Thermodynamic and Raman Spectroscopic Studies of Xe and Kr Hydrates

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The thermodynamic stability boundaries for two noble gas (Xe and Kr) hydrates have been investigated in a pressure range up to 445 MPa and a temperature range of (324.4 to 345.3) K for the Xe hydrate system and (274.4 to 320.0) K for the Kr hydrate system. The Raman spectrum of the intermolecular O−O stretching vibration mode has been evaluated for each hydrate single crystal along with the three-phase coexisting curve. The slope change on the boundary curve and the pressure dependence on the Raman shift for the Kr hydrate crystal reveal that a structural phase-transition point exists at 414 MPa and 319.20 K, whereas the Xe hydrate crystal of structure I does not exhibit any phase transition over the region studied.

Introduction

Gas hydrates have recently attracted the attention of many investigators of petroleum and chemical engineering. The noble gas hydrates are not necessarily essential for practical applications; however, how the noble gases, having a spherical shape and characteristic properties, affect hydrate stability is fundamental for a thermodynamic understanding of gas hydrates. Some important findings have been reported for the noble gas hydrate systems. For example, Kurnosov et al.[1] found that the 14-hedral cavity ($4^2 5^8 6^4$) doubly occupied by Ar generates the tetragonal structure hydrate at very high pressures, and Ohgaki et al.[2] claimed that the Xe hydrate system is the border system that does not have a high-temperature quadruple point in a series of critical temperatures of the guest molecules.

Moreover, it seems to be that the hydrate cage occupied by the small and spherical guest molecules is easily shrunk by pressurization. The Raman spectrum of the intermolecular O−O stretching vibration mode of water molecules gives important information about the constriction ability as well as the structural change in hydrate cages by pressurization. In the previous paper,[3] we found that the hydrate cages occupied by methane shrink gradually by pressurization, whereas the O−O stretching vibration is relatively independent of the pressure in the hydrate systems of ethane,[4] ethylene,[5] and so on.[15,16]

In the present study, the three-phase coexisting curves for two noble gas (Xe and Kr) hydrate systems have been investigated, and the pressure dependence of the Raman O−O vibration shifts has been evaluated along with the equilibrium curve.

Experimental Section

The experimental apparatus used in the present study is essentially the same as that previously described.[6] It was designed and manufactured to establish the equilibrium conditions for measuring the three-phase coexisting curve and to prepare the hydrate single crystal for performing in situ laser Raman spectroscopic analysis. The high-pressure optical cell has a pair of sapphire windows, an inner volume of approximately 0.2 cm^3, and a maximum working pressure is about 500 MPa. The contents were pressurized without changing the total amount of the substances by use of a volume controller attached to the cell.

For the pressure measurement, two different pressure gauges were used according to the working pressure. Up to 75 MPa, a pressure gauge (Valcom VPRT) calibrated by a Ruska quartz Bourdon tube gauge was used with an estimated maximum uncertainty of 0.02 MPa. Over 75 MPa, a pressure transducer (NMB STD-5000K) and digital peak holder (NMB CSD-819) were used with an estimated maximum uncertainty of 2 MPa.

The system temperature was controlled by thermostated water circulating through the jacket attached to the cell. The equilibrium temperature was measured within a reproducibility of 0.02 K using a thermistor probe calibrated by a Pt resistance thermometer (25 Ω) inserted into a hole of the cell wall.

Single crystals of noble gas hydrates in equilibrium were analyzed using a laser Raman microprobe spectrometer with a multichannel CCD detector (Jobin Yvon Ramanor T64000). The laser beam from the object lens irradiated the sample through the upper sapphire window. The backscatter of the opposite direction was taken in with the same lens. The argon ion laser beam of 514.5 nm and 100 mW was condensed to a 2-μm spot diameter. The spectral resolution was about 1 cm^{-1}. The Raman peak of the intermolecular O−O stretching vibrational mode of water molecules that construct hydrate cages was detected around 205 cm^{-1}.

After the preparation of a single crystal in the three-phase coexisting equilibrium (the preparation procedures were described elsewhere[6]), the Raman peak was detected under several pressure conditions. Usually, the single-crystal preparation took a lot of time (a couple of weeks).

