The Development of Novel Methodology for Observing Discontinuous Behaviour of Density of Compresses Gases by Light Scattering

Tetsuo Aida, Shinya Fujiwara, and Toyokazu Shinkai ,*
Department of Biological & Environmental Chemistry,
School of Humanity-oriented Science & Engineering, Kinki University
JAPAN

Summery

A novel methodology for determining the discontinuous behavior of density of compressed gases has been developed based on light scattering method. This method is capable to quantitatively evaluate the degree of heterogeneity of the density of compressed gasses, carbon dioxide, ethane, ethylene or even their mixed gases, on its pulse pattern of UV or visible light scattering, and to determine the precise temperature and pressure conditions. In the case of carbon dioxide, the muximum amplitude of obsorbance was observed at 7.36MPa, indicating its maximum heterogeneity. Also, a maximum of molar polarization has been observed at the same conditions using our dielectric property measurement equipment for determining molecular association, of which detailed experimental data also present at the poster session of this conference.

ntroduction

Although it has long been expected a very attractive supercritical fluid industrial technology in the field of organic synthesis, there seems to be still no clear establishment for that. Since 1987, we have conducted a series of research project[1)] to develop an efficient chemical process using a supercritical carbon dioxide, and are noticing that the characteristic behaviour of supercritical fluid to the chemical reaction could be induced in the very restricted region of density, so-called "*miracle density*" [2)] near the critical point, as shown in Figure 1.

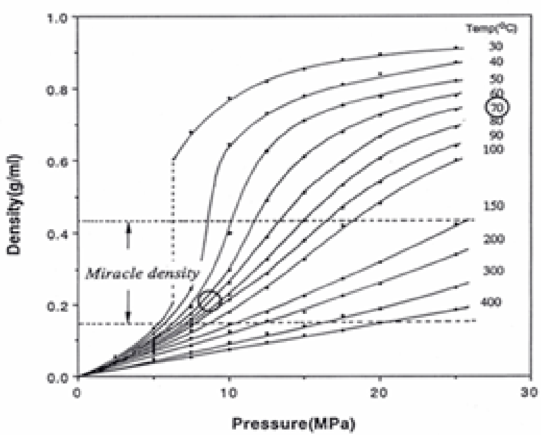

Figure 1 Relation between pressure and density of CO_2

Actually, there seemed to be a general understanding that the most strongest abnormality of supercritical fluid for the chemical reaction must be generated under the reaction condition which the density of the solution with the compressed gas exhibits a maximum discontinuous behaviour used to observed as a characteristic light scattering, so-called "*critical opalescence*", based on the strong molecular association.

In order to determine the precise reaction condition, i.e., temperature, pressure and concentration of reactants, that will induce the "*critical opalescence*" of the supercritical carbon dioxide solution, we have developed a novel methodology which can be quantitatively evaluate the degree of heterogeneity of the density of compressed gasses, carbon dioxide, ethane, ethylene or even their mixed gases, on its pulse pattern of UV or visible light scattering.

In this paper, we will present detailed information of our new instrumentation with experimental data, and discuss potential research projects.

Experimental

The principle of this methodology is demonstrating in Figure 2. Namely, the discontinuous behavior of density of compressed gases can be evaluated as a degree of absorbance of light resulted by the light scattering through the photometric cell.

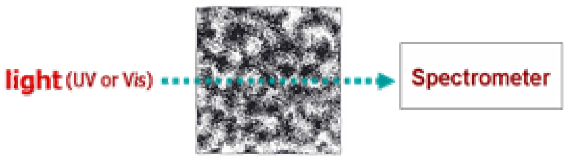

Figure 2 Principle of methodology

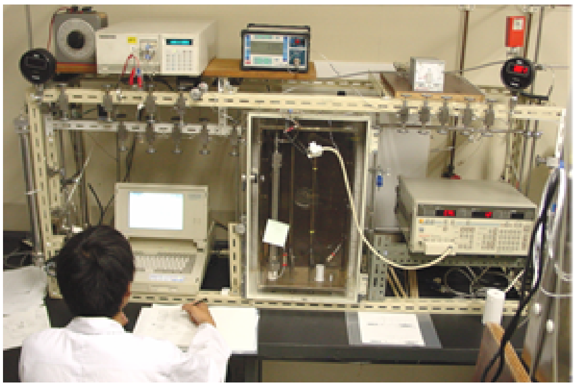

Figure 3 Over view of instrumentation

In Figure 3, the over view of the instrumentation shown, that is composed by a compressor and a spectrometer equipped with specially designed photometric cell, of which pressure can be precisely controlled in the range of 0.005MPa.

In the Figure 4, a typical example of the measurement is demonstrated that was performed by using carbon dioxide. The muximum amplitude of obsorbance is appeared at 7.36Mpa suggesting its maximum heterogeneity of the density.

