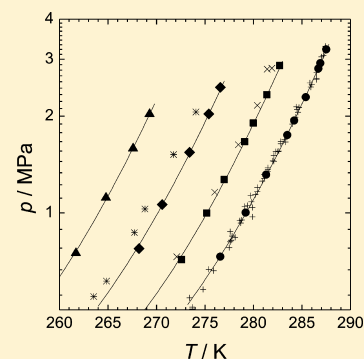


Equilibrium Conditions of Ethane Hydrates in the Presence of Aqueous Solutions of Alcohols, Glycols, and Glycerol

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ABSTRACT: Equilibrium conditions of ethane hydrates in aqueous solutions of methanol, ethanol, ethylene glycol, diethylene glycol, triethylene glycol, and glycerol were experimentally measured at temperatures ranging from (261.6 to 285.9) K and pressures of up to 3.12 MPa using an isochoric method. On a mass fraction basis, the inhibiting effect on ethane hydrate formation decreased in the following order: methanol > ethanol > ethylene glycol > glycerol \approx diethylene glycol > triethylene glycol.



INTRODUCTION

Gas hydrates are crystalline compounds formed by hydrogen-bonded water molecules encapsulating small gas molecules such as methane. Natural gas hydrates containing methane are serious concerns in the gas and oil industry because they can result in the blockage of pipelines and processing facilities. A substantial amount of studies on hydrate stability has been performed to identify ways to inhibit hydrate formation. The addition of chemicals such as alcohols and glycols, which shifts the hydrate equilibria to lower temperatures and higher pressures, is a widely used method in the industry for inhibiting hydrate formation.

The present study is part of a continuing study on gas hydrate equilibria in solutions containing chemical inhibitors. Previously, the inhibiting effects of alcohols, glycols, and glycerol on hydrate equilibria of propane or carbon dioxide were experimentally investigated.^{2,3} In the present study, new experimental data on ethane hydrate equilibria in the presence of chemical solutions over a wide range of concentrations are presented. Ethane is usually found in commercially produced natural gas and can also form a hydrate with water under suitable temperature and pressure conditions. Furthermore, the inhibiting effects of the chemicals on ethane hydrate equilibria were investigated and compared to those on propane and carbon dioxide hydrate equilibria.

The chemicals used in the present study included methanol, ethanol, ethylene glycol, diethylene glycol, triethylene glycol, and glycerol. The measurements of ethane hydrate equilibria were made at temperatures ranging from (261.6 to 285.9) K and pressures of up to 3.12 MPa using an isochoric method. To validate the experimental technique performed in the present study, ethane hydrate equilibria in pure water were also measured.

EXPERIMENTAL SECTION

Materials. Deionized water was distilled before use. Ethane of research grade purity was supplied by Takachiho Chemical Industrial Co., Ltd. The suppliers of the alcohols, glycols, and glycerol used in the present study are listed in Table 1.

Table 1. Chemicals Used for the Experiments with the Corresponding Supplier and Purity

chemical	supplier	purity (mass fraction basis)
methanol	Kanto Chemical Co., Inc.	>99.8 %
ethanol	Wako Pure Chemical Industries, Ltd.	>99.5 %
ethylene glycol	Kanto Chemical Co., Inc.	>99.5 %
diethylene glycol	Wako Pure Chemical Industries, Ltd.	>99.0 %
triethylene glycol	Alfa Aesar	>99.0 %
glycerol	Kanto Chemical Co., Inc.	>99.0 %

Appropriate amounts of the chemicals and distilled water were weighed on an electronic balance with a resolution of 0.01 g and mixed thoroughly at room temperature. The uncertainties in the composition of the solutions were less than ± 0.0002 on a mass fraction basis.

Experimental Apparatus. The experimental apparatus used in the present study is the same as that used in previous studies.^{3,4} A cylindrical stainless-steel cell with a volume of approximately 1000 cm³ was immersed in a glycol–water bath, the temperature of which was controlled by an external heater

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and refrigeration unit. The cell was equipped with a mixer to agitate the solution and hydrate. The temperature and pressure inside the cell were measured with a platinum resistance thermometer and a semiconductor pressure transducer, respectively. The estimated uncertainties of the temperature and pressure were ± 0.2 K and ± 0.04 MPa, respectively.

Experimental Procedures. Hydrate equilibrium conditions were measured using an isochoric method similar to those used in previous studies.^{3,4} In each experimental run, approximately 700 cm³ of solution was charged into the cell. The cell was repeatedly flushed with ethane, and ethane was then introduced into the cell until the desired pressure was reached. The vent valve of the cell was closed, and the temperature was then lowered for hydrate formation.

