Formation of Gas Hydrate with CFC Alternative R-134a

Yasuhiko H. Mori
Tatsushi Mori
Department of Mechanical Engineering
Keio University
Yokohama 223, Japan

Gas hydrates are a class of solids, in which molecules of various compounds (guest species) are enclosed in icelike lattices that are made of hydrogen-bonded water molecules. Some CFC's (chlorofluorocarbons) such as R 11 (trichlorotrifluoromethane; CCl_3F) and R-12 (dichlorodifluoromethane, CCl_2F_2) are known to form gas hydrates, serving as guest species, which can exist at temperatures up to about 281.6 and 285.2 K, respectively (Davidson, 1973). The R-11 and R-12 hydrates had been considered the most favorable substances as cool storage media for residential air conditioning systems (Ternes, 1984; Akiya et al., 1987) till restrictions on the use of CFC's became increasingly tight. R-134a (1,1,1,2-tetrafluoroethane, CF_3CH_2F) is currently considered a prospective substitute for R-12 and is expected to replace the latter in usual refrigeration and air-conditioning equipment. As far as we know, however, no evidence has been reported up to the present time that R-134a can form a gas hydrate possibly usable as a cool storage medium.

In the present work, we intend to reveal if R-134a can form a gas hydrate and, if it can, to determine, with a reasonable accuracy for practical purpose, the highest temperature at which the hydrate can exist, i.e., the temperature of the quadruple point where the hydrate, R-134a in both vaporous and liquid states, and water in liquid state would coexist.

Experimental Studies

The experiments of R-134a hydrate formation were performed using the same apparatus we used before in studying R-12 hydrate formation (Mori and Mori, 1989). It was a small-scale closed-loop vapor-compression refrigerator which incorporated a crystallyzer—gas-hydrate storage tank—as a substitute for the conventional evaporator. The crystallizer was a vertically-oriented, vacuum-jacketed borosilicate-glass-made cylindrical column, 80 mm ID and 600 mm high, having an agitator inserted into it along its central axis. The crystallizer was charged with a specified volume (600 cm^3) of deionized-and-distilled water. R-134a, mostly in liquid state, continuously flowed into the crystallizer at its bottom, resulting in the evaporation of R-134a while in contact with the water and thereby cooling the contents of the crystallizer. R-134a, thus vaporized, flowed out of the crystallizer through its top into the refrigerator loop. The temperature in the crystallizer was detected by three copper-constantan thermocouples inserted in it, and the pressure was measured by a Bourdon gauge connected to the vapor outlet of the crystallizer.

The R-134a sample we used was furnished by Asahi Glass Co., Ichihara, Japan, and its purity was said to be 99.9 wt. % or higher.

Results and Discussion

It was observed that R-134a gas hydrate was formed in the crystallizer just in the same manner as R-12 hydrate. A photographic evidence of R-134a gas hydrate formation is given in Figure 1.

When the hydrate storage in the crystallizer almost completed itself, the circulation of R-134a in the refrigerator loop was stopped. Then the crystallizer was left to be warmed by the laboratory air, which resulted in a slow decomposition of the hydrate into R-134a both in liquid and vapor states and water in liquid state. In the mean time, the temperature and the pressure in the crystallizer showed constant values until the decomposition almost completed itself. These constant values of the temperature and the pressure were regarded as those at the quadruple point, which were 283.1 ± 0.3 K and 0.415 ± 0.009 MPa, respectively.

The quadruple point thus determined is plotted on a pressure vs. temperature diagram in Figure 2 to be compared with a

---

Correspondence concerning this paper should be addressed to Y. H. Mori.

