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Research Article

Separation Process of Nonpolar Gas Hydrate in Food Solution under High Pressure Apparatus

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Separation process of nonpolar gas hydrate formation in liquid food was experimentally studied under high pressure container. Xenon (Xe) gas was selected as hydrate forming gas and coffee solution was used as a sample of liquid food. The high-pressure stainless steel container having the inner diameter of 60 mm and the volume of 700 mL with a U-shaped stirrer was designed to carry out this experiment. A temperature of 9.0°C and Xe partial pressure of 0.9 MPa were set as a given condition. The experiment was designed to examine the effect of steel screen size, formation rate, temperature condition, and amount of Xe gas dissolving in the solution on the separation process which was indicated by concentration efficiency. Screen size of 200 and 280 mesh resulted in higher concentration efficiency than that of 100 mesh. The higher stirring rate caused the higher formation rate of Xe hydrate and created the smaller Xe hydrate crystals. At the condition giving the same solubility in water, temperature of 14.8°C resulted in lower concentration efficiency than 9.0°C. The increase in the amount of Xe gas dissolving in coffee solution caused the concentration efficiency to decrease; however, the concentration ratio between the final and initial concentration of the solution increased.

1. Introduction

There has been an increase in gas hydrate research over the last decade. Interestingly, the research not only has focused on the inhibition of gas hydrate formation, which is of particular relevance to the petroleum industry, but also has evolved into investigations on the promotion of hydrate formation as a potential novel separation technology [1]. Utilization of hydrate formation in a variety of areas has been developed [2]; these areas include desalination [3–5], aqueous solution concentration [6], and waste minimization [7–9]. The process has become of interest in waste minimization (effluent concentration), the food industry, and the concentration of other aqueous solutions [9, 10]. Concentration of fluid materials by gas hydrate forming, such as fruit juices, enzyme suspension, any aqueous fluid containing solutes, and suspended substances, has been reported by many researchers [11–16].

The use of gas hydrate in the concentration method instead of the energy-demanding evaporation in beet sugar industry was reported by Heist Engineering Corporation [17]. Study on the hydrate formation from C_3H_8, CO_2, and a C_3H_8-CO_2 mixture in various mechanical mill effluents and their concentrates has been reported [8]. The hydrate process could operate from 8 to 10°C above the temperature of the freeze concentration process. Although gas hydrate could be applied for the concentration of liquid foods, it was reported that residuals of the hydrate former caused the products to have a bitter aftertaste and a change in both color and odor [14, 15, 18]. To reduce the residuals of gas hydrate, it was suggested that the hydrate of CO_2, N_2O, N_2, or the rare gases would likely be applied to overcome the problem of organoleptic alteration [13, 14]. Therefore, for the application of gas hydrate for the concentration of liquid foods, it must be considered that the use of hydrate forming material will not have a chemical effect on the liquid foods and will not remain after concentration operation.

Among many nonpolar gases that form gas hydrate, inert gases are suitable in the sense that they can be expected not to cause chemical changes in liquid foods because of their low chemical reactivity. Due to their inert activity, these gases could not form covalent compounds easily. Consequently, they have low chemical reactivity [19, 20]. Xenon (Xe) gas has highest solubility in water resulting in the greatest capability of gas hydrate formation among inert gases. Dissolution of Xe causes the change of water structure to a clathrate-like structure and yields an increase in population of hydrogen-bonded water molecules [21–24]. This structured water formation is formed by the hydrophobic hydration between water molecules and Xe molecules [25]. The phenomenon of structured water by dissolution of nonpolar gas has been confirmed by using nuclear magnetic resonance [26].

The fundamental concept of the concentration method was based on the phenomenon that water becomes structured after a nonpolar gas, under appropriate condition, dissolves into water [27]. The concentration process of solution by gas hydrate involving any gas capable of hydrate forming was forced into solution under suitable conditions of both temperature and pressure. The resulting gas hydrate was then separated from relatively concentrated solution [10]. Removal of gas hydrate from the concentrated solution could be achieved by mechanical separation. Gas hydrate was then decomposed by elevating the temperature or by reducing the pressure or by a combination of these to yield the hydrate forming gas and water. The hydrate forming gas was separated from the water and recycled for subsequent gas hydrate formation [11].