Hydrate formation can be detected by a rapid pressure drop due to the encapsulation of ethane in the hydrate. After hydrate formation, the temperature was raised to a temperature slightly lower than the predicted equilibrium temperature. The temperature was subsequently raised in steps of 0.1 K to dissociate the hydrate. At every step, the temperature was kept constant for 3 h to achieve a steady equilibrium state. While the temperature was raised in the presence of the hydrate, a marked increase in pressure was observed at each step due to the partial dissociation of the hydrate. In contrast, once the hydrate completely dissociated, only a small pressure increase was observed due to thermal expansion and fluid phase equilibria. The point at which the slope of the measured pressure to temperature abruptly changed is considered to be the hydrate dissociation point, which is also the hydrate equilibrium condition.

RESULTS AND DISCUSSION

The obtained equilibrium conditions of ethane hydrates in aqueous solutions of alcohols, glycols, and glycerol are summarized in Tables 2, 3, and 4, respectively. The obtained conditions are also shown graphically in Figures 1 to 6 along with the corresponding data from the literature. To validate the experimental technique performed in the present study, the results of ethane hydrate in pure water were compared to previously reported data (Figure 1). The comparison indicated that the present results obtained using the isochoric procedure are consistent with the previous data.

The equilibrium conditions for pure water obtained in the present study were correlated from a least-squares regression to obtain the equation:

$$\ln(p/\text{MPa}) = -2726.64 + 106675/(T/\text{K}) + 416.2985 \ln(T/\text{K}) \quad (1)$$

where p and T are the equilibrium pressure and temperature, respectively. The equation indicates the phase equilibria for an ethane-rich vapor + water-rich liquid + ethane hydrate system. The absolute mean deviation of the calculated pressure (AAD %) is 0.66 % from the following equation:

$$\text{AAD}\% = \frac{1}{N} \sum |(p_{\text{exp}} - p_{\text{cal}})/p_{\text{exp}}| \cdot 100 \quad (2)$$

where N is the number of data. The regression curves are also shown in Figures 1 to 6.

As shown in the figures, the addition of the chemicals shifts the ethane hydrate equilibrium to a lower temperature and higher pressure. The data sets for ethane hydrate equilibria in each solution essentially parallel the regression curve for pure

Table 2. Equilibrium Conditions of Ethane Hydrates in Pure Water and Aqueous Solutions of Alcohols (w = Mass Fraction of Alcohol)

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
Pure Water					
276.6	0.73	283.5	1.74	286.7	2.81
279.2	1.00	284.2	1.94	286.9	2.92
281.3	1.31	285.4	2.29	287.5	3.22
Methanol ($w = 0.10$)					
272.6	0.72	279.1	1.67	282.7	2.87
275.2	1.00	280.0	1.90		
277.0	1.27	281.4	2.33		
Methanol ($w = 0.20$)					
268.2	0.78	273.4	1.54	276.6	2.46
270.6	1.06	275.4	2.03		
Methanol ($w = 0.30$)					
261.7	0.75	267.6	1.59		
264.8	1.12	269.3	2.03		
Ethanol ($w = 0.10$)					
273.5	0.68	280.1	1.63	283.9	2.85
278.0	1.23	282.5	2.28		
Ethanol ($w = 0.20$)					
271.0	0.80	275.9	1.48	279.8	2.62
272.4	0.94	278.3	2.08		
Ethanol ($w = 0.30$)					
265.6	0.73	271.0	1.38	274.9	2.33
268.1	0.97	273.0	1.79		

water. The best-fit curves for different concentrations of solutions, which are parallel to the regression curve for pure water, are also shown in the figures.

As shown in Figure 1, the present results for methanol solutions are in agreement with the data previously reported by Ng and Robinson⁵ for the 0.10 mass fraction methanol solution, while there is disagreement for the 0.20 mass fraction methanol. This discrepancy may be due to the use of an isothermal procedure with visual observation by Ng and Robinson⁵ since visual techniques can lead to inaccurate results for determining the hydrate equilibria, as pointed out by Tohidi et al.⁶ For ethanol and ethylene glycol solutions shown in Figures 2 and 3, the present results are in good agreement with the corresponding previously reported data.^{7–9} New experimental data are presented for ethanol and ethylene glycol solutions of up to 0.30 and 0.40 mass fractions, respectively. Afzal et al.¹⁰ reported on ethane hydrate equilibria in the presence of diethylene glycol solutions of up to 0.163 mass fraction. Additional data for solutions of up to 0.50 mass fraction are shown in Figure 4. The present results for the triethylene glycol and glycerol solutions are in disagreement with some of the previously reported experimental data (Figures 5 and 6). The reason for this discrepancy remains unclear. However, the temperature differences are within approximately 2 K. In the present study, the ethane hydrate equilibria were investigated for solutions of up to 0.50 mass fraction.