Xe was purchased from Daido Hoxan Inc., having a stated minimum purity of 99.995 mol %. The majority of

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Table 1. Three-Phase Coexisting Data for the Xe Hydrate System

T/K	*p*/MPa
324.40	106
326.67	129
329.79	163
332.15	193
334.19	221
335.96	247
337.35	271
338.68	294
340.06	320
341.29	345
342.54	368
343.59	391
344.45	416
345.32	440

Table 2. Three-Phase Coexisting Data for the Kr Hydrate System

T/K	*p*/MPa	*T*/K	*p*/MPa
274.49	1.62	300.89	35.21
275.84	1.82	301.70	39.33
277.15	2.10	302.46	44.23
278.14	2.30	303.04	49.23
278.87	2.51	303.94	56.09
279.77	2.70	305.16	67.57
280.09	2.80	306.20	78
280.75	2.98	307.22	88
281.73	3.28	307.51	89
282.21	3.43	308.37	98
283.22	3.83	309.72	113
284.18	4.23	310.81	129
285.11	4.60	312.04	148
285.62	4.87	313.01	166
286.58	5.36	313.96	180
286.59	5.39	314.86	199
287.59	6.02	315.69	218
288.57	6.68	315.96	226
289.58	7.44	316.55	249
290.57	8.31	317.19	270
291.56	9.31	317.40	285
292.46	10.19	317.90	309
294.26	12.70	318.26	330
295.48	15.10	318.86	353
296.65	17.74	319.00	376
297.39	19.93	319.29	399
298.39	23.34	319.20	414[a]
299.47	27.41	319.37	433[a]
300.26	31.09	320.02	445[a]

[a] New hydrate structure.

the impurity was Kr at 3.78 ppm. Kr was purchased from Neriki Gas Co. Ltd., having a stated minimum purity of 99.999 mol %. Distilled water was obtained from Yashima Pure Chemicals Co. Ltd.

Results and Discussion

The experimental data obtained in the present study for the Xe and Kr hydrate systems are listed in Tables 1 and 2, respectively. Figure 1 shows the pressure temperature relations of two noble-gas hydrate systems accompanied with the literature values.

The S-shaped curve of the Xe hydrate system is the characteristic behavior caused by the differential $p-v-T$ relation around the critical end point, not by hydrate structural changes. The critical end point (the gas and liquid phases become identical in the presence of the hydrate phase) for the Xe hydrate system is at 299.76 K and 5.86 MPa[2], which is very close to the three-phase coexistence curve. The equilibrium curve obtained in the present study (over 75 MPa) is smoothly extrapolated to the previous results in the low-pressure region[2]. Overall, the discrepancy between the present results and the literature values[7] is less than 5% in pressure.

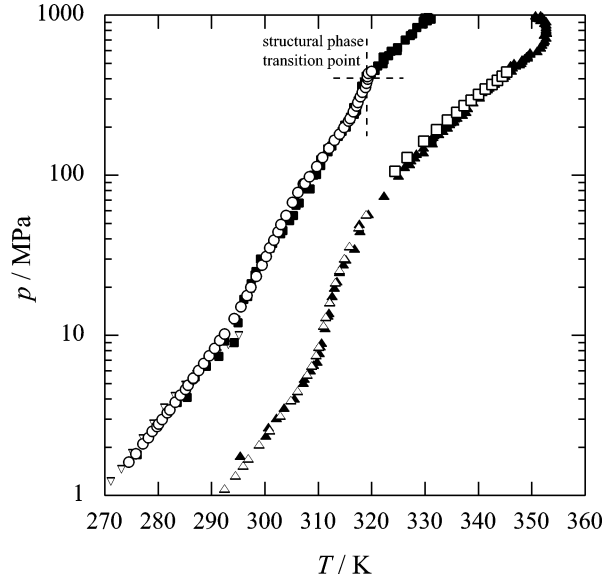

Figure 1. Pressure−temperature relations of hydrate stability boundaries: □, three-phase coexistence curve of the Xe hydrate (present study); ▲, Dyadin et al.;[7] △, Ohgaki et al.[2]; ○, three-phase coexistence curve of the Kr hydrate (present study); ▽, Berecz and Balla-Achs;[12] ■, Dyadin et al.[10] The structural phase-transition point exists at 414 MPa and 319.20 K for the Kr hydrate system.

