Adsorption in structure-I clathrate hydrates described using a single Langmuir site: Evidence from all-atom Monte Carlo molecular simulations

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Clathrate hydrates are a non-stoichiometric ice-like material consisting of a hydrogen-bonded water network forming a network of cavities which contain gas molecules. Natural gas clathrate hydrate deposits can be found in the deep ocean and in tundra permafrost, where the environmental temperature and pressure conditions permit their formation. Methane clathrate hydrate, and several others, typically take on the so-called structure-I lattice structure, which is itself a solution to the Kelvin problem—i.e. a foam of approximately equal-volume bubbles with minimal inter-bubble surface area [D. Weaire, R. Phelan, Phil. Mag. Lett. 69, 107 (1994)]. Commonly, especially within the context of van der Waals-Platteeuw theory [J.H. van der Waals, J.C. Platteeuw, Adv. Chem. Phys. 2, 1 (1959)] used to describe clathrate hydrate phase equilibria, two different cavity types are modelled as Langmuir-type adsorption sites, necessitating the use of four fitted adsorption isotherm parameters [W.R. Parrish, J.M. Prausnitz, Ind. Eng. Chem. Proc. Des. Dev. 11, 26 (1972)]. This study employs all-atom Monte Carlo molecular simulations to examine the suitability of describing the structure-I clathrate hydrate cavities in terms of a single Langmuir-type adsorption site. The use of such an adsorption isotherm model would halve the number of adsorption isotherm parameters typically fitted to experimental phase equilibria. Several different gas species known to form structure-I clathrate hydrates are considered: Carbon monoxide, methane, ethane, ethene, and hydrogen sulphide. This general idea has been used previously for united-atom simulations of methane clathrate hydrate [M. Lasich, A.H. Mohammadi, K. Bolton, J. Vrabec, D. Ramjugernath, Fluid Phase Equilibr. 369, 47 (2014)], and the results of the present work demonstrate the utility and limitations of this approach using more rigorous molecular models across several different systems.