

# Experimental Study of Methane Hydrate Phase Equilibrium in the Presence of Polyethylene Glycol-400 Aqueous Solution

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In this communication, we report dissociation conditions of methane hydrates in the presence of (0.1 and 0.4) mass fractions of polyethylene glycol-400 aqueous solutions in the temperature ranges of (276.8 to 287.3) K and (276.1 to 285.6) K, respectively. The equilibrium data were measured using an isochoric pressure-search method. It is shown that low concentration of polyethylene glycol 400 in aqueous solution has almost no inhibition effect on the dissociation conditions of methane hydrates, while this effect is not ignorable at high concentrations.

## Introduction

Glycols have widely been used to inhibit formation of gas hydrates in natural gas industry.<sup>1</sup> One of the advantages of using glycols is their low loss to the gas phase due to their low vapor pressures leading to effective thermodynamic inhibition of gas hydrate formation.<sup>1</sup> The presence of glycols normally shifts phase equilibrium boundaries of gas hydrates to high pressures/low temperatures. Knowledge of gas hydrate phase equilibrium in the presence of glycol aqueous solutions is therefore of interest to avoid pipeline blockage and other operational problems in the natural gas industry.<sup>1</sup> Most of the experimental data in the literature have been reported for ethylene glycol (EG) containing systems, while the experimental measurements for other glycols containing systems are limited.<sup>1</sup> However, recent progress has been made with regard to diethylene glycol (DEG)<sup>2</sup> and triethylene glycol (TEG)<sup>3,4</sup> containing systems. Polyethylene glycol (PEG) may be used as an alternative to inhibit formation of gas hydrates. The information for this latter chemical is indeed limited.<sup>1</sup> On the other hand, no thermodynamic model has been developed to predict the hydrate inhibition effect of PEG-400 aqueous solutions to our knowledge.

It is the intention of this work to report the dissociation conditions of methane hydrates in the presence of different PEG-400 aqueous solutions at various temperatures (Table 1). The equilibrium data were measured using an isochoric pressure-search method.<sup>2–6</sup> The experimental data generated in this work on dissociation conditions of methane hydrates in the presence of PEG-400 aqueous solutions are compared with the corresponding experimental data in the presence of pure water reported in the literature<sup>6–8</sup> to identify the inhibition effects of the above-mentioned aqueous solutions.

## Experimental Section

Table 2 reports the purities and suppliers of materials used in this work. PEG-400 (produced by BASF) is a polymer with varying amounts of various glycols having an average or

**Table 1. Dissociation Temperature Ranges Studied in This Work for Methane Hydrates in the Presence of PEG-400 Aqueous Solutions**

aqueous solution system	hydrate dissociation temperature range/K
0.10 mass fraction of PEG-400	276.8 to 287.3
0.40 mass fraction of PEG-400	276.1 to 285.6

**Table 2. Purities and Suppliers of Materials<sup>a</sup>**

chemical	supplier	purity %
methane	Messer Griesheim	99.995
PEG-400	BASF (Pluriol-E400)	>99.0

<sup>a</sup> Deionized water was used in all experiments.

**Table 3. Molar Distribution of Various Glycols Constituting PEG-400 Used in This Work**

constituents of PEG-400	mole %
triethylene glycol	0.1
tetraethylene glycol	0.7
pentaethylene glycol	2.1
hexaethylene glycol	7.2
heptaethylene glycol	14.4
octaethylene glycol	19.1
nonaethylene glycol	19.2
decaethylene glycol	15.7
undecaethylene glycol	10.2
dodecaethylene glycol	5.9
tridecaethylene glycol	3.4
tetradecaethylene glycol	1.5
pentadecaethylene glycol	0.5
mean molar mass of PEG-400/g·mol <sup>-1</sup>	414.5

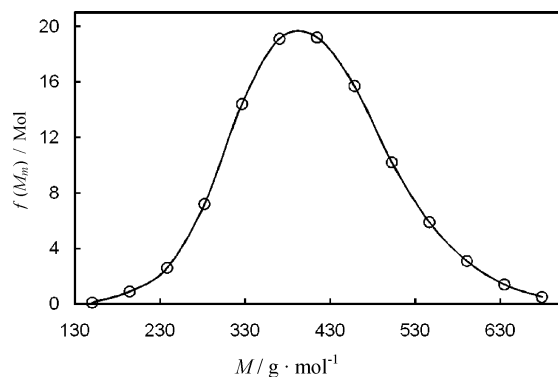
“approximately mean” molar mass of 400 g·mol<sup>-1</sup>. The “exact mean” molecular mass of the PEG-400 used in this work is 414 g·mol<sup>-1</sup>. The molar distribution of our PEG-400 is presented in Table 3. A graph between molar mass and its distribution is presented in Figure 1. PEG-400 was treated with thermal molecular sieves (UOP type 3A) to eliminate any possible impurity before using it for experimental measurements. Special precautions were taken to minimize any possibility of contamination of glycols with water from air because of their hygroscopic nature.