From the slope of the equilibrium curve ($\mathrm{d}p/\mathrm{d}T$), the overall enthalpy change $\Delta_{\mathrm{hyd}}H$ was obtained by using the Clapeyron equation, the Lee−Kesler equation of state,[8] and ideal hydrate assumption. The details are given in the previous paper.[2] The average value of $\Delta_{\mathrm{hyd}}H = 65 \pm 6$ kJ/mol shows good agreement with the previous value of 65 kJ/mol.[2,9,17] A large deviation at high temperatures was mainly caused by the uncertainty in the volumetric properties of the Xe fluid at high pressure.

The Kr hydrate system exhibits curious behavior as shown in Figure 1. In the present study, the structural phase-transition point was determined at 414 MPa and 319.20 K along with the thermodynamic stability boundary. Dyadin et al.[10] have reported the structural change (structure II to structure I) around 415 MPa. However, Desgreniers et al.[11] have claimed that the structure-II Kr hydrate changes to structure I near 300 MPa and to the hexagonal structure near 600 MPa at room temperature. However, there was no unusual pressure−temperature relation around 300 MPa caused by the hydrate structural change. It is possible that the structure-I hydrate near 300 MPa corresponds to the metastable state because the latter's measurements were not performed under three-phase equilibrium conditions. Around 10 MPa and 295 K, the present data show a large disagreement with the literature.[10,12] The literature values indicate a structural phase transition at 10 MPa. However, careful measurement around this point shows a smooth curve in the present study. The average value of $\Delta_{\mathrm{hyd}}H$ is evaluated with the same procedure as that given above. A value of $\Delta_{\mathrm{hyd}}H = 57 \pm 2$ kJ/mol was found in a temperature range of (275 to 305) K, which is in good agreement with the literature value of 56.2 kJ/mol at 273 K.[13]

The Raman spectrum of the intermolecular O−O stretching vibrational mode of water was detected around 205 cm^{-1} in the gas hydrate systems. The typical Raman peaks of the Kr hydrate are shown in Figure 2. The peak

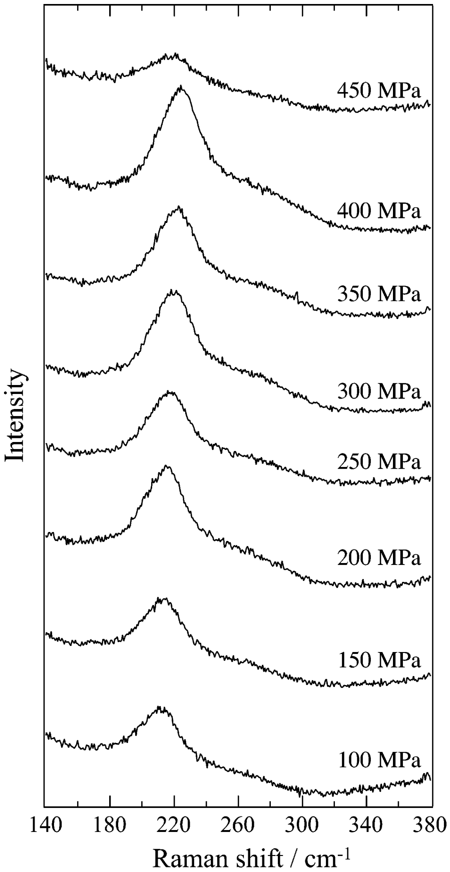

Figure 2. Raman spectra of the O−O stretching vibration for the Kr hydrate crystal on the thermodynamic stability boundary curve.

corresponding to the hydrate cage structured by hydrogen bonds is a peculiar spectrum of the hydrate lattice. Some small peaks at lower than 140 cm^{-1} were not taken up because it was difficult to specify the meaning of peaks from noise on the shoulder of Rayleigh scattering. The Raman peaks show the blue shift in proportion to pressure up to 414 MPa. Over 414 MPa, the peak becomes broad and shifts to a low-energy vibration. The pressure effect on the O−O vibrational mode in the Xe and Kr hydrate crystals is shown in Figure 3. In both systems, the O−O vibrational energy increases with pressure; that is, the hydrate cage constructed of water molecules shrinks gradually by pressurization.

