

DTA characterization of TBPB and TBPB-CO₂ hydrates in porous media

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Due to the current global warming and climate change, international commitments aiming at reduce CO₂ emissions in several fields of activity. Refrigeration activity is one of the most concerned because using harmful primary refrigerants for the greenhouse effect. Secondary refrigeration is a method using a neutral fluid in order to confine primary refrigerants and to reduce their quantities. Two-phase refrigerants (solid-liquid) are relevant for this method since their energy density is higher than that of single-phase secondary refrigerant thanks to the melting latent heat of the solid [1]. Clathrate hydrate slurries are composed of phase change materials (PCM) dispersed in a liquid phase [2-3]. Gas hydrates are non-stoichiometric ice-like compounds in which gas molecules are trapped inside a cage of water molecules. They form in conditions of low temperature and high pressure. By example CO₂ hydrate form at 273.93 K at 1.37 MPa or 282.91 K at 4.46 MPa [4-5]. Adding of promoters like, perylkammonium salt enable to decrease the equilibrium pressure but create a kind of hydrates known as semiclathrates [6-7].

The present work investigates the use of mixed hydrates formed from CO₂ + tetra-*n*-butylphosphonium bromide (TBPB) + water mixtures, as appropriate media for cold storage and distribution in refrigeration applications. These hydrates have equilibrium conditions required for air-conditioning applications, with melting temperature between 282 and 289 K for moderate pressure between 0.5 and 2 MPa [6-9].

DTA device was used for determining dissociation enthalpies and equilibrium conditions of mixed and single TBPB hydrates under various stability conditions (P, T) and salt concentrations in bulk and porous media. The results reveal that mixed hydrates are formed in porous media at lower temperature than in bulk conditions for a constant pressure due to capillary forces.

Keywords : *TBPB, hydrate, DTA, porous media, secondary refrigeration*

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