To investigate the inhibiting effect of the chemicals on ethane hydrate formation, the temperature difference, ΔT , between ethane hydrate equilibria in pure water and each chemical solution was obtained, assuming that each set of ethane hydrate equilibria in a solution ran parallel to the regression curve obtained for pure water. The temperature difference was calculated using the following equation:

Table 3. Equilibrium Conditions of Ethane Hydrates in Aqueous Solutions of Glycols (w = Mass Fraction of Glycol)

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
Ethylene Glycol ($w = 0.10$)					
275.1	0.84	281.2	1.73	284.3	2.79
278.8	1.30	283.0	2.27		
Ethylene Glycol ($w = 0.20$)					
270.9	0.68	276.5	1.40	280.5	2.52
274.6	1.10	279.0	1.99		
Ethylene Glycol ($w = 0.30$)					
267.7	0.74	273.5	1.58	276.4	2.46
270.7	1.09	275.4	2.07		
Ethylene Glycol ($w = 0.40$)					
263.1	0.84	268.3	1.64		
266.3	1.24	270.3	2.10		
Diethylene Glycol ($w = 0.10$)					
276.1	0.78	281.8	1.68	285.9	3.12
279.5	1.22	284.1	2.31		
Diethylene Glycol ($w = 0.20$)					
273.2	0.72	279.4	1.59	282.9	2.60
276.7	1.14	281.8	2.21		
Diethylene Glycol ($w = 0.30$)					
271.1	0.76	276.4	1.52	280.4	2.74
273.8	1.06	279.0	2.18		
Diethylene Glycol ($w = 0.40$)					
267.4	0.79	273.6	1.75		
271.3	1.30	275.8	2.38		
Diethylene Glycol ($w = 0.50$)					
261.6	0.77	267.2	1.55		
265.1	1.18	269.1	2.01		
Triethylene Glycol ($w = 0.10$)					
276.9	0.83	280.6	1.36	285.1	2.53
279.8	1.22	283.3	1.95	286.3	3.09
Triethylene Glycol ($w = 0.20$)					
273.7	0.70	281.1	1.77	284.7	3.03
278.4	1.24	283.4	2.44		
Triethylene Glycol ($w = 0.30$)					
272.3	0.76	278.0	1.59	281.9	2.81
274.8	1.04	280.3	2.20		
Triethylene Glycol ($w = 0.40$)					
269.8	0.84	275.5	1.75		
273.1	1.27	277.9	2.43		
Triethylene Glycol ($w = 0.50$)					
264.4	0.82	269.8	1.60		
266.9	1.10	272.2	2.24		

$$\Delta T = T_0 - T_s \quad (3)$$

where T_0 and T_s are the hydrate equilibrium temperatures at a given pressure for pure water and a solution, respectively. The calculated ΔT values are shown in Table 5 and Figure 7.

The inhibiting effects of the different chemicals on ethane hydrate equilibria can be observed by comparing the temperature differences for solutions containing the same mass fraction of each chemical. As shown in Figure 7, methanol is the most effective in inhibiting ethane hydrate formation, followed by ethanol and ethylene glycol. Glycerol is more effective than diethylene glycol for solutions of up to 0.40 mass fraction, while diethylene glycol is slightly more effective than glycerol for a solution of 0.50 mass fraction. Triethylene glycol has the least inhibiting effect on ethane hydrate formation. Therefore, on a mass fraction basis, the inhibiting effect of

Table 4. Equilibrium Conditions of Ethane Hydrates in Aqueous Solutions of Glycerol (w = Mass Fraction of Glycerol)

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
Glycerol ($w = 0.10$)					
275.2	0.73	280.8	1.49	285.6	3.06
277.9	1.02	283.8	2.26		
Glycerol ($w = 0.20$)					
271.2	0.59	277.3	1.25	282.1	2.41
273.3	0.75	279.9	1.75	283.2	2.84
Glycerol ($w = 0.30$)					
271.5	0.82	278.2	2.02		
275.2	1.33	279.9	2.65		
Glycerol ($w = 0.40$)					
266.8	0.74	273.9	1.83		
271.2	1.29	275.7	2.46		
Glycerol ($w = 0.50$)					
263.2	0.88	267.7	1.60		
264.9	1.11	269.4	2.09		