Basic study on the concentration of liquid food using Xe hydrate was reported [27]. Their works resulted that Xe hydrate was possible to grow in coffee solution with time and higher temperature and lower Xe pressure yielded the larger size of Xe hydrate. At temperature-pressure combinations giving the same solubility in water, higher temperature resulted larger size of Xe hydrate. In practical operation, the condition resulting in the larger size of Xe hydrate is required to achieve better separation process between Xe hydrate and solution. The objective of this study was to experimentally examine the application of Xe hydrate formation for the concentration of liquid food to provide technical data for subsequent process evaluation and development.

2. Material and Methods

2.1. Material. Coffee solution was used as a sample of liquid food. The sample was prepared by dissolving 20 g of freeze-dried coffee in 380 g of distilled water. Xe gas (99.995%), purchased from Iwatani Sangyo Co., Ltd., Japan, was selected as hydrate forming gas.

2.2. Experimental Apparatus. Figure 1 shows the experimental apparatus. The formation of Xe hydrate occurs in the high-pressure container constructed from stainless steel having the inner diameter of 60 mm and the volume of 700 mL. The apparatus was equipped with the glass windows on the front and backsides to make possible observation of Xe hydrate formation. Coffee solution was poured into the high-pressure container from the top by opening the upper lid. After closing it, Xe gas was injected to the high-pressure container from the top through the pipe. A U-shaped stirrer made of Teflon was used to mix the solution in the high-pressure container. This design of stirrer was introduced to minimize the buildup of gas hydrate on the wall of high-pressure container. The clearance between the Teflon rod and the wall of high-pressure container was about 2 mm. The power of stirrer was supplied by a DC motor with the speed range from 0 to 1000 rpm and the torque of 35 Ncm.

The temperature of solution was measured by thermistor, which was inserted through the upper lid, protected by the pipe, and placed near the bottom of the container. Thermorecorder with an accuracy of 0.1°C (model RT-10, ESPEC-Japan) was used for recording temperature. A pressure gauge with the measurement range of −0.10 to 2.00 MPa (Taiatsu Techno, Japan) was used to measure the pressure of the gas in the high-pressure container. Once the crystals have formed, the concentrated solution was drained from the container through the discharge pipe fitted with a removable stainless steel screen. For setting temperature of solution, the apparatus was placed in a constant temperature room.

2.3. Sampling Procedure. After 300 mL of coffee solution was poured into the container, the upper lid was closed and the stirrer was stirred; Xe gas was then injected. The change in Xe partial pressure during the hydrate formation was monitored continuously. The hydrate formation at the surface of the solution was observed from the glass windows. At residence time of 24 h, the solution was discharged under a relatively constant pressure condition. This condition was required to minimize the collapse of Xe hydrate when the concentrated solution was discharged.

The discharge process was done by opening Valves 1 and 2 (Valve 3 remained closed). By this way, the concentrated solution was allowed to pass through the screen fitted between Valves 1 and 2 and entire tube was filled. The Xe hydrate still remained on the upper side of the screen. Afterwards, Valves 1 and 2 were closed and by opening Valve 3, the concentrated solution in part A was discharged, as sample 1. As a next step, Valve 2 was opened (Valve 3 closed) to allow the concentrated solution between Valves 1 and 2 (parts B and C) to flow to part A. Valve 2 was closed and Valve 3 was opened; the material in part A could be obtained as sample 2. The remaining Xe hydrate was obtained by releasing the lower part.