A description of the experimental setup used in this study is given elsewhere.<sup>2–4</sup> Figure 2 shows a schematic picture of the

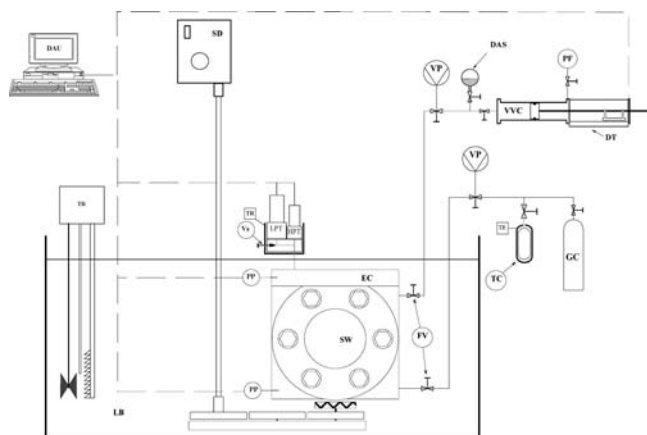
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**Figure 1.** Molar distribution [ $f(M_m)$ ] of various glycol fractions constituting polyethylene glycol-400 (PEG-400) used in this work. Symbols are based on information in Table 3, and the solid curve is the tendency curve (Source: Institut français du pétrole (IFP)).



**Figure 2.** Schematic picture of the apparatus used for measuring hydrate dissociation conditions. DAS, degassed aqueous solution; DAU, data acquisition unit with central desktop computer; DT, displacement transducer; EC, equilibrium cell; FV, feeding valve; GC, gas cylinder; HPT, high pressure transducer (in service); LB, liquid bath for controlled cooling and heating cycles; LPT, low pressure transducer (out of service); PF, pressurizing fluid; PP, platinum resistance thermometer (platinum probe) for temperature; SD, stirring device coupled magnetically with the equilibrium cell; SW, sapphire window; TC, temperature controller; TR, temperature regulator; VP, vacuum pump; Vs, separating valve of LPT; VVC, variable volume cell.

apparatus used in this work. Briefly, the main part of the apparatus is a cylindrical vessel, which can withstand pressures higher than 40 MPa. The vessel has a volume of 57.5 cm<sup>3</sup> with two sapphire windows. A magnetic stirrer ensures sufficient agitation to facilitate reaching equilibrium. The vessel was immersed inside a temperature-controlled bath to maintain the temperatures of study. Two platinum resistance thermometers (Pt100) inserted into the vessel were used to measure temperature and check for equality of temperatures within temperature measurement uncertainties, which is estimated to be less than 0.1 K. This temperature uncertainty estimation comes from careful calibration against a 25  $\Omega$  reference platinum resistance thermometer. The pressure in the vessel was measured with a DRUCK pressure transducer (Druck, type PTX611 for pressures up to 20 MPa). Pressure measurement accuracies are estimated to be better than 5 kPa. The hydrate dissociation points were measured with the isochoric pressure-search procedure.<sup>2–6</sup> The vessel containing the aqueous solution (10 % by volume of the vessel was filled by 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 vessel. Note that the vessel was evacuated before the

**Table 4.** Experimental Dissociation Data for Methane Hydrates in the Presence of PEG-400 Aqueous Solutions

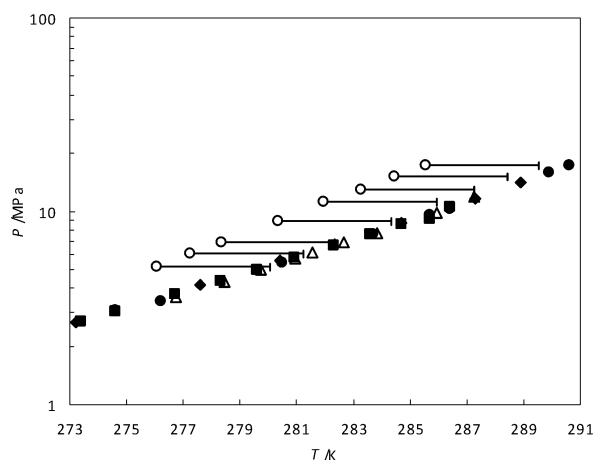
$T/K^a$	$P/MPa^b$
0.10 mass fraction PEG-400 aqueous solution	
276.8	3.58
278.5	4.34
279.8	5.01
281.0	5.67
281.6	6.15
282.7	6.88
283.9	7.70
286.0	9.83
287.3	11.90
0.40 mass fraction PEG-400 aqueous solution	
276.1	5.15
277.3	6.08
278.4	6.96
280.4	8.93
282.0	11.15
283.3	12.97
284.5	15.20
285.6	17.37