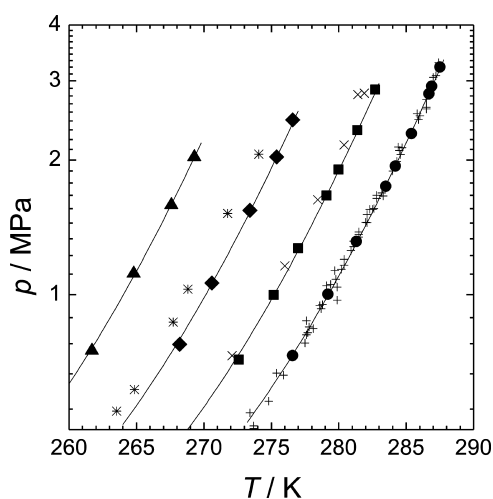


Figure 1. Ethane hydrate equilibrium conditions in pure water and aqueous methanol solutions. ●, present study (pure water); ■, present study ($w = 0.10$); ◆, present study ($w = 0.20$); ▲, present study ($w = 0.30$); +, ref 1 (pure water); ×, ref 5 ($w = 0.10$); *, ref 5 ($w = 0.20$). Solid curves are best-fit curves for each set of experimental data which are parallel to the regression curve obtained for pure water.

chemicals on ethane hydrate equilibria decreases in the following order: methanol > ethanol > ethylene glycol > glycerol \approx diethylene glycol > triethylene glycol. The order of the inhibiting effect is the same as those obtained for propane and carbon dioxide hydrate equilibria,^{2,3} although the temperature difference for ethane hydrate is slightly smaller than those for propane and carbon dioxide hydrates for the same concentration of the solutions.

Alternatively, to approximate the temperature suppression due to the addition of chemicals, Hammerschmidt¹³ presented a semiempirical equation:

$$\Delta T = \frac{1297W}{100M - MW} \quad (4)$$

where ΔT is the temperature difference in K, M is the molecular weight of the chemical, and W is the concentration of the chemical measured as mass percent in the solution. The

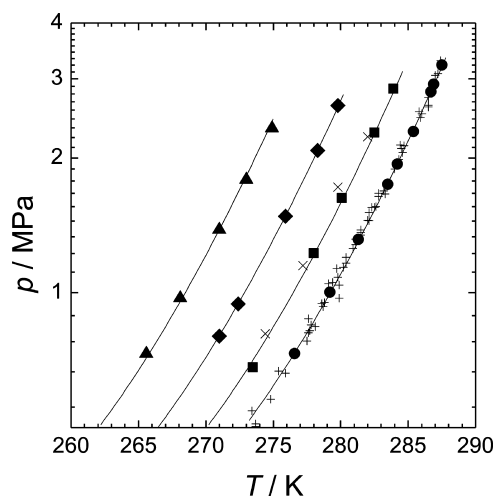


Figure 2. Ethane hydrate equilibrium conditions in aqueous ethanol solutions. ●, present study (pure water); ■, present study ($w = 0.10$); ◆, present study ($w = 0.20$); ▲, present study ($w = 0.30$); +, ref 1 (pure water); ×, ref 7 ($w = 0.10$).

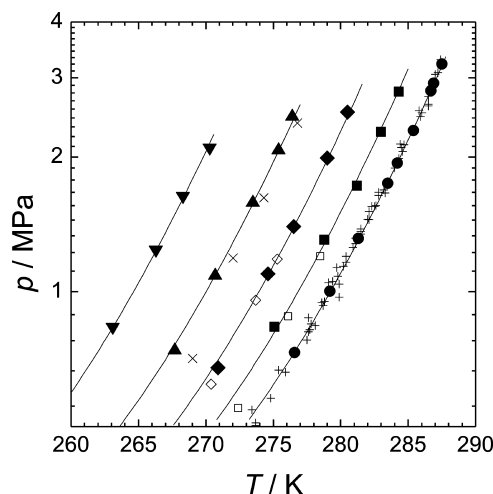


Figure 3. Ethane hydrate equilibrium conditions in aqueous ethylene glycol solutions. ●, present study (pure water); ■, present study ($w = 0.10$); ◆, present study ($w = 0.20$); ▲, present study ($w = 0.30$); ▼, present study ($w = 0.40$); +, ref 1 (pure water); □, ref 8 ($w = 0.10$), ◇, ref 8 ($w = 0.20$), ×, ref 9 ($w = 0.30$).

calculated values from the Hammerschmidt equation are also shown in Table 5.