The concentration of solution was determined by oven drying (Constant Temperature Oven model DNF 44, Yamato Scientific Co., Ltd., Japan) at 105°C for 24 h. About 5 g of solution was used as a sample. The concentration of solution was calculated from the weight of dry matter divided by the initial weight of solution and expressed as wt.%. Before

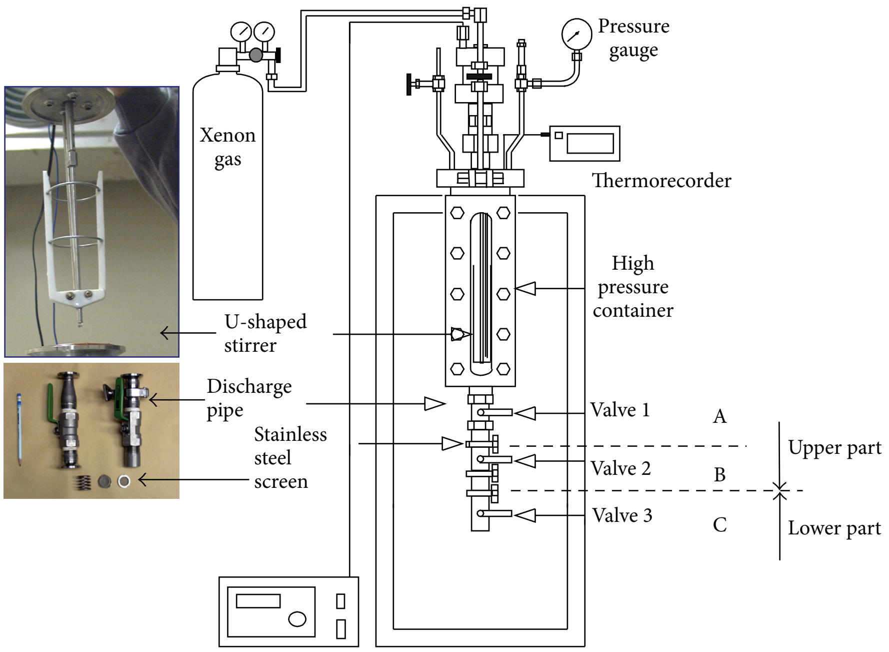

Figure 1: Experimental apparatus.

measuring the weight of solution, the sample was placed in desiccators for about 30 minutes to make the temperature of dry matter constant. The weight of solution was measured by an electronic balance (Model AT261 Delta Range, Mettler Toledo, Switzerland). The concentration measurement of solution was done for the initial concentration of solution and the concentrated solution (final concentration). Concentration efficiency was calculated by using the initial, final, and theoretical concentrations. The theoretical concentration is the concentration that can be achieved if all of Xe hydrate is pure crystal (8Xe $46H_2O$) and Xe hydrate can be entirely removed from the solution. Two replications were carried out for all of the experimental conditions.

2.4. Determination of Screen Size. This experiment was designed to determine the screen size that could be used for the separation process of the Xe hydrate crystals and the concentrated solution. The temperature of 9.0°C, the Xe partial pressure of 0.90 Mpa, and the stirring rate of 200 rpm were given as the common conditions. Using the graph of hydrate forming pressure with Xe gas [27], it was confirmed that the condition of temperature of 0.9°C and Xe partial pressure of 0.90 MPa assured the formation of Xe hydrate. The screen size was examined among 100 mesh (150 μm), 200 mesh (75 μm), and 280 mesh (53 μm).

2.5. Effect of Formation Rate. The stirring rate at 100, 200, and 400 rpm was set to determine the effect of the rate of Xe hydrate formation on the concentration efficiency, with the fixed screen size of 200 mesh. A given condition used in this experiment was the temperature of 9.0°C and the Xe partial pressure of 0.90 MPa.

