

Research Article

Isotope Effect on Eutectic and Hydrate Melting Temperatures in the Water-THF System

C. Y. Jones,¹ J. S. Zhang,² and J. W. Lee²

¹Department of Chemistry, Hamilton College, Clinton, NY 13323, USA

²Department of Chemical Engineering, The City College of the CUNY, NY 10031, USA

Correspondence should be addressed to C. Y. Jones, cyjones@hamilton.edu

Received 24 July 2009; Accepted 3 December 2009

Academic Editor: Angelo Lucia

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Differential scanning calorimetry was used to study the effect of isotopic substitution on the eutectic and melting temperatures in the water-tetrahydrofuran (THF) system with THF molar fractions near the stoichiometry of the hydrate phase. Deuteration of the host causes an opposite effect from that of the guest with respect to the hydrate liquidus curve and eutectic melting temperature. The eutectic temperature in D₂O-containing systems is approximately 3.7 K higher than that in H₂O-containing systems. The melting temperatures of THF and deuterated THF hydrates increase by roughly 3.5 K with heavy water. The inclusion of deuterated THF causes a depression of the hydrate liquidus temperatures and a small but measurable effect on the eutectic temperature.

1. Introduction

Tetrahydrofuran (THF, C₄H₈O) hydrate plays a prominent role in the study of numerous hydrate properties, for example, their formation [1], structure [2], and dynamics [3]. The reasons for this prominent role are practical ones: THF is water-soluble, is readily available as both hydrogenated and fully deuterated compounds of high purity, and its aqueous solutions form hydrates under mild conditions at atmospheric pressure. Maximum melting points for THF hydrate have been reported in the range of (277.15–278.15) K [4–8]. Because of the ease with which THF hydrate forms, and the fact that at room temperature water and THF are completely miscible, the rather complex phase behavior taking place in this system is not apparent. In fact, the tetrahydrofuran-water system displays complex liquid-phase behavior, with regions of high-temperature and low-temperature immiscibility; several features of the *P-T-x* space of the THF-water system are shown in Figure 1. Matouš et al. [4] identified a broad, closed loop with lower and upper consolute temperatures of approximately 344 K (53.5 wt%) and 410 K (48 wt%), respectively. Their study, and a more recent one by Balevicius et al. [5], were undertaken to characterize the critical behavior in the system and clarify and describe

substantial isotope effects on liquid miscibility. Rosso and Carbonnel [6] and Carbonnel and Rosso [7] determined the phase diagram at low temperatures and found a miscibility gap with a critical temperature of approximately 286 K and a peritectic reaction at 278 K forming the structure II clathrate hydrate at a composition of 17 : 1 H₂O : THF. This makes the structure II hydrate an incongruently melting phase. A transformation of the structure II hydrate to the structure I form has been observed at 255 K and 34 MPa [8] and 77 K and 131 MPa [9]. Manakov et al. [10] characterized the THF-water system at high pressure and found a high-temperature hydrate phase with room temperature stability in the range of 4.9–30 MPa.

Studies have been conducted on both the hydrogenated and deuterated forms of THF hydrate, depending on the nature of the property being investigated. However, the dramatic nature of the H/D isotope effect causes changes in both the physical and chemical properties of binary mixtures or water and water-miscible organic solvents. Oleinikova and Weingärtner [11] studied the effect of the H/D isotopic composition on the shape of the immiscibility loop in the THF-water binary system. In these studies, they observed a shrinking of the miscibility gap in the presence of THF-*d*8 and a widening of the gap in the presence of D₂O. Isotope