In addition, Østergaard et al.¹⁴ also presented the correlation of temperature suppression of hydrate equilibria caused by the chemicals as the following equation:

$$\Delta T = (C_1 W + C_2 W^2 + C_3 W^3) \cdot (C_4 \ln(P) + C_5) \cdot (C_6 (P_0 - 1000) + 1) \quad (5)$$

where P is pressure of the system (in kPa), W is the concentration of the chemicals in aqueous phase (in mass %), P_0 is the dissociation pressure of hydrocarbon in the presence of pure water at 273.15 K (in kPa), and C_1 to C_6 are constants which depend on the chemicals. Since the correlation depends on the pressure of the system, the values were calculated assuming that the pressure of the system is 1.5 MPa, as shown in Table 5.

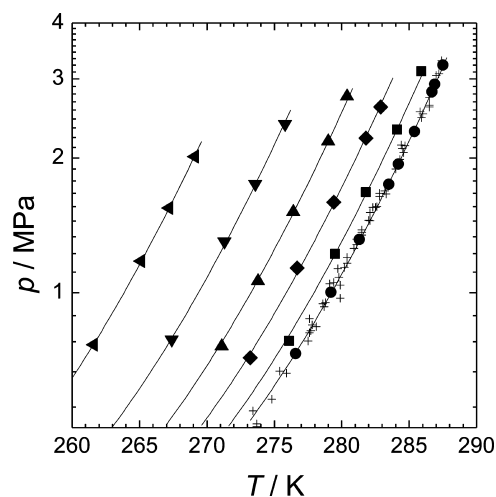


Figure 4. Ethane hydrate equilibrium conditions in aqueous diethylene glycol solutions. ●, present study (pure water); ■, present study ($w = 0.10$); ◆, present study ($w = 0.20$); ▲, present study ($w = 0.30$); ▼, present study ($w = 0.40$); ◀, present study ($w = 0.50$); +, ref 1 (pure water).

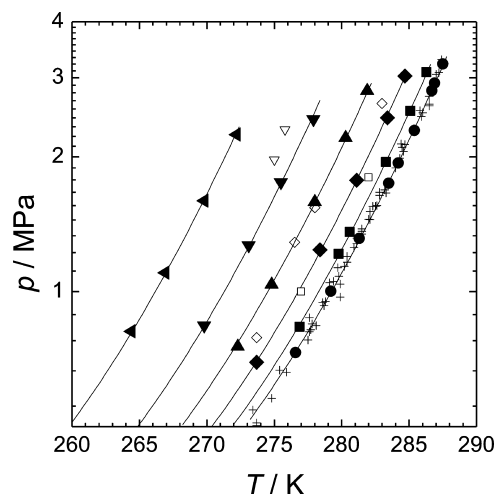


Figure 5. Ethane hydrate equilibrium conditions in aqueous triethylene glycol solutions. ●, present study (pure water); ■, present study ($w = 0.10$); ◆, present study ($w = 0.20$); ▲, present study ($w = 0.30$); ▼, present study ($w = 0.40$); ◀, present study ($w = 0.50$); +, ref 1 (pure water); □, ref 11 ($w = 0.10$); ◇, ref 11 ($w = 0.20$); ▽, ref 11 ($w = 0.40$).

The order of inhibiting effects obtained experimentally is the same as that calculated by the Hammerschmidt equation for lower concentrations of solutions. However, the experimental and calculated values are slightly different. On the other hand, the values calculated from the correlation of Østergaard et al. are in good agreement with the present results over the whole concentrations range of the chemicals except for glycerol.