The pressure dependence of the O−O vibration in the N_2 and CO_2 hydrate crystals is also shown for comparison in Figure 3. The N_2 and CO_2 hydrates are well known as typical crystals of structure-II and structure-I hydrates in the present pressure region, respectively. They show a common pressure dependence on the O−O vibration; however, the N_2 hydrate[14] exhibits higher vibration energy than the CO_2 hydrate[6] at the same pressure. The distinction proceeds from a size difference of the pentagonal dodecahedron hydrate cages; that is, the dodecahedron cage of the structure-II hydrate is slightly smaller than that of the structure-I hydrate. The Xe hydrate system shows good agreement with the CO_2 hydrate system (dotted line). However, the Kr hydrate system agrees well with the N_2 hydrate system (solid line) up to 414 MPa. Above that pressure, it shows a discontinuous line, and the O−O vibrational energy becomes lower than that of structure-I hydrates. This fact reveals that the structural phase transition in the Kr hydrate crystal occurs around 400 MPa and that the average ridge-line length of hydrate cages becomes longer than that of structure-I hydrates.

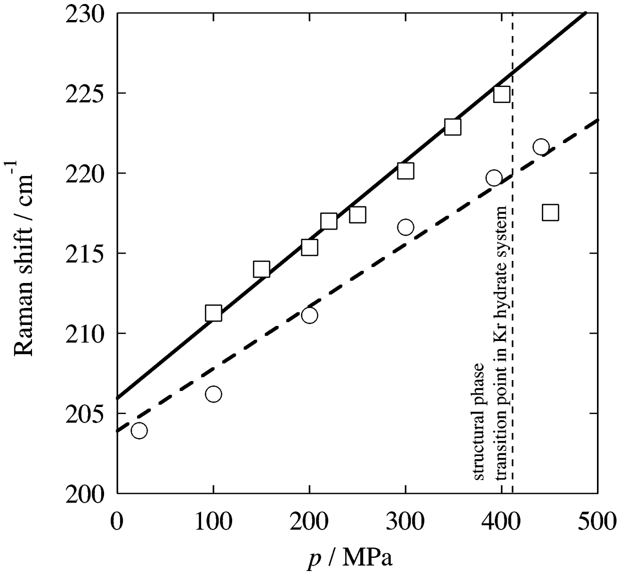

Figure 3. Pressure dependence on the Raman shift corresponding to the O−O stretching vibration for the Xe and Kr hydrate systems: ○, Xe hydrate; □, Kr hydrate; −, N_2 hydrate (structure II);[14] - - -, CO_2 hydrate (structure I).[6] The Xe hydrate crystal belongs to the structure-I hydrate over the whole experimental region. In the Kr hydrate system, the structure-II hydrate crystal exists up to 414 MPa and changes to a different structure.

The pressure dependence of the Xe and Kr hydrates indicates the shrinkage of the hydrogen-bonded cage or the large free volume in the hydrate cage for these guest molecules. It is also important that the structure-I Xe hydrate crystal never changes its structure over the whole pressure range, whereas the structure-II Kr hydrate exhibits a structural change around 400 MPa. The hydrate structure observed at over 414 MPa would be the hexagonal crystal, as speculated on by Desgreniers et al.[11]

Conclusions

Three-phase coexisting curves of Xe and Kr hydrate systems were obtained up to 445 MPa by use of a high-pressure optical cell. Each single crystal of Xe and Kr hydrates was analyzed in situ by the use of laser Raman spectroscopy. The pressure dependence of the intermolecular O−O stretching vibrational mode reveals that the Xe hydrate crystal belongs to the structure-I hydrate over the whole experimental region. For the Kr hydrate system, the structure-II hydrate crystal exists up to 414 MPa and changes to a different structure (probably hexagonal). Both noble gas hydrate crystals indicate a considerable shrinkage of the hydrate cage by pressurization.

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