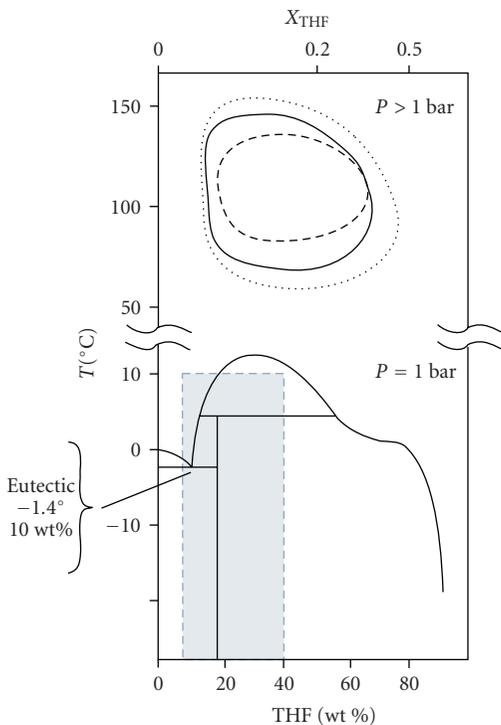


FIGURE 1: Schematic of the T - x phase diagram of the water-THF system (solid lines), taken from the published phase diagrams of Rosso and Carbonnel ($T < 50^\circ\text{C}$), Carbonnel and Rosso ($T < 50^\circ\text{C}$) and Balevicius et al. ($T < 50^\circ\text{C}$). The gray solvus curves represent the widening (dotted) and narrowing (dashed) of the miscibility gap with deuteration of water and THF, respectively.

effects are also evident in the crystal structure determinations of clathrate hydrates, due to the covalent distances being longer and the hydrogen bonds being stronger in D_2O than those in H_2O .

Understanding how the behavior in the THF-water and other hydrate systems is affected by isotope substitution is critical to developing a complete understanding of their stability. Hanley et al. [12] previously measured the isotope effect on cooling curves in the THF-water system, where substitution with D_2O shifts the curve to higher temperatures. Based on the results of Balevicius et al. [5] a guest isotope effect on the phase equilibria of the solid phases might be predicted as well. In this work, we use differential scanning calorimetry (DSC) to study the effect of isotopic substitution in both THF and water on the eutectic and hydrate melting temperatures in water-tetrahydrofuran systems. The quantum effects responsible for the H/D isotope effect on the tetrahedral, hydrogen-bonded structures formed by H_2O and D_2O are well known; however, the H/D effects on hydrate crystal structure parameters and the effect of guest H/D substitution on hydrate properties have not been studied systematically, even though results from studies of both hydrogenated and deuterated hydrates are used routinely as models for natural hydrate systems.

2. Experimental

2.1. Materials. Tetrahydrofuran with a purity of +99% was purchased from Sigma-Aldrich. Tetrahydrofuran- d_8 with 99.9 atom% D and deuterium oxide with 99.5% D were obtained from Sigma-Aldrich. All chemicals were used as received without further purification. Deionized water was produced in our lab with a resistivity of $18\text{ M}\Omega\text{ cm}$.

2.2. Apparatus and Procedures. The eutectic and melting points were determined with a MicroDSC purchased from Setaram. A detailed description of the MicroDSC was given in a previous paper [13]. The solutions were prepared gravimetrically. The sample cells were charged with approximately 20 mg of solution, and the reference cell was empty. The sample and reference cell were cooled down to a low temperature at a rate of 3 K min^{-1} , which was usually below 248 K, and then heated to a temperature below the eutectic point at a rate of 1.2 K min^{-1} , followed by heating the cells at a rate of 0.1 K min^{-1} up to 280 K or 285 K, to allow both the ice and hydrate phases to melt. The cycle of cooling-heating was repeated at least three times for each sample, and the average values are reported in this work. The onset temperature of the eutectic melting peak is taken as the eutectic temperature, and the maximum temperature of hydrate melting peak is taken as the melting temperature.

3. Results and Discussion

3.1. Cooling Behavior. Figures 2–4 present typical cooling and heating thermograms for water-rich and THF-rich solutions. In the water-rich region, as shown in Figure 2, only a single exothermic peak is detected in the first cooling step, which is due to the freezing of hydrates and ice simultaneously. However, two exothermic peaks are observed in the subsequent cooling steps. The first and second peaks correspond to the freezing of hydrates and ice, respectively. The freezing temperature of hydrates in the subsequent cooling steps is much higher than that in the first one, which comes from the “memory effect” [14]. It should be noted here that freshly prepared THF or d -THF solutions are cloudy, but they become clear after one cooling-heating cycle. Whether the memory effect is due to the state of solutions is unclear at this point. In the THF-rich region, only one peak is observed in all cooling steps, which corresponds to the freezing of hydrates.

