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A thermodynamic study of the (difluoromethane + water) system

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ABSTRACT

A study of the (difluoromethane + water) system was conducted at temperatures between (255 and 298) K, and pressures from (0.06 to 1.30) MPa. The solubility of difluoromethane in liquid water was measured from (280 to 298) K, at pressures up to the hydrate formation pressure. The (p, T) behavior of the (liquid + hydrate + vapor) three-phase equilibrium was measured from (274 to 292) K. The (p, T) behavior of the (ice + hydrate + vapor) three-phase equilibrium was measured from (257 to 273) K. Solubility-corrected enthalpies of dissociation were determined at the lower quadruple point (Q1) using the Clapeyron equation. The de Forcrand method was used to determine the hydration number of the hydrate at Q1. The results show that not all of the cages in the SI hydrate structure are filled.

1. Introduction

Difluoromethane readily forms hydrates of structure SI at moderate pressures. Difluoromethane hydrate has been mentioned for possible applications in refrigeration [1] and desalination [2]. Despite this interest, no complete study of the hydrate formation equilibria have been published to date. The liquid–hydrate–vapor (LHV) curve has been reported by Akiya *et al.* [3] and Hashimoto *et al.* [4], but neither determined the {ice + hydrate + vapor (IHV)} equilibrium. Also, there have been no reports of the vapor–liquid behavior (solubility) of difluoromethane in water near the hydrate formation region. All of these data sets are required in order to utilize the so-called “de Forcrand” method [5] to determine the hydration number of the hydrate at the lower quadruple point (Q1). In this work, the LHV measurements were repeated at high precision and agreed well with the previous studies. The IHV curve was determined for the first time. Extensive measurements of solubility were also made at various temperatures as a function of pressure, up to the hydrate formation pressure.

The equilibria of interest in this study are summarized in the following list.

$$CH_2F_2 \cdot nH_2O(s) \rightleftarrows (1 - nx)CH_2F_2(g) + nH_2O(l, sat) \tag{R1}$$

$$nH_2O(l, sat) \rightleftarrows nxCH_2F_2(g) + nH_2O(l) \tag{R2}$$

$$CH_2F_2 \cdot nH_2O(s) \rightleftarrows CH_2F_2(g) + nH_2O(l) \tag{R3}$$

$$CH_2F_2 \cdot nH_2O(s) \rightleftarrows CH_2F_2(g) + nH_2O(s) \tag{R4}$$

$$nH_2O(s) \rightleftarrows nH_2O(l) \tag{R5}$$

The equilibrium (R1) expresses the dissociation of hydrate to form a nearly pure difluoromethane vapor (the water vapor pressure being small) and a solution of liquid water saturated with difluoromethane. The hydration number n is unknown at first. (R2) depicts the solution equilibrium in reverse. Adding (R1) and (R2) gives (R3), in which all components are in their standard states as pure phases. (R4) is the analogue to (R3), except that it applies to temperatures below Q1, where water exists as a solid. The low vapor pressure of ice and the extremely low solubility of gases in ice guarantees that reactants and products in the actual system are in their standard states. (R5) is the difference (R4) and (R3) and simply shows the melting of n moles of ice. The essence of the “de Forcrand” method is that if the enthalpy changes of (R3) and (R4), and hence (R5) are measured, n may be determined.

2. Experimental

All measurements were conducted in a stainless steel autoclave (see figure 1) with a volume of $(6.33 \pm 0.05) \cdot 10^{-4}$ m^3. The autoclave was completely immersed in a thermostatic bath of 50% ethylene glycol in water. A magnetically coupled stirring bar provided mixing. The temperature was controlled by circulating the coolant with a Neslab® RTE 140 chiller. Temperature inside the autoclave was measured by an Omega® thermistor which had been calibrated against an ASTM 63C mercury thermometer. The temperature measurement is believed to be accurate to better than ±0.1 K. Pressure was measure by Heise® bourdon-type absolute pressure gauges of (0 to 100) psi {(0 to 0.7) MPa} or (0 to 200) psi {(0 to 1.4) MPa} range. These gauges were calibrated by means of a deadweight tester. Absolute accuracy of pressure measurements is believed to be ±700 Pa.

Difluoromethane was supplied by DuPont, with a stated purity of greater than 99.9%. Distilled water was degassed by boiling.

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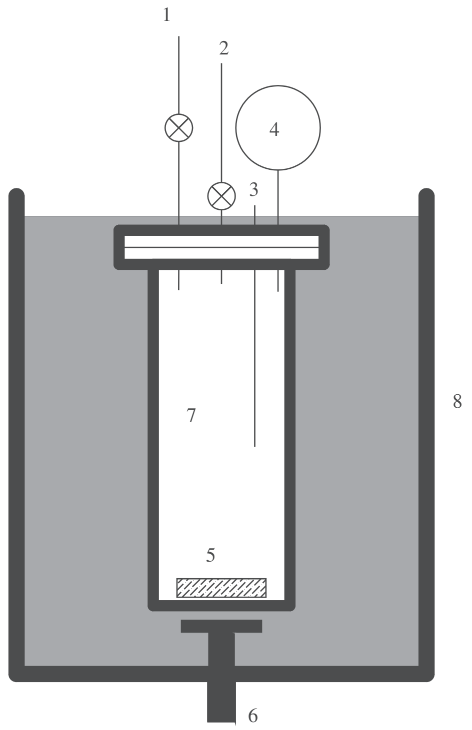

FIGURE 1. Schematic of autoclave. 1 – water inlet, 2 – gas inlet, 3 – thermistor, 4 – pressure gauge, 5 – magnetic stirring bar, 6 – stirring motor, 7 – pressure vessel, 8 – thermostatic bath.

