spinodal line measurement. Indeed, through windows of a static cell, we cannot observe darken windows due to light scattering. However, when we used a continuous flow apparatus for vapor-liquid equilibrium measurement, we found that water showed two opaque points[1]. If our observation means spinodal points, it will contribute to develop an equation of state.

EXPERIMENTAL

Apparatus and Procedure

Fig.1 shows experimental apparatus.

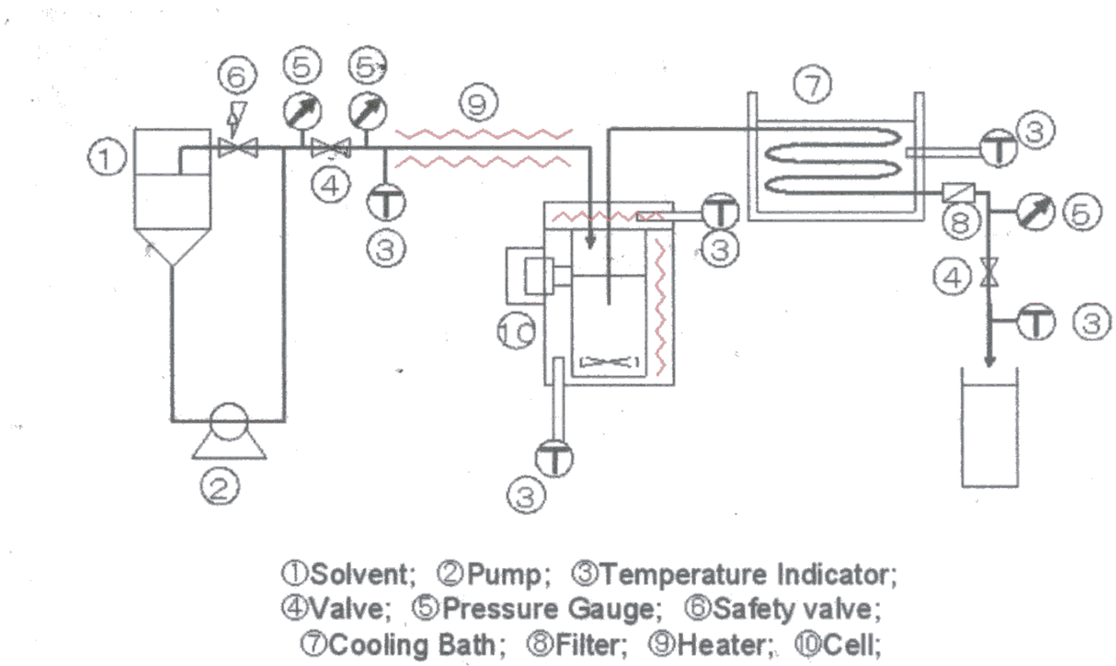

Fig.1 Experimental continuous flow apparatus

Distilled water in a tank (1) flows at 40ml/min with a pump (2) and preheated with heater (9). The critical temperature of water is 374 °C and the critical pressure is 22.12MPa and pressure in set over the critical pressure with valve (4). Reaching the supercritical state, the heater was shut down. Temperature is naturally cooling. Pressure is controlled with a valve (4). Finding an opaque state through a cell window, we recorded the value of temperature and pressure.

Experimental Results

Through windows of a static cell, we cannot observe darken windows due to light scattering. However, when we used a continuous above mentioned flow apparatus for vapor-liquid equilibrium measurement, we found that water showed two opaque points at a temperature ranging from 570 K to the critical temperature and higher temperature opaque points than the vapor pressure line down to 430K and 5 MPa shown in blue points. Several times experiments revealed excellent reproducibility. Measured spinodal point pressure was higher and a little bit lower than that from the Peng-Robinson equation of state. So it suggests that experimental results will contribute the development of a novel equation of state.

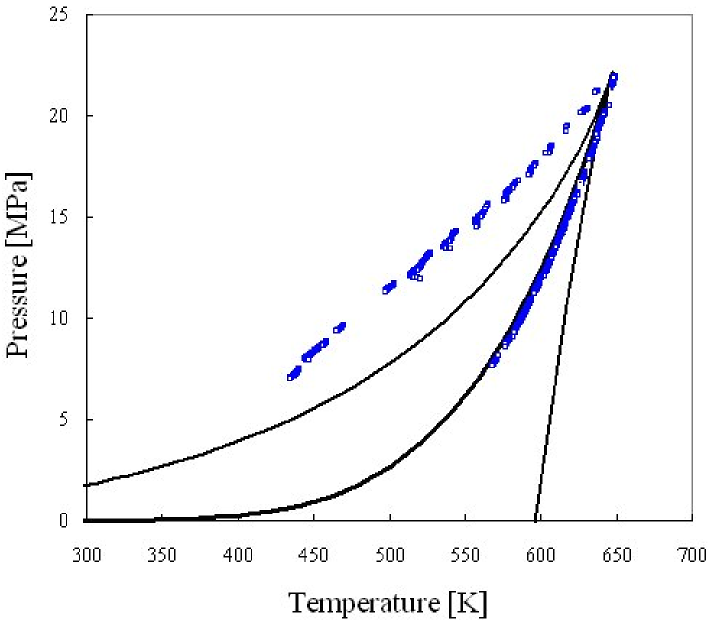

Fig.2. Experimental results. Blue plots : experimental spinodal points, Bold line: binodal line, two solid lines: spinodal curves calculated with Peng-Robinson EOS.