3.2. Heating Behavior. Figures 3 and 4 show heating behaviors in the H_2O -rich and THF-rich regions, respectively. In the H_2O -rich region, a sharp endothermic peak corresponds to the melting of the ice and some hydrate simultaneously, followed by a broad exothermic peak that is due to the dissociation of the rest of the hydrate sample. The small peak before the bulk melting event occurs where the heating rate was changed from 1.2 to 0.1 K min^{-1} . The heating rate of 0.1 K min^{-1} was selected based on measurements of the eutectic and liquidus (also called “melting”) temperatures as a function of the heating rate, as shown in Table 1.

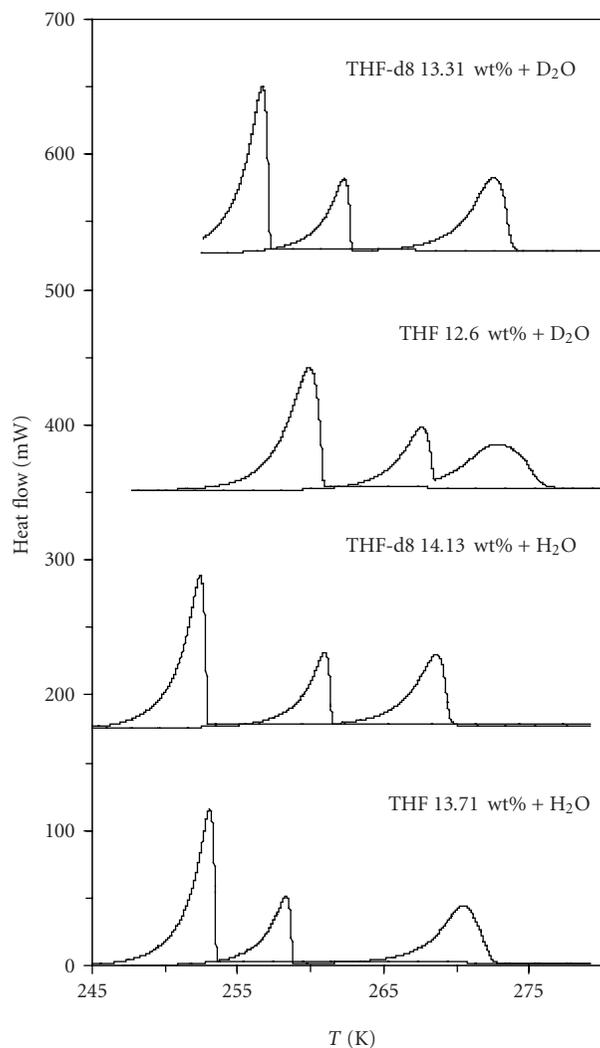


FIGURE 2: Cooling thermograms in H_2O - and D_2O -rich regions. The thin line trace is the first cooling step; the heavy line is the subsequent cooling step.

TABLE 1: Eutectic and hydrate melting temperatures as a function of the heating rate for THF (15.89 wt%)+ H_2O .

Heat rate (K min^{-1})	Eutectic melting (K)	Hydrate melting (K)
0.1	272.03	278.09
0.2	272.02	278.10
0.5	271.96	278.23
1.0	271.58	278.29

At a heating rate below 0.2 K s^{-1} , the eutectic temperature determined by the DSC used in this work is very close to the one (272.01 K) reported by Delahaye et al. [15], and the melting temperature does not change significantly under the same conditions. In the THF-rich regions, only one endothermic peak is observed that comes from the melting of hydrates.