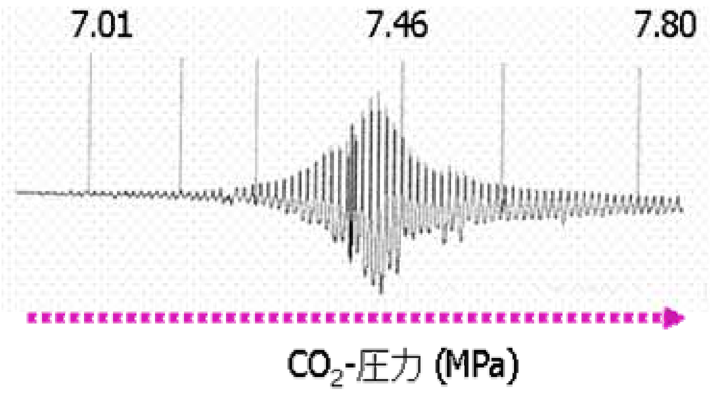

Figure 4 Example of spectrum for measuring light scattering of CO2

Results and Disscussion

Figure 5 is demonstrating the discontinuous behavior of density of compressed carbon dioxide under various temperature conditions measured by this method. The amplitude of absorbance was determind on the redording chart as shown in Figure 4, and plotted with the the pressure of carbon dioxide.

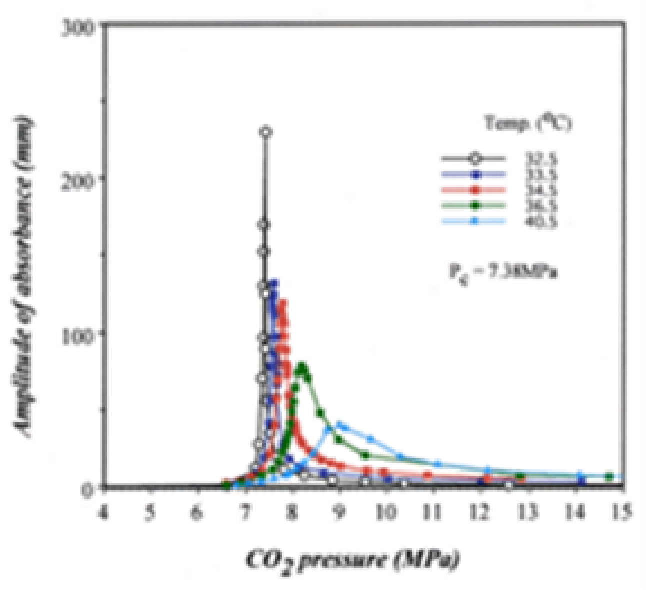

Figure 5 Pressure and temperature dependence on light scattering of CO_2

There are several interesting features in this Figure. The first of all, a very sharp peak of the light scattering was observed around the critical pressure 7.38Mpa of carbon dioxide, meanwhile almost no amplitude was observed in the lower pressure and higher pressure range spressure than that. This is exactly identical behaviour of "*critical opalescence"* which is expected to be induced near the critical point. The second of all, the absolute value of the amplitude was decreasing as higher temperature condition. At the same time, the peak was shifted to higher pressure region. All of these phenomena seem to suggest that the very strong molecular association of carbon dioxide is taking place.

If it is true, a very serious question will rise in our mind, that is, we had ever made wrong setting of reaction condition toward the supercritical chemical reaction. Because as shown in Figure 4, the peak of abnormality exists in a very narrow range of pressure, i.e., within ca. 0.50MPa span under 35.0^{o}C temperature, and can not be observed over 60.0 ^{o}C. This means that there was no chance to get the advantageous supercritical effect on chemical reaction as far as we ignored this very restricted density, "*miracle density*".

In order to get general understanding of such characteristic behaviour of carbon dioxide as a supercritical fluid, we have conducted same experiment by using ethane and nitrous oxide, and the experimental results obtained are demonstrated in Figures. 5 and 6, respectively.

Although both compounds have similar critical conditions as carbon dioxide, the physico-chemical property is thought to be quite different. All of those measurements exhibit a common pattern of the light scattering around their critical points, indicating that the heterogeneity of the density of compressed gasses could be induced by such mechanism as a characteristic molecular association of supercritical fluid.

