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Note

The Melting Curve of Tetrahydrofuran Hydrate in D_2O

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Melting points for the tetrahydrofuran/D_2O hydrate in equilibrium with the air-saturated liquid at atmospheric pressure are reported. The melting points were measured by monitoring the absorbance of the solution. Overall, the melting-point phase boundary curve is about 2.5 K greater than the corresponding curve for the H_2O hydrate, with a congruent melting temperature of 281 ± 0.5 K at a D_2O mole fraction of 0.936. The phase boundary is predicted to within 5% if the assumption is made that the THF occupancy in the D_2O and H_2O hydrates is the same. We measure an occupancy of 99.9%. The chemical potential of the empty lattice in D_2O is estimated to be 5% greater than in H_2O.

KEY WORDS: absorbance; chemical potential; deuteriohydrate; heavy water; lattice occupancy; melting points; tetrahydrofuran hydrate.

1. INTRODUCTION

The phase diagram of the tetrahydrofuran (THF) deuteriohydrate is required to support measurements on hydrate dynamics, and studies of the mechanisms of hydrate nucleation, by neutron scattering. We report the hydrate–liquid phase boundary at atmospheric pressure in this note.

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The possibility of using the small-angle neutron scattering technique of contrast matching was the prime motivation for the work. Contrast matching allows species in a mixture to be distinguished by exploiting differences in their scattering length density [1]. For example, recent work on the nucleation and growth of zeolite crystals from an aluminosilicate gel has demonstrated the power and versatility of the technique to probe the structure of mixtures with very diverse species and to investigate the kinetics of phase changes in such mixtures [2]. We believe that a similiar approach could be applied to a study of the formation and structure of hydrates.

Hydrates [3] are crystalline molecular complexes, or clathrates, formed from a lattice of water molecules around a guest molecule, and the scattering density of the unit cage can be markedly different from that of water or the guest molecule when D_2O is substituted for H_2O. Thermodynamic data for a D_2O–hydrate are scarce, however, and only the D_2O–cyclopropane system has been studied in depth [4]. (Some measurements were made for the krypton and xenon hydrates [5], and the motion of the guest tetrahydrofuran molecule in the D_2O lattice at very low temperatures has been discussed by Davidson and coauthors [6].)

2. EXPERIMENTAL

The phase boundary of the hydrate mixture was determined by recording the melting points of the solid hydrate in equilibrium with the solution as a function of THF mole fraction. The melting point of the mixture at a given temperature (*T*) was estimated by the optical turbidity, measured by the change in apparent beam absorbance using a commercial uv/vis spectrophotometer. The solid has an absorbance of about 1, whereas the absorbance of the liquid is essentially zero.

We first worked with THF/H_2O solutions to establish the method. The THF/H_2O hydrate phase diagram is well known [7–9]. A solution was prepared from 99.9% pure THF and doubly distilled H_2O at a given mass fraction of THF and placed in a standard spectrophotometer cell fitted with a mechanical stirrer and a calibrated copper–constantan thermocouple. The temperature was estimated to be accurate to 0.05 K, and temperature gradients in the sample cell were negligible. For all runs, the spectrophotometer was balanced with the sample cell at about 1 K above its estimated hydrate freezing temperature with respect to an identical cell containing an 0.8 mole fraction THF/H_2O solution at room temperature. The balance was not affected by temperature over the limited range of our experiments, or by the rate of stirring of the sample. The sample solution was cooled rapidly with agitation to just above the ice point to initiate hydrate formation and then set to equilibrate with stirring at about a degree kelvin below the estimated hydrate melting point of the temperature of interest. We found that although nucleation would take hours or even days without agitation in general, nucleation was essentially instantaneous (of the order of seconds) for H_2O mole fractions less than 0.7.

After equilibration at constant temperature and absorbance, the temperature of the sample was ramped-up at $0.1\ K \cdot min^{-1}$, and the absorbance and temperature were plotted as a function of time. The melting point was taken to be the temperature at which the absorbance fell. The assignment of a definite break in the absorbance curve was the principle source of uncertainty in determining the transition temperature since the absorbance was affected by how rapidly the hydrate crystals dispersed. Repeated runs for a given sample reduced this uncertainty to between 0.1 and 0.7 K, depending on the THF mole fraction. Our THF/H_2O melting points agreed with the literature values [7, 8] to within 0.2 K at corresponding mole fractions.