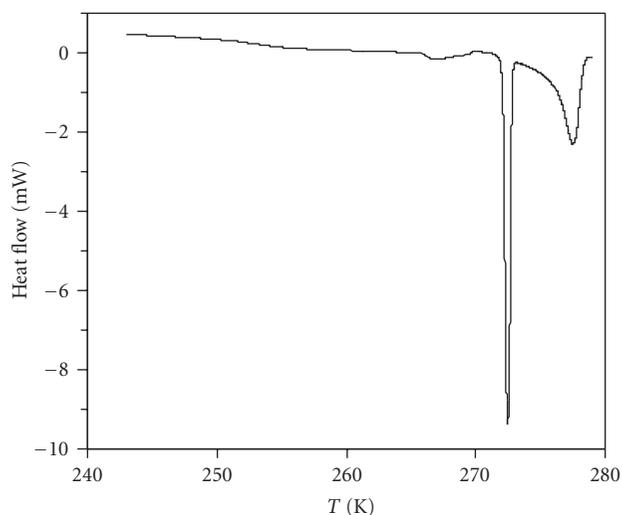
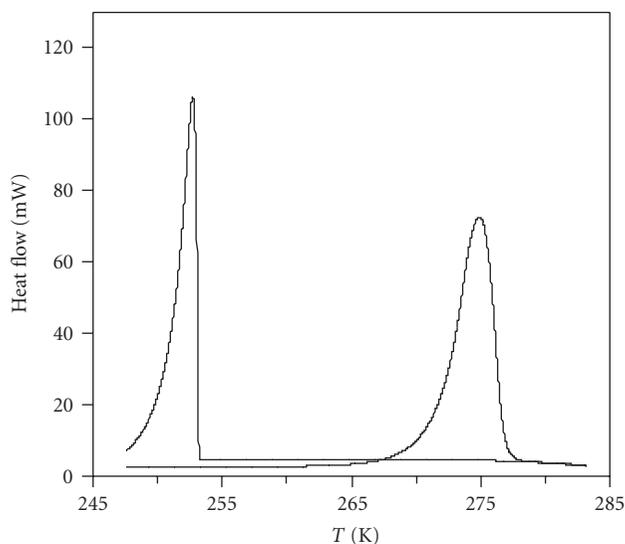


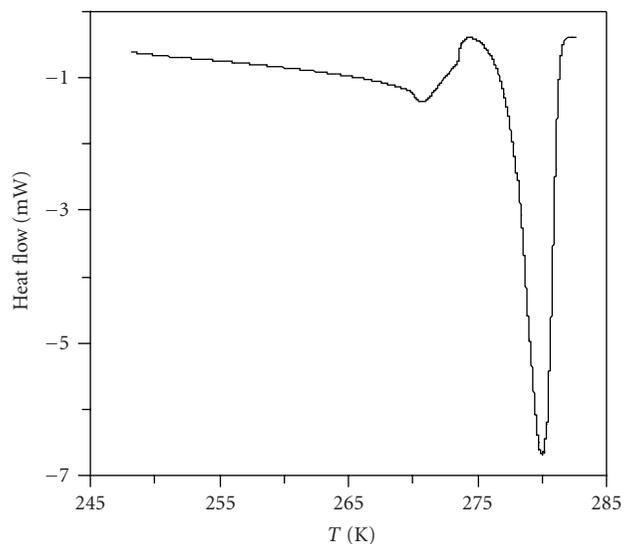
FIGURE 3: Heating thermogram for the THF (13.71%)- H_2O system.

3.3. Isotope Effects. The eutectic and melting temperatures are listed in Table 2, and the melting temperatures are also plotted in Figure 5. For both the host and the guest, the substitution of deuterium for hydrogen gives rise to statistically significant differences in the location of the liquidus. Several trends are observed. First, an increase of approximately 3–4 K in the hydrate melting temperature with heavy water is observed. Second, the eutectic temperatures increase by roughly 3.8 K with heavy water. These increases are close to difference (3.8 K) in the melting temperatures of ice and deuterated ice. Third, inclusion of deuterated THF causes an unexpected depression of the hydrate melting temperatures. The decrease ranges from (0.4–1.2) K for hydrogenated host and (0.6–1.0) K for deuterated host. Fourth, the eutectic temperature of THF-containing systems is (0.03–0.18) K higher than that in THF-*d8*-containing systems for both H_2O and D_2O . The eutectic temperatures of $\text{C}_4\text{H}_8\text{O}-\text{H}_2\text{O}$, $\text{C}_4\text{D}_8\text{O}-\text{H}_2\text{O}$, $\text{C}_4\text{H}_8\text{O}-\text{D}_2\text{O}$, and $\text{C}_4\text{D}_8\text{O}-\text{D}_2\text{O}$ systems are 272.06, 271.95, 275.78, and 275.68 K, respectively.

