A model to predict phase equilibrium of CH$_4$ and CO$_2$ clathrate hydrate in aqueous electrolyte solutions

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ABSTRACT

A thermodynamic model to predict phase equilibrium of methane and carbon dioxide hydrate in aqueous electrolyte solutions is presented. Using the Pitzer model to account for the variation of water activity due to electrolytes and dissolved gas in aqueous solutions, we extended the model based on ab initio molecular potential developed recently by us for the CH$_4$-H$_2$O and CO$_2$-H$_2$O binary systems to the CH$_4$-(or CO$_2$)-H$_2$O-salts system. Comparison of the model with extensive experimental data indicates that this model can accurately predict the phase equilibrium of CH$_4$ hydrate and CO$_2$ hydrate in various electrolyte solutions (such as aqueous NaCl, KCl, CaCl$_2$, NaCl + KCl, NaCl + Na$_2$CO$_3$ solutions, and seawater) from zero to high ionic strength (about 6 m) and from low to high pressures.

Keywords: Methane hydrate, carbon dioxide hydrate, thermodynamic stability, electrolyte solution, phase equilibrium, formation conditions

INTRODUCTION

Gas hydrates are non-stoichiometric crystalline compounds that consist of a hydrogen-bonded network of host water molecules and enclathrated guest molecules. They are generally stable at low temperatures and high pressures. When electrolytes are present in the liquid water, the hydrate formation is inhibited. It is of great importance to predict the phase equilibrium of gas hydrate in aqueous electrolyte solutions for many engineering, environmental, and geochemical problems, such as inhibiting the formation of hydrate in natural gas pipelines (Sloan 1998), exploring and exploiting methane hydrate reservoirs in marine sediments, sequestering CO$_2$ on the ocean floor, analyzing the salinity of fluid inclusions (Collins 1979; Diamond 1994), and desalinating seawater (Barduhn et al. 1962; Smirnov 1990).

In the last half century, various thermodynamic models for the calculation of phase equilibrium properties of the gas hydrate system were developed, such as the models proposed by Parrish and Prausnitz (1972), Ng and Robinson (1976), John et al. (1985), and Lee and Holder (2002). Most of these models are based on the statistical mechanical model proposed by van der Waals and Platteeuw (1959) and calculate Langmuir constants from the Kihara potential model with parameters determined from phase equilibrium data of gas hydrates. Recently, we proposed a new method to compute the Langmuir constant from angle-dependent ab initio intermolecular potentials (Sun and Duan 2005). This method can accurately predict both phase equilibria and cage occupancy of methane hydrate and carbon dioxide hydrate in gas-water binary systems.

Electrolytes cannot enter the lattice of hydrates, but they act by lowering the activity of water in the coexisting liquid phase, causing hydrates to form at lower temperatures and higher pressures compared to their formation in pure water. Using the Pitzer-Mayorga activity coefficient model (Pitzer and Mayorga 1973) to account for the activity depression of water in aqueous electrolyte solutions, Englezos and Bishnoi (1988) presented a method to predict gas hydrate formation in aqueous solutions of electrolytes. Because the Pitzer-Mayorga model doesn’t consider the neutral species dissolved in aqueous solution, Englezos and Bishnoi (1988) neglected the effect of the dissolved gas component on water activity in aqueous solution. Although it can produce good results for systems with substances sparingly soluble in water (e.g., light hydrocarbons, nitrogen), it leads to systematic errors for soluble gases (such as CO$_2$), because the effect of soluble gas on water activity is significant. Englezos (1992) tried to predict the formation condition of CO$_2$ hydrate in aqueous NaCl solution from the Aasberg-Petersen’s model (Aasberg-Petersen et al. 1991). However, the average absolute deviation of this model for CO$_2$ stability in 10 wt% NaCl solution is more than 11%. Tse and Bishnoi (1994) examined three models [including Chen and Evans (1986), Zuo and Guo (1991), and Aasberg-Petersen et al. (1991)] that can treat the aqueous electrolyte phase, and found that the model of Zuo and Guo (1991) gave the best results for predicting incipient equilibrium condition of CO$_2$ hydrate in aqueous single salt solutions. Tohidi et al. (1995) predicted the inhibition effect of electrolyte on phase equilibrium of gas hydrates based on their thermodynamic model for aqueous electrolyte solution. Dickens and Quinby-Hunt (1997) predicted methane hydrate stability in seawater from the Pitzer-Mayorga model and achieved good agreement with experiments. Dubessy et al. (1992) and Bakker et al. (1996) predicted the CO$_2$ hydrate stability field in CO$_2$-H$_2$O-salts system from the Pitzer-Mayorga model, using an approximate method to include CO$_2$ solubility and to calculate the activity of water in CO$_2$-H$_2$O-salts system.

In general, the previous models can predict phase equilibria...