The procedure was repeated for 99.75 D-% D_2O as the solvent. The results with our estimate of error are given in Table I and plotted in Fig. 1 as a function of the mole fraction of $D_2O(x_d)$. Included in Fig. 1 is a composite of our THF/H_2O data and data from Ref. 8, plotted at roughly equivalent mole fractions of $H_2O(x_w)$. Given that the congruent melting

Table I. The Melting Points of THF Hydrate in D_2O and H_2O

THF mass fraction	x_d	m.p. in D_2O (K)	x_w	m.p. in H_2O (K)
0.068	0.980	276.4 ± 0.8	0.982	273.3[a]
0.069		—	0.982	273.7 ± 0.2
0.111	0.966	278.8 ± 0.2	0.970	276.5[a]
0.115		—	0.969	276.5 ± 0.3
0.120	0.964	280.0 ± 0.2	0.967	277.0[a]
0.155	0.952	280.3 ± 0.3	0.956	278.0[a]
0.210	0.931	281.0 ± 0.5	0.938	278.1[a]
0.220		—	0.934	278.1 ± 0.1
0.238	0.920	280.8 ± 0.2	0.928	278.0[a]
0.261	0.911	280.8 ± 0.7	0.919	277.8[a]
0.345	0.872	279.6 ± 0.3	0.884	277.1[a]
0.373		—	0.871	277.0 ± 0.2
0.502	0.781	278.4 ± 0.2	0.799	275.8[a]
0.559	0.740	276.6 ± 0.3	0.759	275.3[a]
0.562		—	0.757	275.4 ± 0.2
0.682	0.627	276.7 ± 0.3	0.651	274.2[a]
0.720		—	0.609	274.4 ± 0.4

[a] Values for the H_2O hydrate interpolated from our data and the data of Ref. 8.

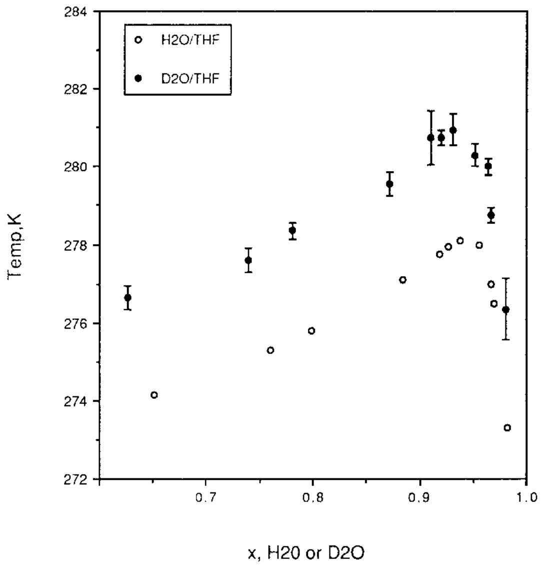

Fig. 1. Plot of the melting points of the THF/D_2O hydrate (filled circles) as a function of the water mole fraction. Also shown are the equivalent points for the THF/H_2O hydrate (open circles) from our own work and from Ref. 8.

temperature of the H_2O hydrate was found to be 278.2 ± 0.5 K at a mole fraction of 0.936—in agreement with the literature [7–9]—we estimate a congruent melting temperature of 281.0 ± 0.5 K for the THF/D_2O hydrate.

3. RESULTS

The THF/D_2O data were analyzed as follows. Let us first consider coexistence between the hydrate and the liquid for the THF/H_2O system. Assuming, as is the common practice, that the hydrate is a solid solution, we have $\mu_w^L = \mu_w^H$, where μ_w^L is the chemical potential of water in the liquid mixture and μ_w^H is the chemical potential in the hydrate. Further, one has

$$\mu_w^L(T) = \mu_w^0(T) + RT \ln \gamma_w x_w \qquad (1)$$

where $\mu_w^0(T)$ is the chemical potential for pure water at the temperature of the experiment, γ_w is the activity coefficient of water, and R is the gas constant. The hydrate forms a structure II lattice [3], with the THF molecules occupying the large cavities, and from the theory [10] of Van der Waals and Platteeuw for the structure II hydrate,

$$\mu_w^H = \mu_w^\beta + RT \ln(1 - y_{THF})/17 \tag{2}$$

where μ_w^β is the chemical potential of the unoccupied lattice cavity, and y_{THF} is the occupancy probability of finding a THF molecule in a lattice. Whence the relationship between the water mole fraction and the temperature at phase equilibrium is given by

$$\ln x_w = \mu_w^\beta/RT - \mu_w^0(T)/RT - \ln \gamma_w + \ln(1 - y_{THF})/17 \tag{3}$$