CONCLUSIONS

The equilibrium conditions of ethane hydrates in aqueous solutions of methanol, ethanol, ethylene glycol, diethylene glycol, triethylene glycol, and glycerol were experimentally measured at temperatures ranging from (261.6 to 285.9) K and pressures of up to 3.12 MPa using the isochoric method. The set of ethane hydrate equilibria for each chemical solution essentially paralleled the results obtained for pure water. The

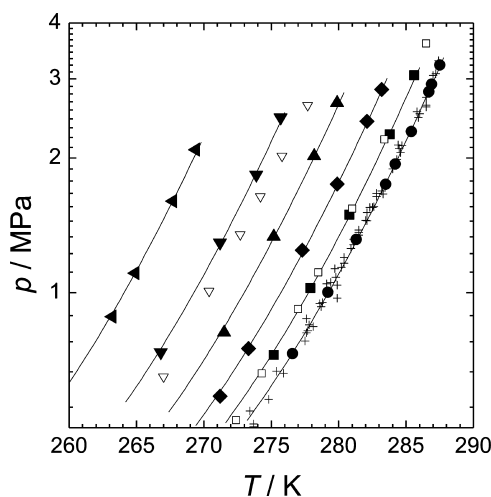


Figure 6. Ethane hydrate equilibrium conditions in aqueous glycerol solutions. ●, present study (pure water); ■, present study ($w = 0.10$); ◆, present study ($w = 0.20$); ▲, present study ($w = 0.30$); ▼, present study ($w = 0.40$); ◀, present study ($w = 0.50$); +, ref 1 (pure water); □, ref 12 ($w = 0.10$); ▽, ref 12 ($w = 0.40$).

Table 5. Temperature Differences in Ethane Hydrate Equilibria between Each Chemical Solution ($w = \text{Mass Fraction of the Chemical}$) and Pure Water

chemical	w	ΔT^a	ΔT^b	ΔT^c	ΔT^d	ΔT^e
		K	K	K	K	K
methanol	0.10	4.0	4.5	4.9	4.5	4.4
	0.20	9.1	10.1		10.1	9.8
	0.30	15.2			17.3	16.3
ethanol	0.10	2.8	3.2	3.5	3.1	3.0
	0.20	6.4	6.9		7.0	6.9
	0.30	10.8			12.1	12.7
ethylene glycol	0.10	2.4	2.6	2.8	2.3	2.7
	0.20	5.3	5.8	6.4	5.2	5.4
	0.30	9.2	10.0		9.0	8.9
	0.40	14.6			13.9	14.0
diethylene glycol	0.10	1.3	1.5	1.7	1.4	1.5
	0.20	3.3	3.7	4.1	3.1	3.3
	0.30	6.0	6.6		5.2	5.8
	0.40	9.9			8.1	9.8
	0.50	15.4			12.2	15.4
triethylene glycol	0.10	0.9	1.1	1.2	1.0	1.6
	0.20	2.5	2.8	3.1	2.2	2.8
	0.30	4.7	5.2		3.7	4.6
	0.40	8.0	8.7		5.8	7.8
	0.50	13.1			8.6	13.3
glycerol	0.10	1.5	1.7	1.9	1.6	1.0
	0.20	3.5	3.9	4.3	3.5	2.9
	0.30	6.3	6.8		6.0	5.4
	0.40	10.0			9.4	8.7
	0.50	15.2			14.1	12.7

^aPresent study for ethane hydrate. ^bMaekawa³ for carbon dioxide hydrate. ^cMaekawa² for propane hydrate. ^dHammerschmidt equation.¹³ ^eCalculated by the correlation proposed by Østergaard et al.¹⁴ (assuming $P = 1.5$ MPa).

inhibiting effect of chemicals on ethane hydrate equilibria on a mass fraction basis decreased in the following order: methanol > ethanol > ethylene glycol > glycerol \approx diethylene glycol > triethylene glycol.

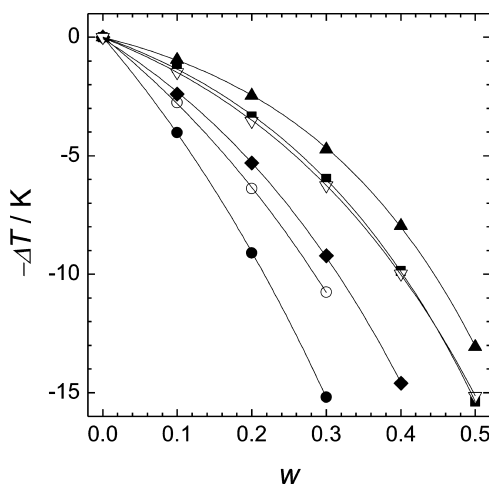


Figure 7. Temperature suppression for ethane hydrate equilibria due to the addition of chemicals. ●, methanol; ○, ethanol; ◆, ethylene glycol; ■, diethylene glycol; ▲, triethylene glycol; ▽, glycerol. Solid curves are best-fit curves for the temperature suppressions for the different chemicals.

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