2.6. Effect of Temperature. The effect of temperature, at condition giving the same Xe solubility in water, on the concentration efficiency was examined. The temperature of 9.0°C, Xe partial pressure of 0.90 MPa, screen size of 200 mesh, and stirring rate of 100 rpm were used as a given condition. The effect of temperature on the concentration efficiency was observed by increasing the temperature from 9.0 to 14.8°C at the condition giving the same Xe solubility in water. At condition of 9.0°C and 0.90 MPa, the Xe solubility in water was 1.14×10^{-3} mol Xe/mol H_2O [18]. When the temperature was increased to 14.8°C, the same value of Xe solubility in water as in the condition of 9.0°C and 0.90 MPa was achieved by increasing the Xe partial pressure to 1.09 MPa. The equilibrium of Xe partial pressure in the high-pressure container was 0.38 MPa for conditions of 9.0°C and 0.90 MPa and 0.68 MPa for 14.8°C and 1.09 MPa. The difference in the equilibrium of Xe partial pressure caused the difference in the amount of Xe gas to be dissolved in the solution. The amount of Xe gas dissolved in the 300 mL of coffee solution was 8.19×10^{-2} mol for conditions of 9.0°C and 0.90 MPa and 6.33×10^{-2} mol for 14.8°C and 1.09 MPa. The difference in the amount of Xe gas dissolved in the solution caused the difference in the amount of Xe hydrate to be formed in solution. Consequently, the amount of water that can be removed was also theoretically different.

2.7. Effect of Amount of Dissolved Xe Gas. This experiment was designed to examine the effect of the amount of Xe gas dissolved in the solution on the concentration of solution. The temperature of 9.0°C, Xe partial pressure of 0.90 MPa, screen size of 200 mesh, and stirring rate of 100 rpm were used as

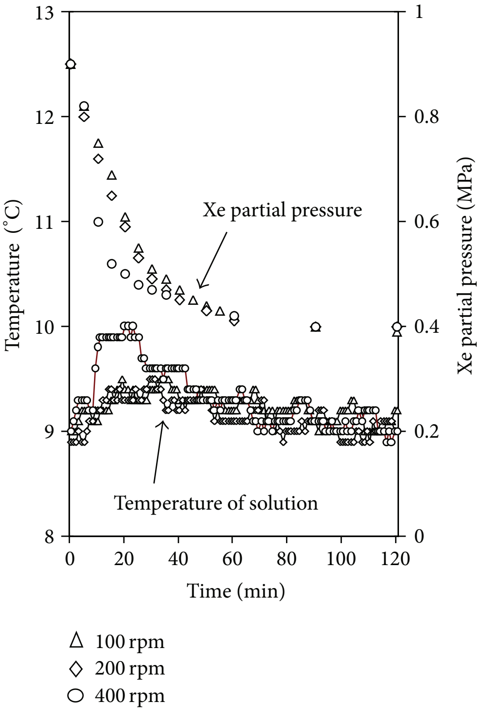

Figure 2: Change in Xe partial pressure and temperature of solution during the formation of Xe hydrate at different stirring rate (temperature: 9.0°C, Xe partial pressure: 0.90 MPa).

a given condition. At this condition, the amount of Xe gas dissolved in the 300 mL of coffee solution was 8.19×10^{-2} mol. The effect of the amount of Xe gas dissolved in the solution on the concentration of solution was examined by increasing the amount of Xe gas dissolved in the 300 mL of solution from 8.19×10^{-2} to 23.4×10^{-2} mol Xe.

3. Results and Discussions

3.1. Effect of Screen Size. Table 1 shows the concentration measurement for screen size of 100, 200, and 280 mesh. The final concentration was the average concentration of the concentrated solution measured at each sampling process. The use of screen size of 200 and 280 mesh resulted in higher concentration efficiency (58.3%) than that of 100 mesh (33.3%). It was considered that the screen size of 100 mesh with a perforation size of 150 μm might have caused the small gas hydrate to pass through the screen and to be mixed with the concentrated solution. Hence, the concentration efficiency became less. Because the small Xe hydrate melted easily, the use of screen size of 200 and 280 mesh resulted in the similar concentration efficiency.

Table 1: Screen size and concentration efficiency.

Screen size (mesh)	Concentration (wt.%)			Concentration efficiency (%)
	Initial	Final	Theoretical	
100	4.75	4.79	4.87	33.3
200	4.69	4.76	4.81	58.3
280	4.71	4.78	4.83	58.3

Table 2: Effect of stirring rate on the concentration efficiency.