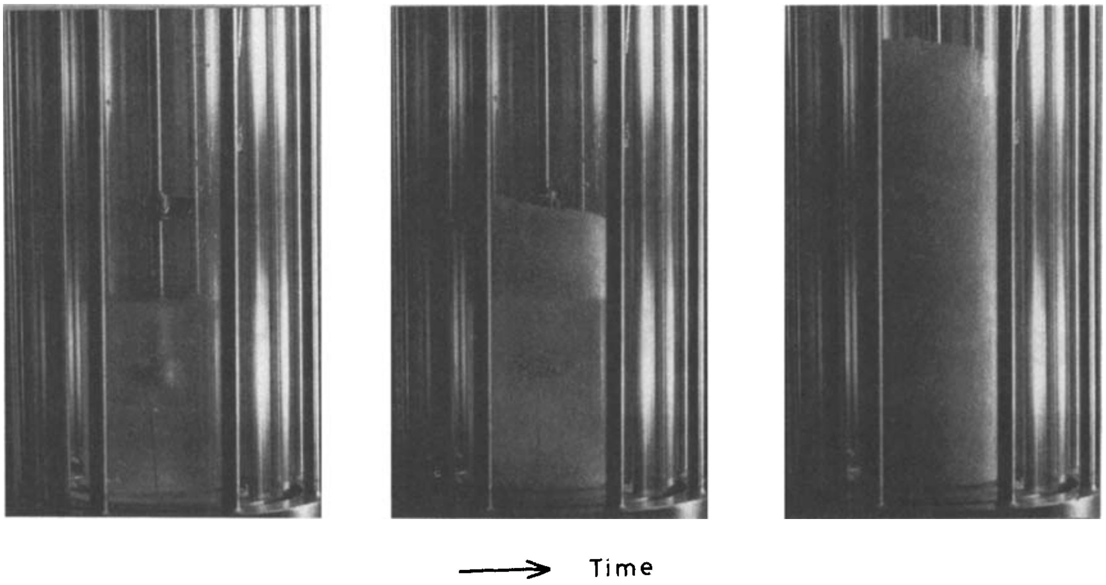

Figure 1. Typical sequence of accumulation of R-134a gas hydrate in the crystallizer.

curve representing the sum of saturated vapor pressures of R-134a and water. The vapor pressure of R-134a was predicted by the correlation given by Piao et al. (1988) based on their experimental data. As for the vapor pressure of water, the data given in the *JSME Data Book* (1983) were used. It is recognized that the quadruple point determined in this work falls within its measurement uncertainties on the curve, and thus it is consistent with the newly-obtained R-134a vapor pressure data of Piao et al.

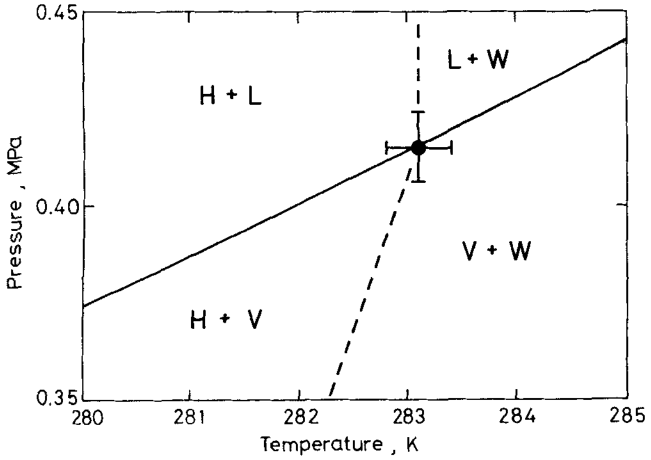

Figure 2. Phase diagram for R-134a/water system.

●, quadruple point determined in this work with uncertainties indicated by the vertical and horizontal bars superposed; ——, the sum of saturated vapor pressures of R-134a and water (Piao et al., 1988; *JSME Data Book*, 1983); ---, phase boundaries indicated only for illustrative purpose; *H*, gas hydrate; *V*, vapors of R-134a and water; *L*, R-134a in liquid state; *W*, water in liquid state.

Conclusions

R-134a can form a gas hydrate. The temperature and the pressure at the quadruple point—the highest temperature and the highest pressure for the existence of the hydrate—are 283.1 ± 0.3 K and 0.415 ± 0.009 MPa, which are lower than those of R-12 gas hydrate by about 2 K and 0.018 MPa, respectively.

Acknowledgments

We are indebted to Asahi Glass Co., Ichihara, for providing us the R-134a sample we used in this work. Our thanks are also due to F. Isobe, a student at the Department of Mechanical Engineering, Keio University, for his assistance in the experiments.

Literature Cited

Akiya, T., M. Owa, M. Nakaiwa, S. Kawasaki, M. Minemoto, and Y. Ando, "Cool Storage Using Gas Hydrate," *Int. Cong. of Refrigeration Proc.*, **E**, 166 (1987).

Davidson, D. W., "Clathrate Hydrate," *Water, A Comprehensive Treatise*, F. Franks, ed., Plenum Press, New York, **2**, 115 (1973).

JSME Data Book: The Thermophysical Properties of Fluids, Japan Soc. Mech. Engrs., Tokyo (1983).

Mori, T., and Y. H. Mori, "Characterization of Gas Hydrate Formation in Direct-Contact Cool Storage Process," *Int. J. Refrig.*, in press (1989).

Piao, C.-C., H. Sato, and K. Watanabe, "A Study of Thermodynamic Properties of CFC Alternative R 134a," in Japanese, *Proc. Japan Symp. on Thermophysical Properties*, 235 (1988).

Ternes, M. P., "Characterization of Refrigerant-12 Gas Hydrate Formation for Heat Pump Cool Storage Applications," ASME Paper 84-AES-12 (1984).

Manuscript received Jan. 20, 1989.