Recently, we had revealed the specific behavior [3] of supercritical fluid with the dielectric property measurement of carbon dioxide near the critical point by using our handmade apparatus. The detailed information of this research is available with some supplimental data in the poster session of this conference (T13-P98). Advantage of our instrumentation is the unique capability to provide reasonably accurate experimental data concerning delicate behaviours of the static relative permittivity (ε_r) of even very diluted vapor phase system which was not detected previously.[4]

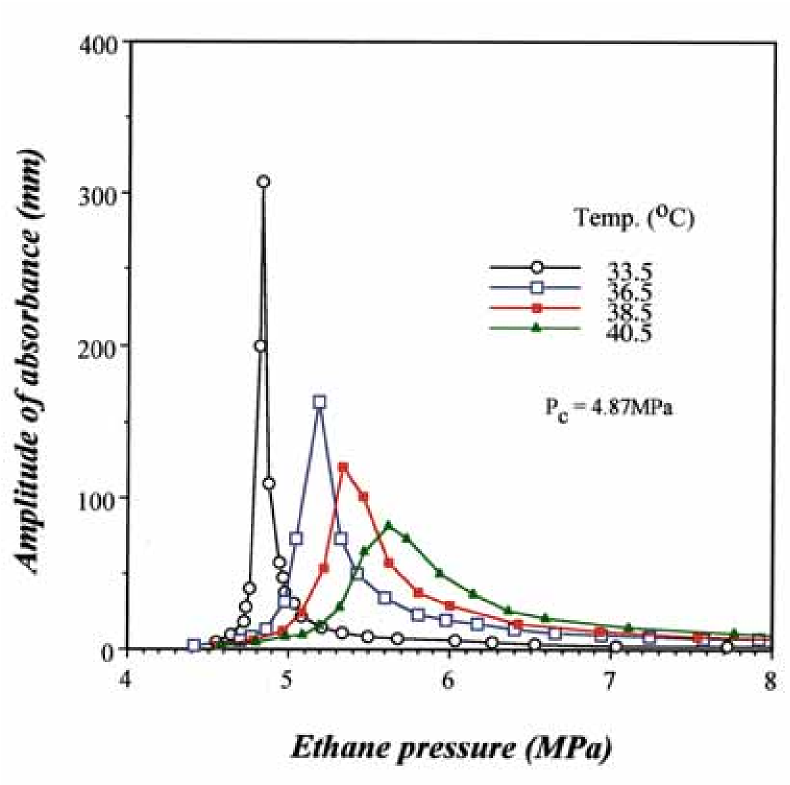

Figure 5 Pressure and temperature dependence on light scattering of ethane

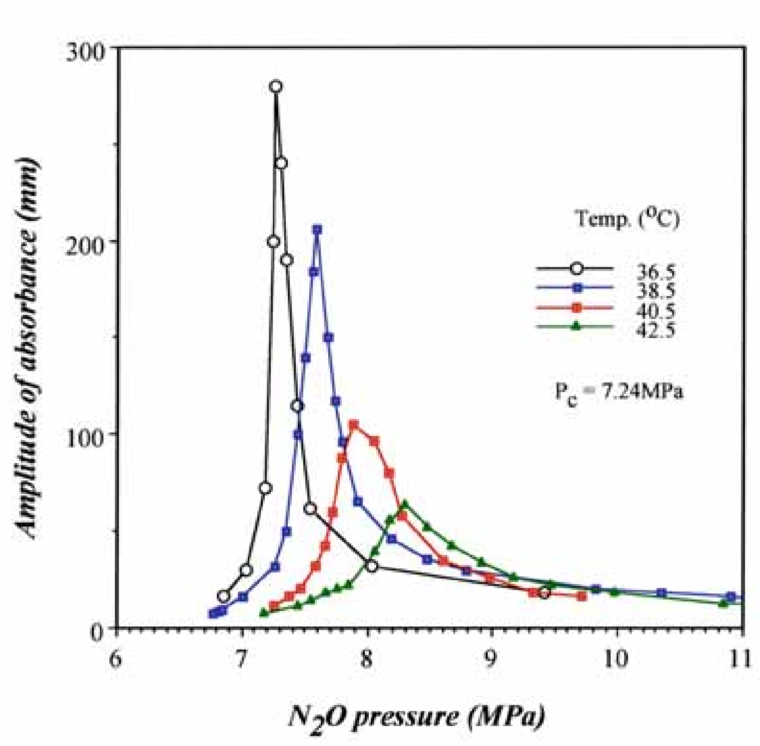

Figure 6 Pressure and temperature dependence on light scattering of N_2O

In Figure 7, the relationship between the molar polarization of carbon dioxide and the density with a function of temperature is cited. Very interestingly, it is obvious that the molar polarization was significantly enhanced near the critical density, and futhermore the trend of the peaks such as temperature depencence and pressure dependence seemed to be exactly identical to those of the light scattering describe above.