Stirring rate (rpm)	Concentration (wt.%)			Concentration efficiency (%)
	Initial	Final	Theoretical	
100	4.75	4.82	4.87	58.3
200	4.69	4.76	4.81	58.3
400	4.75	4.81	4.88	46.2

3.2. Effect of Formation Rate. Figure 2 shows the change in temperature and Xe pressure in the high-pressure container during the formation of Xe hydrate from 0 to 120 minutes for stirring rate of 100, 200, and 400 rpm. The initial temperature of solution was 9.0°C and Xe partial pressure was 0.9 MPa. In all conditions, Xe pressure decreased rapidly during the first 20 minutes and was kept almost constant after 60 minutes. The decrease in Xe pressure was followed by the increase in temperature of solution. The increase in temperature indicated the dissolution of Xe gas. For stirring rate of 400 rpm, the decrease in Xe partial pressure and the increase in temperature of solution were more rapid than those of 100 and 200 rpm. Consequently, the Xe dissolution rate at 400 rpm was higher than those of 100 and 200 rpm.

After 60 minutes, Xe partial pressure in the container was stable at 0.38 MPa. At condition with stirring rate of 100 and 200 rpm, the first formation of Xe hydrate was observed at the surface of solution after 10 minutes, while at condition with stirring rate of 400 rpm, Xe hydrate was found after 5 minutes. This phenomenon showed that higher stirring rate enhanced the formation rate of gas hydrate. The same phenomenon of the effect of stirring rate on the hydrate formation has been reported by many researchers [7, 8, 13, 14, 28, 29].

Table 2 shows the concentration efficiency of 100, 200, and 400 rpm. It was found that the stirring rate of 100 and 200 rpm resulted in the same concentration efficiency (58.3%). However, the stirring rate of 400 rpm resulted in a lower concentration efficiency (46.2%). This can be explained by that the dissolution rate at the condition with stirring rate of 400 rpm was higher than those of 100 and 200 rpm. The higher dissolution rate means the higher formation rate of Xe hydrate. The higher formation rate created the smaller Xe hydrate crystals. The small Xe hydrate caused the separation process to be more difficult and as a result, the concentration efficiency became less. In the case of stirring rate of 100 and 200 rpm, the decrease in Xe pressure and the increase in temperature of solution were almost the same and resulted in the same concentration efficiency.

3.3. Effect of Temperature. Figure 3 shows the change in temperature of solution and Xe partial pressure in the high-pressure container during the formation of Xe hydrate from 0 to 120 minutes for the conditions of 14.8°C, 1.09 MPa and 9.0°C, 0.90 MPa. The amount of Xe dissolved in the solution was 6.33×10^{-2} mol for conditions of 14.8°C, 1.09 MPa and

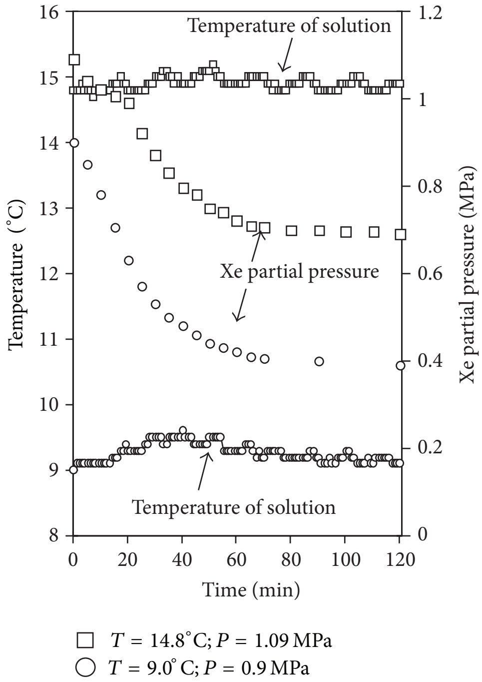

Figure 3: Change in Xe partial pressure and temperature of solution during the formation of Xe hydrate for conditions of 14.8°C, 1.09 MPa and 9.0°C, 0.90 MPa.

