ABSTRACT

Clathrate hydrate is an ice-like crystalline compound that is formed by hydrogen-bonded water network with small-sized molecules trapped into their cage-like structures. The natural gas hydrates occurring in seafloor and permafrost region are regarded as a sustainable energy resource for the upcoming century as they are mostly composed of methane gas. Besides, the gas hydrates technology is a potential tool to separate, store and transport the gases, de-saline or purify the seawater and ensure trouble-free fluid flow through the pipelines located in the low temperature regions. The statistical thermodynamics based van der Waals-Platteeuw theory provides a fundamental approach to understand the phase behavior of clathrate hydrates. However, the critical assumptions made in the theory limit the implementation of the theory for polar and large-sized guest molecules. In this contribution, we formulated the *ab initio* methodology that is computationally feasible and it accurately estimates the cavity potential for both small and large sized guests. Using this technique, we address the lattice distortion by larger guests, e.g. liquid (cyclic ethers and ketones) and gaseous (refrigerants) promotors. Subsequently, the multiple-occupancy of smaller guests at high pressure conditions is considered. This apart, an advanced mixing rule is developed for the mixture containing clathrate hydrates. With these proposed modifications, the modified van der Waals-Platteeuw theory is applicable for wide ranges of guests and operating conditions.

Keywords: Clathrate hydrate, thermodynamic modelling, *ab initio*, cavity potential, lattice distortion, multiple-occupancy, mixing rule

.