An experiment was started by evacuating the autoclave to less than 15 Pa by means of a mechanical vacuum pump. Next difluoromethane was admitted to the approximately desired pressure. The system was stirred and equilibrated, after which accurate temperature and pressure measurements were made. REFPROP8® software [6] was used to determine the molar density of difluoromethane, from which the number of moles present was calculated. REFPROP8 uses the very accurate equation of state developed by Tilner-Roth and Yokozeki [7]. Next the desired volume of water was added by means of a screw-driven piston whose internal area was well known.

For solubility measurements, the autoclave was cooled to a temperature just above the temperature at which hydrates would form. The system was allowed to stabilize for approximately 2 h, after which a (p, T) measurement was made and the system temperature was raised by 2.00 K. The process was repeated up to a temperature of 298.15 K. REFPROP8 was used again to find the amount of difluoromethane remaining in the gas phase, from which the amount dissolved was found by difference. REFPROP8 is unable to calculate (vapor + liquid) equilibria for mixtures of hydrocarbons and water, since its simple mixing rules do not work for very dissimilar components. Therefore, the vapor was assumed to be pure difluoromethane. Since the vapor pressure of water is as much as 0.5% of the pressure of difluoromethane in some cases, an error in the third significant figure of the solubility value may be introduced.

For (liquid + hydrate + vapor) phase equilibrium measurements, the autoclave was cooled to a temperature near 273 K. Hydrate formation, signaled by a sudden drop in pressure, usually occurred within 30 min of initial cooling. After allowing approximately two hours for equilibration, the autoclave was warmed slightly, and 2 h were allowed for the autoclave to stabilize at the new temperature. (p, T) data were taken and the process repeated in small temperature increments up to the vicinity of the second quadruple point near 293 K.

For ice–hydrate–vapor measurements, a slight refinement was necessary to prevent the ice from immobilizing the stirring bar. A piece of very fine stainless steel mesh was inserted around the inside surface of the autoclave so as not to block the stirring bar. With vigorous stirring during the initial cooling, ice formed on the mesh and not on the stirring bar. An additional benefit was that the ice phase had a large surface area which facilitated hydrate formation. Hydrates formed readily and equilibration required no more than about 4 h. (p, T) measurements proceeded in the same way as in the LHV case.

A common theme in many hydrate studies is the very long time that may be required for the system to come to equilibrium. In extreme cases the researchers wait for as long as 24 h after the temperature has stabilized before they record the equilibrium pressure. This was not found to be necessary in the present case. Stable pressures were always reached within a few hours of temperature stabilization, and the measured pressures were reproducible and did not depend on whether the temperature was approached from above or below. Accuracy of equilibrium pressures is believed to be within ±0.002 MPa. It is believed that the high rate of stirring was responsible for the rapid equilibration. Good agitation causes the hydrate crystals to be small, such that they can equilibrate rapidly with their surroundings. The excellent agreement of our equilibrium pressures with those of Hashimoto *et al.* [4] is further evidence for the correctness of our method.

3. Results and analysis

3.1. Solubility

The data were fitted to the Krichevsky–Kasarnovsky [8] equation, as given below

$$\ln(f/x) = \ln(K_H) + \frac{(p - p_s)\overline{V}^{\infty}}{RT}. \tag{1}$$

In equation (1), f is the fugacity, x the dissolved mole fraction, K_H the Henry's law constant, and p_s is the solvent vapor pressure, which will be neglected. $\overline{V}^{\infty}$ is the partial molar volume of the solute at infinite dilution.

In figure 2, a plot of ln(*f*/*x*) *vs.* *p* at each temperature yields $\overline{V}^{\infty}$ from the slope and $\ln(K_H)$ from the intercept.

The enthalpy of solution at infinite dilution is found by the van't Hoff [9] equation.

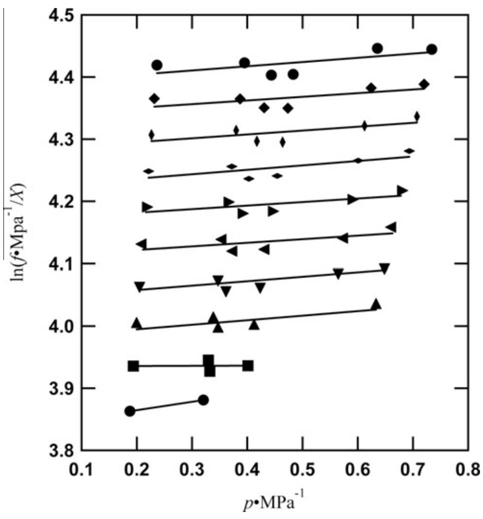

FIGURE 2. Krichevsky–Kasarnovsky plot for the solubility of difluoromethane in water, in 2.0 K increments from (280.15 to 298.15) K, starting at the bottom.