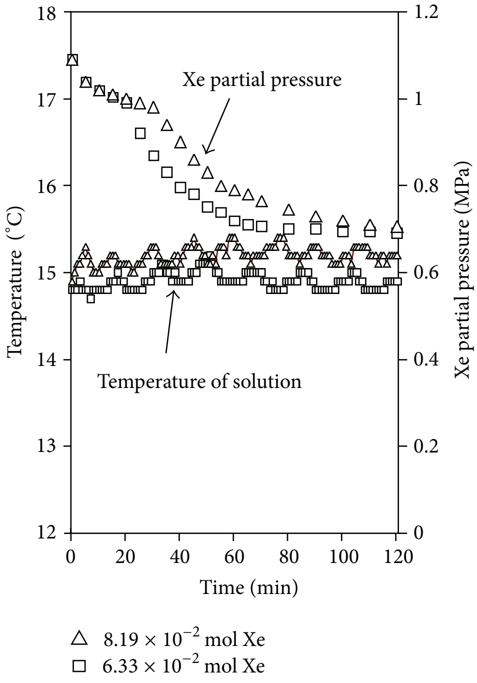

Figure 4: Change in Xe partial pressure and temperature of solution during the formation of Xe hydrate at conditions of 14.8°C and 1.09 MPa.

8.19×10^{-2} mol for conditions of 9.0°C, 0.90 MPa. For conditions of 14.8°C and 1.09 MPa, Xe partial pressure decreased slowly during the first 25 minutes. Afterwards, it decreased rapidly up to 80 minutes. After 120 minutes, it was kept almost stable at 0.68 MPa. The same occurred at 9.0°C, 0.90 MPa; the decrease in Xe pressure was followed by the increase in temperature of solution. This indicated the dissolution of Xe gas. At condition of 14.8°C, 1.09 MPa, although an increasing trend in temperature of solution was observed, it was not so clearly seen at condition of 9.0°C, 0.90 MPa. At this condition, Xe hydrate was found firstly at the surface of the solution after 15 minutes or about 5 minutes longer than that required for condition of 9.0°C, 0.90 MPa.

Effect of temperature on the concentration efficiency was also examined for the temperature of 14.8°C and Xe partial pressure of 1.09 MPa and at condition giving the same amount of Xe gas dissolved in the 300 mL solution as for the temperature of 9.0°C and Xe partial pressure of 0.90 MPa. The change in temperature of solution and Xe partial pressure is shown in Figure 4. It was also plotted data for condition of 14.8°C, 1.09 MPa and the amount of Xe gas dissolved in the 300 mL of solution (6.33×10^{-2} mol Xe). The decrease in Xe partial pressure and the increase in the temperature of solution for both conditions were not exactly the same; however, the trends were similar. Increasing the amount of Xe gas dissolved in the solution increased the peak of temperature of solution. This showed that due to higher dissolution of Xe gas in the solution, the heat that was released for condition of 8.19×10^{-2} mol was higher than that for 6.33×10^{-2} mol.

Effect of temperature on the concentration measurement and efficiency is shown in Table 3. Higher temperature created larger size of crystal [27]. Consequently, the concentration efficiency at higher temperature was better than that at lower temperature condition. However, in this work, the concentration efficiency at the condition of 14.8°C, 1.09 MPa for both the amount of Xe dissolved in the solution of 6.33×10^{-2} mol and 8.19×10^{-2} mol was lower than that at conditions of 9.0°C and 0.90 MPa. It was considered that the amount of Xe hydrate melting during the separation process at 14.8°C was greater than that at 9.0°C. The melted Xe hydrate was mixed with the concentrated solution and this caused the concentration efficiency to decrease. This phenomenon was supported that, at lower temperature (9.0°C), when the remaining Xe hydrate crystals were discharged, some crystals remained on the stainless screen. However, this was not found at temperature of 14.8°C. This finding suggested that for better separation process the optimum combination of temperature and Xe partial pressure should be found.