DISCUSSION

Metastable

Fig.3 shows a P-ρ diagram of a pure substance. We can see a spinodal curve below critical temperature Tc. At a temperature T_1, pressure increases from R to A with density in Fig.3. A material shows two ways of traces from A. The first trace goes along AD and has a property of stable vapor by saturation. Curves produced changing temperature is called binodal lines. The second trace goes along AB and has a property of supersaturated vapor and disappears at a spinodal point of B. Pressure decrease from S, density reached D. A material shows two ways of traces from D same as time of steam. The first trace goes along DA and has a stable liquid property. Similarly the trace along DC has a property of superheated liquid droplet and disappears at a spinodal point of C. The area enclosed by spinodal curve and binodal curve is called metastable state.

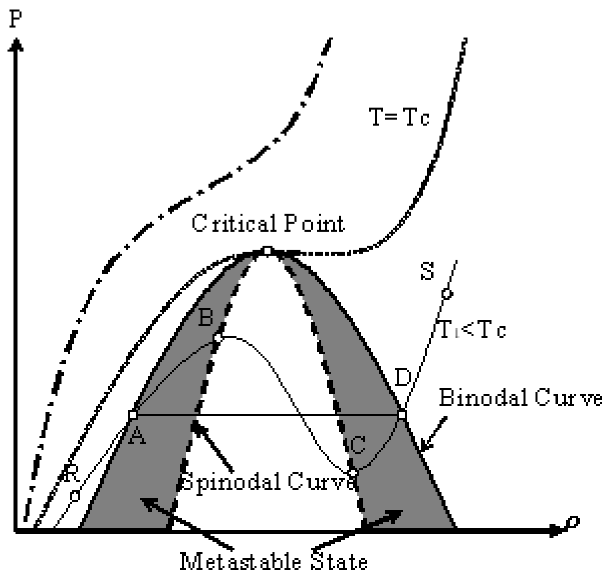

Fig.3 Pressure vs. Density of pure substance

Spinodal Lines

If our observation means spinodal points, the lower pressure spinodal line is just a little lower and the higher one is a few MPa higher than the vapor pressure line of water. It suggests that a curve of an equation of state will be strongly asymmetric in the metastable region. We cannot measure density in our experiment. However, based on equal area principle for phase equilibrium, Fig. 4, for example, can be drawn in comparison with the Peng-Robinson EOS calculations. We believe that our spinodal measurement will develop an equation of state.

CONCLUSION

Using a continuous flow apparatus for supercritical fluids, we found that water had two opaque points at a temperature ranging from 570K to the critical temperature. We believe a strong possibility that the spinodal points of water were measured. It will contribute the development of a novel equation of state. Measured spinodal point pressure was higher than that from the Peng-Robinson equation of state. At vapor-liquid phase equilibrium, an equation of state should satisfy both vapor and liquid phase densities and also equal areas on the border of a vapor pressure. In addition to these conditions, a novel equation of state should pass through the measured two spinodal pressures, i.e., higher and a little lower pressures than the vapor pressure at a fixed temperature whose densities are unknown and inside of a binodal. According to the above conditions, we guess that a novel equation of state features a dash-dot line in the figure. A low density side line is sharp and narrow and a high density side line is shallow and wide.

REFERENCE

１）H.Nishiumi, K.Yamada,”Spinodal Curve Measurements of Pure Substance”,MTMS2006, Chiba, Japan (2006)

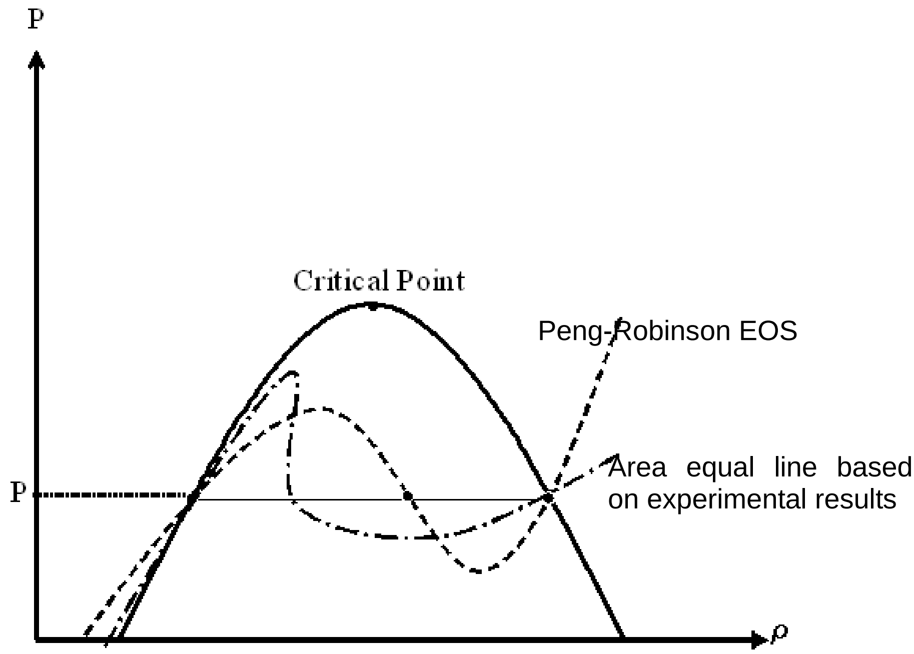

Fig.4 Comparison of the calculated results from Peng-Robinson equation of state (dash-dot line) and experimental results (dot line)