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Short Articles

Experimental Gas Hydrate Dissociation Data for Methane, Ethane, and Propane + 2-Propanol Aqueous Solutions and Methane + 1-Propanol Aqueous Solution Systems

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In this work, experimental gas hydrate dissociation data for methane + 0.164 mass fraction 2-propanol, ethane + 0.05 mass fraction 2-propanol, propane + 0.05 mass fraction 2-propanol, and methane + 0.16 mass fraction 1-propanol aqueous solution systems are presented. The new experimental data have been measured using a reliable isochoric method. The hydrate dissociation data for the methane + 0.164 mass fraction 2-propanol aqueous solution system are compared with the experimental data reported in the literature. Good agreement between the data indicates the reliability of the experimental technique reported in this study.

Introduction

Gas hydrates are a group of nonstoichiometric, icelike crystalline compounds formed through a combination of water and suitably sized guest molecules under low temperatures and elevated pressures. In the gas hydrate lattice, water molecules form hydrogen-bonded cagelike structures, encapsulating the guest molecules, which generally consist of low molecular diameter gases and organic compounds.[1] The most common hydrate structures are those of structure I (*s*I) and structure II (*s*II), where each structure is composed of a certain number of large and small cavities formed by water molecules.[1] For a molecule to enter a cavity, its size should be smaller than a certain value. Large molecule guests, which can enter only a limited number of large cavities, require smaller "help gas" molecules to fill some smaller cavities sufficiently to stabilize hydrate crystals.[1] Suitable conditions for gas hydrate formation commonly occur during hydrocarbon production and exploration operations.[1] Gas hydrate formation can cause flow restriction and blockage, which can lead to serious operational, economic, and safety problems. Thermodynamic inhibitors, such as alcohols and glycols, are normally used to inhibit gas hydrate formation.[1] The presence of inhibitors normally reduces the activity of water in the aqueous phase, which shifts hydrate phase boundaries to high pressures/low temperatures.[1]

Reliable gas hydrate equilibrium data for natural gas main components in the presence/absence of inhibitors are necessary to develop and validate thermodynamic models for predicting hydrate phase boundaries of natural gases in the presence/absence of inhibitors. Many data have been reported for gas hydrates of these components in the presence/absence of methanol and ethylene glycol aqueous solutions.[1] However, information for other alcohols and glycols is limited.[1]

In this work, we report experimental hydrate dissociation data for methane, ethane, and propane + 2-propanol aqueous solutions and methane + 1-propanol aqueous solution systems, which have been measured using a reliable isochoric technique.[2] The hydrate dissociation data have been measured for methane + 0.164 mass fraction 2-propanol aqueous solution in the temperature range of (276.3 to 281.0) K, for ethane + 0.05 mass fraction 2-propanol aqueous solution in the temperature range of (277.2 to 281.6) K, for propane + 0.05 mass fraction 2-propanol aqueous solution in the temperature range of (274.1 to 278.2) K, and for methane + 0.16 mass fraction 1-propanol aqueous solution in the temperature range of (273.2 to 279.8) K. The new gas hydrate dissociation data for the methane + 0.164 mass fraction 2-propanol aqueous solution system are found in good agreement with the literature data indicating the reliability of the experimental technique used in this study.

Experimental Section

Purities and suppliers of materials are provided in Table 1. A detailed description of the experimental setup used in this study is given elsewhere.[3] Briefly, the main part of the apparatus was a cylindrical vessel with two sapphire windows, which can withstand pressures higher than 10 MPa. A stirrer was installed in the vessel to agitate fluids and hydrate crystals inside the vessel. The vessel is immersed in a temperature-controlled bath to maintain the temperature inside the vessel at a prescribed level. Two platinum probes (Pt100) are inserted into the vessel to measure the temperatures. Temperature measurement uncertainties are estimated to be less than 0.1 K. The pressure in the vessel is measured with a DRUCK pressure transducer, and pressure measurement uncertainties are estimated to be less than 5 kPa. The hydrate equilibrium conditions are measured with the batch, isochoric procedure.[2] The vessel containing the aqueous solution was immersed into the temperature-controlled bath, and the gas was supplied from a high-pressure cylinder through a pressure-regulating valve into the evacuated vessel.

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Table 1. Purities and Suppliers of Materials[a]

chemical	supplier	purity
methane	Messer Griesheim	99.995
ethane	Messer Griesheim	99.995
propane	Messer Griesheim	99.995
2-propanol	Acros Organics	99.5
1-propanol	VWR Prolabo Chemicals	99.5

[a] Deionized water was used in all experiments.