3.4. *Effect of the Amount of Xe Gas Dissolved in the Solution.*

Effect of the amount of Xe gas dissolved in the solution on the concentration of the concentrated solution was examined at temperature of 9.0°C and Xe partial pressure of 0.90 MPa. Figure 5 shows the change in Xe partial pressure and temperature of solution in the high-pressure container during the formation of Xe hydrate at condition of Xe gas dissolved in the solution of 23.4×10^{-2} mol/300 mL. Temperature of solution was recorded at 9.2°C when the Xe gas was injected

Table 3: Effect of temperature conditions on the concentration efficiency.

Temperature (°C)	Xe gas dissolved in solution (mol)	Concentration (wt.%)			Concentration efficiency (%)
		Initial	Final	Theoretical	
9.0	8.12×10^{-2}	4.75	4.82	4.87	58.3
14.8	6.33×10^{-2}	4.65	4.69	4.73	50.0
14.9	8.12×10^{-2}	4.74	4.80	4.86	50.0

to the high-pressure container. Data at the same condition of temperature and Xe partial pressure for Xe gas dissolved in the solution of 8.12×10^{-2} mol was also plotted. During the first 20 minutes, the decrease in Xe partial pressure in both conditions was almost the same. However, after residence time of 20 minutes, the decrease in Xe partial pressure for condition of Xe gas dissolved in the solution of 23.4×10^{-2} mol was lower than that of 8.12×10^{-2} mol. After residence time of 120 minutes, Xe partial pressure condition was almost stable at 0.44 MPa. The equilibrium of Xe partial pressure for the condition of Xe gas dissolved in the solution of 23.4×10^{-2} was higher than that of 8.12×10^{-2} mol.

It was observed that the peak of temperature for condition of Xe gas dissolved in the solution of 23.4×10^{-2} mol occurred in the range of residence time of 40 to 80 minutes. The change in temperature was different as occurred at condition of Xe gas dissolved in the solution of 8.12×10^{-2} mol. The maximum difference in the peak of temperature between the both conditions was about 1°C. Increasing the amount of Xe gas dissolved in the solution increased the dissolution of Xe gas in the solution. The increase in the dissolution of Xe gas increased the amount of the heat that was released. Heat of reaction of Xe gas with water to form hydrate at 101 kPa is -15.5 ± 0.2 kJ/mol Xe [30]. At residence time of 24 h, the temperature of solution was kept at 9.4°C. It was considered that the difference in the change of temperature caused the difference in the formation of Xe hydrate.

In order to obtain the change in temperature of solution during the formation of Xe hydrate similar to that which occurred at condition of 9.0°C and 0.90 MPa, the temperature was set at 8.1°C. Figure 6 shows the change in temperature of solution and Xe partial pressure during the formation of Xe hydrate for initial temperature of solution of 8.1 and 9.2°C. It was found that, for temperature of 8.1°C, the maximum temperature of 8.8°C was observed in the range of residence time of 40 to 80 minutes. The peak of temperature for condition of 9.0°C and 0.90 MPa was 9.4°C.

When the amount of Xe gas dissolved in solution was increased about three times (increasing the Xe gas dissolved in the solution from 8.12×10^{-2} to 23.4×10^{-2} mol), the concentration efficiency decreased from 58.3% to 30.8% for temperature of 9.2°C and 35.0% for temperature of 8.1°C (Table 4). Increasing the amount of Xe gas dissolved in the solution from 8.12×10^{-2} to 23.4×10^{-2} mol caused the concentration efficiency to decrease. However, the concentration ratio between final and initial concentration increased from 1.01 to 1.03 times.