The melting points in the THF- H_2O and THF- D_2O systems are close to those reported by Hanley et al. [12]. Figure 6 shows their results along with the melting temperatures obtained in this study. These results show clearly the stabilizing effect of deuteration of the host, due to an increase in the strength of the hydrogen bonds, and the results presented here also indicate a small but statistically significant depression of the melting temperature when deuterated guests are enclathrated. Thus, the deuteration of the host causes an opposite effect on the melting temperatures from that of the guest. One possible explanation for this is that, for a given isotopic makeup of the host, the hydrogenated guest provides a greater entropic stabilization [16] of the hydrate structure relative to the liquid components. The mode of entropic stabilization involves guest vibrational motions, which for THF-*d8* encompass a lower range of frequencies than those of hydrogenated THF. In terms of hydrate properties, guest vibrations have



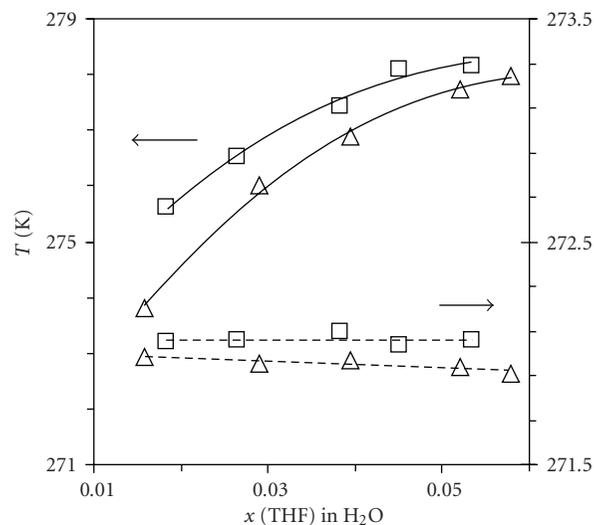
(a)



(b)

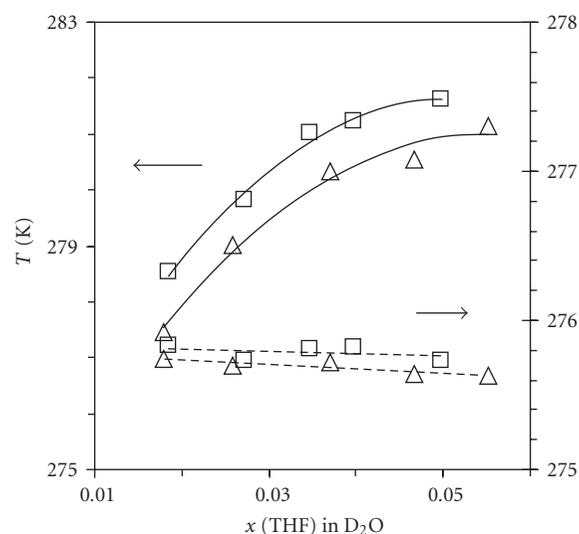
FIGURE 4: Cooling (a) and heating (b) thermograms for the THF (40.47 wt%)-D₂O system.

an enormous impact: low-frequency guest vibrations have been shown unambiguously to contribute to the low-thermal conductivity of clathrate hydrates by means of resonant scattering of lattice acoustic vibrations [17]. Beyond their impact on the thermal conductivity, guest vibrations must also play a role in the stability of the hydrate through guest-host interactions. More specifically, the rotational dynamics of large guests in general, and of large, polar guests such as THF in particular, might change sufficiently with deuteration to affect their ability to rotate within the cage potential. For polar guests, dipolar interactions and hydrogen bonding with the host could increase and lead to a decrease in the stability of the hydrate. Studies of deuterated guest molecules



□ THF
△ THF-d8

(a)



□ THF
△ THF-d8

(b)

FIGURE 5: Effect of the isotopic composition of the THF guests on the melting points of hydrates (—) and eutectic melting of hydrate/ice mixtures (---) in H₂O (a) and D₂O (b).

could therefore provide a means of examining the effect of a change in guest vibrations on thermal conductivity and other properties, while keeping the size of the guest constant.