Table 2. Experimental Hydrate Dissociation Data for Methane + 2-Propanol, Ethane + 2-Propanol, Propane + 2-Propanol, and Methane + 1-Propanol Aqueous Solution Systems (w_1 = mass % of Propanol in Aqueous Solution)

T/K ± 0.1 K[a]	P/MPa ± 5 kPa[b]
Methane + 2-Propanol Aqueous Solution ($w_1 = 16.4$)	
276.3	2.78
277.8	3.27
280.1	4.29
281.0	4.76
Ethane + 2-Propanol Aqueous Solution ($w_1 = 5$)	
277.2	0.65
279.3	0.86
281.6	1.15
Propane + 2-Propanol Aqueous Solution ($w_1 = 5$)	
274.1	0.17
276.6	0.25
278.2	0.32
Methane + 1-Propanol Aqueous Solution ($w_1 = 16$)	
273.2	2.45
274.5	2.84
275.9	3.41
278.3	4.39
279.8	5.16

[a] Uncertainty on temperatures through calibrated platinum probes. [b] Uncertainty on pressures through a calibrated pressure transducer.

After temperature and pressure stabilized, the valve in the line connecting the vessel and the cylinder was closed. Subsequently, temperature was decreased to form hydrate. Hydrate formation in the vessel was detected by a pressure drop. The temperature was then increased with steps of 0.1 K. At every temperature step, the temperature was kept constant for 4 h to achieve a steady equilibrium state in the vessel. In this way, a pressure−temperature diagram was obtained for each experimental run, from which we determined the hydrate dissociation point. If the temperature was increased in the hydrate-forming region, hydrate crystals partially dissociate, thereby substantially increasing the pressure. If the temperature was increased outside the hydrate region, only a smaller increase in the pressure was observed as a result of the change in the phase equilibria of the fluids in the vessel.[4] Consequently, the point at which the slope of pressure−temperature data plots changes sharply was considered to be the point at which all hydrate crystals dissociate and hence as the dissociation point.

Results

Experimental hydrate dissociation data for methane + 0.164 mass fraction 2-propanol, ethane + 0.05 mass fraction 2-propanol, propane + 0.05 mass fraction 2-propanol, and methane + 0.16 mass fraction 1-propanol aqueous solution systems are reported in Table 2. Figure 1 shows the logarithm of hydrate dissociation pressure versus temperature for all the systems studied in this work. The data have been shown on a semilogarithmic scale to show the consistency of the data, as logarithm of hydrate dissociation pressure versus temperature has approximately linear behavior. Figure 1 also shows a comparison between the new experimental data for the hydrate dissociation conditions of the methane + 0.164 mass fraction 2-propanol aqueous solution system and the previously reported experimental data by Østergaard et al.[5] and Ohmura et al.[4] for this system. As can be seen, the data are in good agreement indicating the reliability of the experimental technique reported in this work.

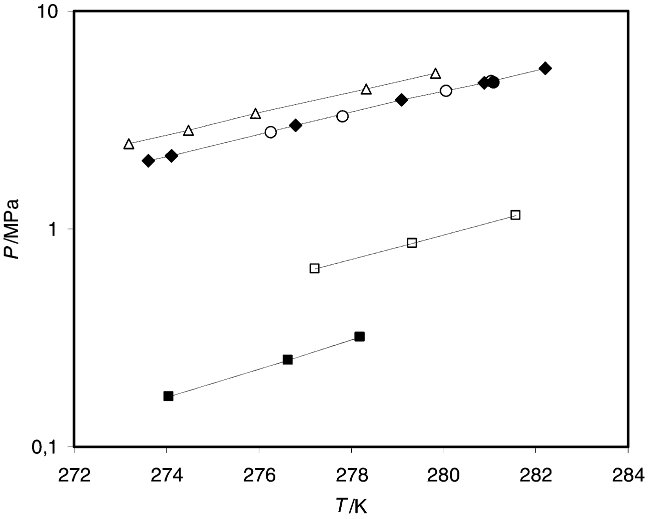

Figure 1. Experimental hydrate dissociation data for methane + 2-propanol aqueous solution (○, this work; ◆, Ohmura et al.;[4] ●, Østergaard et al.,[5] $w_1 = 16.4$), ethane + 2-propanol aqueous solution (□, this work, $w_1 = 5$), propane + 2-propanol aqueous solution (■, this work, $w_1 = 5$), and methane + 1-propanol aqueous solution (△, this work, $w_1 = 16$) systems. Solid lines: the best fit through experimental points (w_1 = mass % of propanol in aqueous solution).

Conclusions

Gas hydrate dissociation data for methane + 0.164 mass fraction 2-propanol, ethane + 0.05 mass fraction 2-propanol, propane + 0.05 mass fraction 2-propanol, and methane + 0.16 mass fraction 1-propanol aqueous solution systems were reported in this work. A reliable isochoric method was used for performing all the measurements. The experimental data for the methane + 0.164 mass fraction 2-propanol aqueous solution system were compared with the literature data, and the good agreement indicated the reliability of the experimental technique used in this study.

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