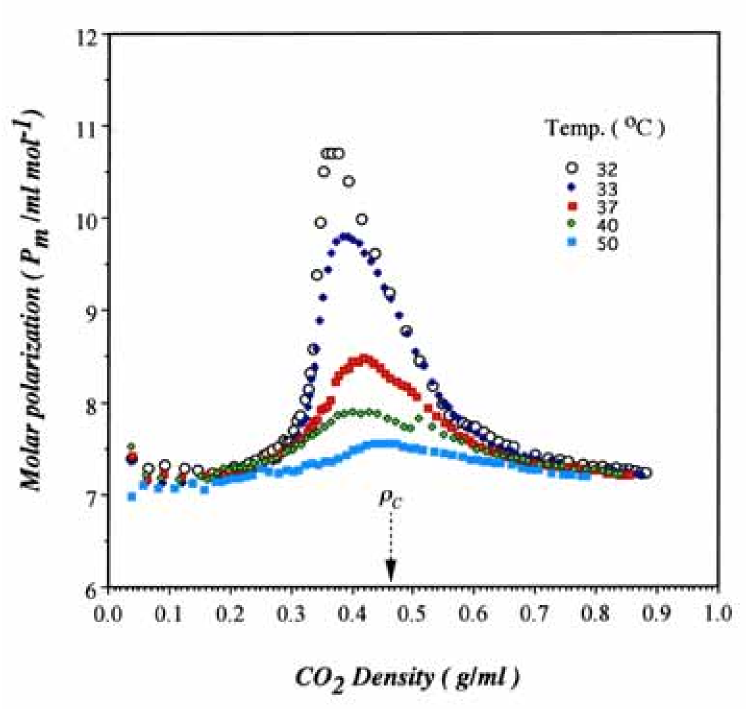

Figure 7 Density and temperature dependence on molar polarization of CO_2

Actually, the comparison of both data on the map of temperature and pressure induced the muximum peak revealed a fine lenear relationship as shown in Figure 8.

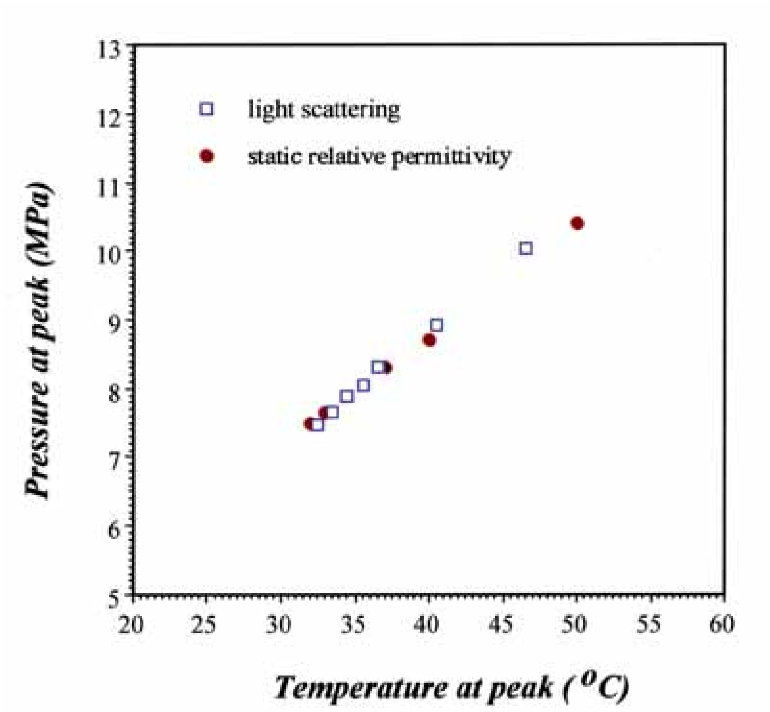

Figure 8 Relationship between molar polarization and light scattering of CO_2

Conclusion

A novel methodology for determining the discontinuous behavior of density of compressed gases has been developed based on light scattering method. This method is capable to quantitatively evaluate the degree of heterogeneity of the density of compressed gasses, carbon dioxide, ethane, ethylene or even their mixed gases, on its pulse pattern of UV or visible light scattering, and to determine the precise temperature and pressure conditions, which is expected to be a breakthrough the establishment of advantageous industrial processes using spercritical fluide. It is also revealed that there is a very reasonable linear relationship between the maximum of molar polarization and the light scattering near the critical point strongly suggesting the characteristic molecular association.

Reference

(1) T. Aida, and T.G. Squires, *ACS-Symposium Series* ***329*****,** 58(1987)

(2) T. Aida, *Proc. of Joint ISHR & ICDSTR, Kochi, Japan, 32(2000)*

(3) H. Ikeya, T. Shinkai, T. Aida, and G.P. Aida, *Annual Meeting of Japan Society of Chemical Engineering*, 3(2003)

(4) T. Moriyoshi, T. Kita, and Y. Uosaki, *Ber. Bunzeneges. Phys. Chem*., **97**, 589(1993)