<sup>a</sup> Uncertainty on temperatures through calibrated platinum resistance thermometers is estimated to be less than 0.1 K. <sup>b</sup> Uncertainty on pressures through calibrated pressure transducer is estimated to be less than 5 kPa.

introduction of any liquid and gas. After getting temperature and pressure stability (far enough from the hydrate formation region), the valve between the vessel and the cylinder was closed. Subsequently, the temperature was slowly decreased to form the 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 with sufficient time 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 is increased in the hydrate forming region, hydrate crystals partially dissociate, thereby substantially increasing the pressure. If the temperature is increased outside the hydrate region, only a smaller increase in the pressure is observed as a result of the change in the phase equilibria of the fluids in the vessel.<sup>9</sup> Consequently, the point at which the slope of pressure–temperature data plots changes sharply is considered to be the point at which all hydrate crystals have dissociated and hence reported as the dissociation point.

## Results and Discussion

All the experimental data are reported in Table 4 and are plotted in Figure 3. A semilogarithmic scale has been used in this figure to show the data consistency, as the logarithm of hydrate dissociation pressure versus temperature has approximately linear behavior. The experimental data on the dissociation conditions of methane hydrates in the presence of pure water reported in the literature<sup>6–8</sup> have also been shown in this figure to identify the thermodynamic inhibition effects of aqueous solutions. In Figure 3, it is observed that the inhibition effect of PEG-400 aqueous solution is ignorable at 0.10 mass fraction (0.0048 mol fraction) of PEG-400 as the hydrate dissociation conditions of methane in the presence of 0.10 mass fraction PEG-400 aqueous solution cover the dissociation conditions of methane hydrates in the presence of pure water. The thermodynamic inhibition effect is however considerable at 0.40 mass fraction (0.0282 mol fraction) of PEG-400. The presence of 0.40 mass fraction PEG-400 in the aqueous solution suppresses the hydrate dissociation temperatures to approximately 4 K. The



**Figure 3.** Experimental dissociation conditions of methane hydrates in the presence of pure water and PEG-400 aqueous solutions. Symbols, experimental data: ○, 0.40 mass fraction PEG-400 aqueous solution, this work; △, 0.10 mass fraction PEG-400 aqueous solution, this work; ●, pure water, literature data;<sup>6</sup> ◆, pure water, literature data;<sup>7</sup> ■, pure water, literature data.<sup>8</sup> Band: 4 K. The best fits to experimental data have not been shown to eliminate any confusion.

corresponding hydrate suppression temperatures due to the presence of 0.40 mass fraction (0.1621 mol fraction) EG, 0.40 mass fraction (0.1016 mol fraction) DEG, and 0.40 mass fraction (0.0740 mol fraction) TEG in the aqueous solutions are approximated (16, 10.5, and 8.5) K, respectively,<sup>10</sup> indicating that although a high concentration of PEG-400 in aqueous solutions thermodynamically inhibits dissociation of methane hydrates its inhibition is much less than the corresponding inhibitions with the EG, DEG, or TEG aqueous solutions.

## Conclusions

We reported experimental data on dissociation conditions of methane hydrates in the presence of different PEG-400 aqueous solutions at various temperatures (Table 1). An isochoric pressure-search method<sup>2–6</sup> was used in all the measurements. The experimental data on hydrate dissociation conditions of methane in the presence of PEG-400 aqueous solutions were compared with the corresponding experimental data reported in the literature in the presence of pure water<sup>6–8</sup> to study thermodynamic inhibition effects of PEG-400 aqueous solutions. It was shown that 0.10 mass fraction PEG-400 aqueous solution has almost no thermodynamic inhibition effect on methane

hydrates, while the corresponding effect with 0.40 mass fraction PEG-400 aqueous solution is considerable. Using the predictions of a reliable general correlation,<sup>10</sup> it was shown that the thermodynamic inhibition effect of 0.40 mass fraction PEG-400 aqueous solution is much less than the corresponding inhibition effects when using EG, DEG, or TEG aqueous solutions.

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