Estimation of the Enthalpy of Dissociation of Simple and Mixed Carbon Dioxide Hydrates using the Clausius-Clapeyron Equation

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Carbon dioxide hydrate slurries have the potential to be applied as a two-phase (solid-liquid) refrigerant [Darbouret et al., 2005]. The melting temperatures of these hydrate slurries are consistent with the temperature needed in applications such as air conditioning and their enthalpies of dissociation have been found to be suitable for refrigeration applications [Martínez et al., 2008]. The use of hydrate slurries in refrigeration requires a high enthalpy of dissociation and appropriate stability conditions of the hydrate crystals at the working temperatures and pressures of the refrigeration systems [Delahaye et al., 2006]. In the present work, the stability conditions of simple and mixed carbon dioxide and tetrahydrofuran hydrates are experimentally measured. Considering the difficulties of obtaining the enthalpy of dissociation data through direct measurements, the enthalpies of dissociation for these hydrates are estimated from the measured equilibrium data by using the Clausius-Clapeyron equation. The results of the calculated enthalpy of dissociation for simple carbon dioxide hydrates are presented and discussed. It is found that the enthalpy of dissociation and hydration number of simple carbon dioxide hydrate estimated by this equation varied from 56.85 to 75.37 kJ/mol and 5.98 to 8.54 as the temperature is reduced from 282.06 to 273.15 K. The enthalpy of dissociation of mixed carbon dioxide and tetrahydrofuran are found in the region of 112.37 up to 152.27 kJ/mol depending on the concentration of tetrahydrofuran in the hydrate forming systems. A rationale for this significant increase of the enthalpy of dissociation of the mixed hydrates will be discussed.

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