4. Conclusion

In this study, we have used microcalorimetry to determine the effect of isotopic substitution on the eutectic and hydrate

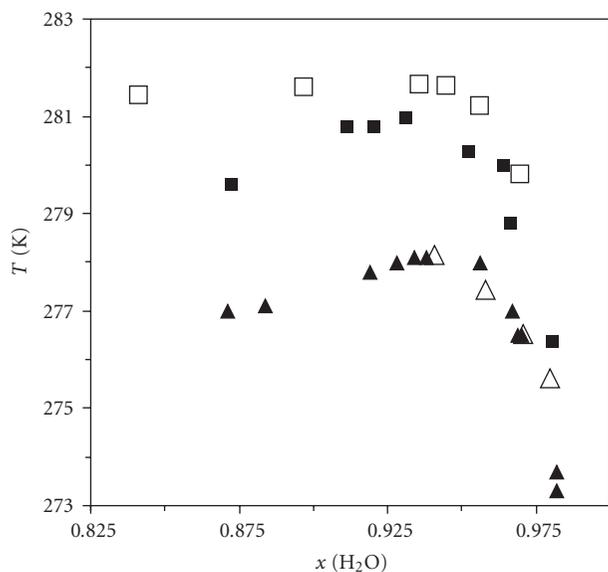


FIGURE 6: Melting points of THF-H₂O (triangles) and THF-D₂O (squares) mixtures obtained by Hanley and coworkers (filled symbols) and in this work (open symbols).

TABLE 2: Eutectic and melting points for the four isotopic THF-water mixtures. The temperatures reported are averages of 3–6 measurements; standard errors are reported for the 95% confidence limit.

Wt%	Eutectic	Hydrate melting
THF+H ₂ O		
6.95	272.05 ± 0.00	275.62 ± 0.04
9.80	272.06 ± 0.01	276.52 ± 0.08
13.71	272.10 ± 0.01	277.44 ± 0.03
15.89	272.04 ± 0.01	278.09 ± 0.02
18.43	272.06 ± 0.00	278.15 ± 0.03
THF- <i>d</i> 8+H ₂ O		
6.02	271.98 ± 0.00	273.82 ± 0.02
10.67	271.96 ± 0.01	276.02 ± 0.06
14.13	271.97 ± 0.01	276.89 ± 0.02
18.00	271.94 ± 0.00	277.73 ± 0.02
19.72	271.91 ± 0.01	277.98 ± 0.03
THF+D ₂ O		
7.00	275.83 ± 0.01	278.53 ± 0.03
10.08	275.73 ± 0.05	279.82 ± 0.04
12.60	275.81 ± 0.02	281.02 ± 0.02
14.19	275.82 ± 0.02	281.22 ± 0.02
17.34	275.73 ± 0.02	281.61 ± 0.01
THF- <i>d</i> 8+D ₂ O		
6.78	275.74 ± 0.01	277.46 ± 0.02
9.57	275.70 ± 0.00	279.01 ± 0.04
13.31	275.72 ± 0.00	280.33 ± 0.02
16.39	275.64 ± 0.01	280.54 ± 0.05
18.91	275.63 ± 0.02	281.14 ± 0.02

melting temperatures in water-THF system. We observed an increase of approximately 3–4 K in the hydrate melting temperature with heavy water and similar increases in the eutectic temperatures with heavy water. Enclathration of deuterated THF causes a depression of the hydrate melting temperatures by (0.4–1.2) K for hydrogenated host and (0.6–1.0) K for deuterated host. In addition, the eutectic temperature of THF-containing systems is (0.03–0.18) K higher than that in THF-*d*8-containing systems for both H₂O and D₂O. These results suggest that guest motions affect the thermodynamic stability of hydrates and call for more extensive calorimetric studies of phase equilibria and guest motions of deuterated molecules in a variety of clathrate hydrates as a test of the generality of the effects of guest vibrations on thermal conductivity and other properties, while the size of the guest is kept constant.

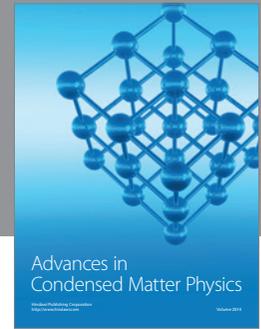
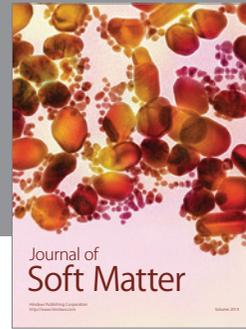
Acknowledgment

The authors are grateful for the support of National Science Foundation for this work under Grant no. CBET-0854210.

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