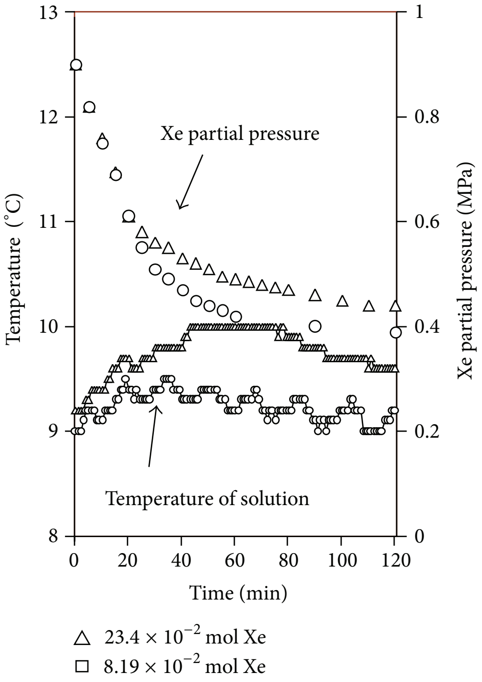

Figure 5: Change in Xe partial pressure and temperature of solution during the formation of Xe hydrate for conditions of 9.0°C and 0.90 MPa.

4. Conclusion

Concentration process of coffee solution through Xe hydrate formation was experimentally demonstrated. The apparatus in which Xe hydrate formation and growth occur in one container was designed and built. It was found that the use of screen size of 200 and 280 mesh resulted in a higher concentration efficiency than that of 100 mesh. Higher formation rate of Xe hydrate resulted in lower concentration efficiency. Increasing the amount of Xe gas dissolving in the solution decreased the concentration efficiency. However, the concentration of the concentrated solution could be increased. Effect of temperature, at condition giving the same Xe solubility in water, showed that when temperature of solution increased, the concentration efficiency became less. When the amount of Xe gas dissolved in solution was increased, the concentration effciency decreased. However, the concentration ratio between final and initial concentration increased. This work was the first effort to use Xe gas hydrate for the concentration of liquid food. Further work

Table 4: The amount of Xe gas dissolved in the solution, the concentration of solution, and the concentration efficiency.

Temperature (°C)	Xe gas dissolved in solution (mol)	Concentration (wt.%)			Concentration efficiency (%)	Concentration ratio*
		Initial	Final	Theoretical		
9.0	8.12×10^{-2}	4.75	4.82	4.87	58.3	1.01
9.2	23.4×10^{-2}	4.62	4.74	5.01	30.8	1.03
8.1	23.7×10^{-2}	4.75	4.89	5.15	35.0	1.03

*Concentration ratio = final concentration/initial concentration.

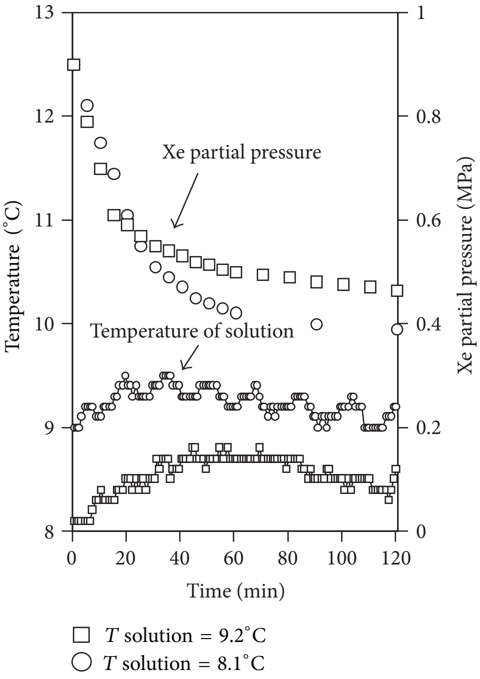

Figure 6: Change in Xe partial pressure and temperature of solution during the formation of Xe gas for condition of 0.9 MPa and Xe dissolved in the solution of 23.4×10^{-2} mol for initial solution temperatures of 9.2 and 8.1°C.

should be done to examine the availability of the use of higher solution sample, recycle process of Xe gas, and continuous separation process.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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