We calculated the chemical potential of pure water from the standard equations given by Haar et al. [11]. We used the value of 937 $J \cdot mol^{-1}$ for the potential for the empty structure II lattice as reported by one of us [12]; see, however, Ref. 13. Strictly, this value is an estimate of the difference between the potentials of the empty lattice and that of ice but the potential for ice is close to zero [11]. The activity coefficients were estimated from the data of Ref. 14, fitted [15] to a Margules equation with constants of $A_{12} = 2.5196$ and $A_{21} = 2.0223$. Given x_w as a function of T, the term $\ln(1 - y_{THF})/17$ was found to vary from -0.429 for the water-rich portion of the phase diagram ($x_w > 0.967$) to -0.513 for the THF-rich part. We note that this corresponds to an occupancy of at least 99.9%. This factor is perhaps high but not inconsistent with the >98% estimate of Gough and Davidson [9].

The phase boundary for the deuteriohydrate was predicted from the equivalent of Eq. (3) (that is, with x_d and γ_d for x_w and γ_w, etc.), with the assumption that the lattice occupancy for THF/D_2O is the value found for THF/H_2O at the same mole fraction. The chemical potential of pure D_2O was calculated from the formulation of Kestin et al. [16], with the reference state adjusted to be the equivalent to that of water; that is, the specific internal energy and the specific entropy are set to zero at the triple point (276.97 K). As for the water mixture, the activity coefficients were evaluated from a fit of the data from Ref. 17 to a Margules equation [15] with constants $A_{12} = 2.8471$ and $A_{21} = 1.9381$. We first estimated 947 $J \cdot mol^{-1}$ for the chemical potential of the empty structure II D_2O lattice from the cyclopropane deuteriohydrate data of Ref. 5, given $\mu_w^\beta \sim 937$ $J \cdot mol^{-1}$. A few iterations, however, between calculated and experimental values of $\ln x_d$ indicated that a value for μ_d^β of about 1000 $J \cdot mol^{-1}$—or 5% greater than μ_w^β—was more satisfactory. Figure 2 plots the percentage deviation in D_2O mole fraction between calculation and observation as a function of temperature.

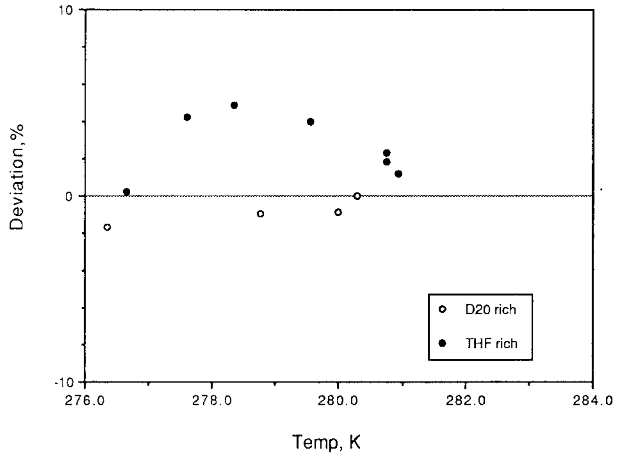

Fig. 2. Deviation curve, $(x_{\text{calc}} - x_{\text{exp}}) * 100/x_{\text{exp}}$, for THF/$D_2O$, where x_{calc} is calculated from Eq. (3) for D_2O with an adjusted value of μ_d^β of 1000 J·mol^{-1} (see text). The open circles represent the water-rich part of the curve in Fig. 1, $x_d \geqslant 0.952$. The filled circles represent the THF-rich part.

4. DISCUSSION AND CONCLUSION

Experimental melting points for the THF/D_2O hydrate in equilibrium with the liquid at atmospheric pressure have been reported. Figure 2 indicates that the data can be represented satisfactorily assuming (a) that the hydrate is a solid solution, (b) that the cage occupancy is the same for the H_2O and the D_2O hydrates, and (c) that the activity coefficients are represented by the Margules equation. The deviations between calculation and experiment for the water-rich, $x_d \geqslant 0.952$, segment of the phase boundary (i.e., $\ln \gamma_d \Rightarrow 0$) are less than 2%. The deviations for the THF-rich curve are 5% or less, but are systematic. Reasons for the deviations cannot be established with certainty from the data, but the most probable cause is an inadequate representation of the activity coefficients. We verified that the predictions did not depend significantly on the choice of the form, or the coefficients, of the expression used for γ_w and γ_d. Nevertheless, the activity coefficients are based on data [14, 15, 17] taken at temperatures well above the hydrate congruent melting points. Thus we have neglected the temperature dependence of the activity coefficients in the temperature range of interest. Furthermore, we have only approximated the mole fraction dependence of the THF occupancy.

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