



An improved model for the phase equilibrium of methane hydrate inhibition in the presence of ionic liquids



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ABSTRACT

In this work, a thermodynamic model is developed and used to predict the phase stability conditions for methane hydrate–ionic liquid (IL)–water system. The hydrate phase is computed from modified van der Waals–Platteeuw model. The Peng–Robinson equation of state (PR-EoS) and developed activity model as a combination of Pitzer–Mayorga–Zavitsas–hydration model is used to evaluate the fugacities of gas and liquid phases, respectively. The hydrate phase stability prediction is also computed using the liquid phase activity predicted by NRTL and Pitzer–Mayorga models, separately, and is compared with the results predicted from the developed model. The model predictions are compared with experimental results on the phase stability of methane hydrate reported in open literatures for 21 ILs. The 21 ILs chosen from various ionic groups such as tetraalkylammonium, pyrrolidinium, imidazolium cationic family with various anion group such as halides (Cl, Br, I), sulphate (HSO₄, ethylsulphate), tetrafluoroborate (BF₄) and dicyanamide (DCA). The absolute average relative deviation in predicted pressure (AARD-P) with developed Pitzer–Mayorga–Zavitsas–hydration–model is improved to 1.60% and non-random two liquid (NRTL), Pitzer–Mayorga model showed 2.02% and 1.77% with 120 data points in the temperature range of 272.1–291.59 K and pressure range of 2.48–20.67 MPa. For 120 data points of phase stability conditions of 21 ILs, 39.2% of the predicted equilibrium pressures (47 data points) were within relative absolute deviation of 0.0–1.0%, 29.2% of the equilibrium pressures (35 data points) were within absolute deviation of 1.01–2.5%, 25.8% of data (31 data points) were within 2.51–7.5% which are mainly for data with low concentrations of ILs and only 5.8% of data (7 data points) showed relative absolute deviations above 7.5% which are observed mainly for data with high concentrations of ILs. Further, the model is used to calculate the inhibition effect of selected 21 ILs on methane hydrate formation.

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1. Introduction

Gas hydrates are crystalline solid structures consisting of stabilized water molecules network formed by hydrogen bonding which encapsulates suitable ‘guest’ gas molecules such as methane (CH₄), ethane (C₂H₆), propane (C₃H₈), iso-butane (C₄H₁₀), hydrogen sulphide (H₂S) and carbon dioxide (CO₂), etc. [1]. The structure of gas hydrates depends upon type of ‘guest’ gas molecule occupied by the cavities of water molecules. The common structures of gas hydrates are structure I, II and H [1]. Gas hydrates formation in oil and gas industry is problematic due to its ability to block gas transmission lines, damage of process equipment causing huge economic losses as well as safety risks [2]. The four different

methods are used to prevent the hydrate formation, viz., depressurization, de-watering, heat addition and inhibition by injecting inhibitors. Out of these four methods, the inhibitors injection method is most commonly adopted by the oil and gas industry. There are two kinds of inhibitors used to prevent the hydrate formation such as, low dosage kinetic inhibitors (LDKIs) and thermodynamic inhibitors. The performance of LDKIs is to slow down the hydrate nucleation and growth rates. Thermodynamic inhibitor inhibit the hydrate formation by shifting hydrate (H)–liquid (L)–vapor (V) phase equilibrium conditions to high pressures and/or low temperature conditions [1]. The most common thermodynamic inhibitors are alcohols, glycols and electrolytes/salts. The alcohols and glycols form hydrogen bond through hydroxyl group with water molecules. An electrolyte (salts) ionizes with dipoles of water molecules to produce strong Columbic bonds. This phenomenon helps in reducing the water activity which shifts the H–L–V equilibrium conditions to high pressures and/or lower temperature conditions [3,4].

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Nomenclature	
IL	ionic liquid
LDKI	low density kinetic inhibitors
NRTL	non-random-two-liquid model
eEOS	electrolyte cubic equation of state
PR-EoS	Peng–Robinson equation of state
MHV1	modified Huron–Vidal
COSMO-SAC	conductor-like screening model for segment activity coefficient
UNIFAC	universal quasi chem. Functional group activity coefficients
AARD	absolute average relative deviation
[N _{1,1,1,1}][Cl]	tetramethylammonium chloride
[N _{1,1,1,eOH}][Cl]	hydroxyethyl-trimethylammonium chloride
[N _{2,2,2,1}][Cl]	tetraethylammonium chloride
[HEMP][BF ₄]	<i>N</i> -(2-hydroxyethyl)- <i>N</i> -methylpyrrolidinium tetrafluoroborate
[BMP][BF ₄]	<i>N</i> -butyl- <i>N</i> -methylpyrrolidinium tetrafluoroborate
[EMIM][Cl]	1-ethyl-3-methylimidazolium chloride
[OH-C ₂ MIM][Cl]	1-(2-hydroxyethyl)-3-methylimidazolium chloride
[BMIM][Cl]	1-butyl-3-methylimidazolium chloride
[EMIM][Br]	1-ethyl-3-methylimidazolium bromide
[BMIM][Br]	1-butyl-3-methylimidazolium bromide
[MMIM][I]	1,3-dimethylimidazolium iodide
[EMIM][I]	1-ethyl-3-methylimidazolium iodide
[PMIM][I]	1-propyl-3-methylimidazolium iodide
[BMIM][I]	1-butyl-3-methylimidazolium bromide
[EMIM][EtSO ₄]	1-ethyl-3-methylimidazolium ethylsulfate
[EMIM][HSO ₄]	1-ethyl-3-methylimidazolium bisulfate
[BMIM][MeSO ₄]	1-butyl-3-methylimidazolium methylsulfate
[EMIM][BF ₄]	1-ethyl-3-methylimidazolium tetrafluoroborate
[OH-EMIM][BF ₄]	1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate
[BMIM][BF ₄]	1-butyl-3-methylimidazolium tetrafluoroborate
[BMIM][DCA]	1-butyl-3-methylimidazolium dicyanamide
List of symbols	
f	fugacity (MPa)
v'_i	number of cavities of type i per water molecule in hydrate structure
T	hydrate dissociation temperature (K)
R	universal gas constant
C_{ij}	Langmuir adsorption constant for guest gas (j) in interaction with each type cavity (i)
A_{ij} , B_{ij} , C_{ij} and D_{ij} ,	fitted parameters in Langmuir adsorption constant Eqs. (4) and (5)
f_j	fugacity of the hydrate former in gaseous phase (MPa)
Z	compressibility factor
A , B	constants in Eq. (6)
P	equilibrium pressure (MPa)
p	vapor pressure (MPa)
v	molar volume (m ³ kmol ⁻¹)
x	mole fraction
M	molecular weight
a_w	activity of water
v_l	number of ions in IL formula
m_i	molality of i th ion
I	ionic strength
a, b	constants in Pitzer–Mayorga model
A_ϕ	Debye–Hückel constant
h	hydration number
$G_{sw} - G_{ss}$	interaction parameter between solute–solvent (water)
$G_{ws} - G_{ww}$	interaction parameter between solvent (water)–solute
f^ϕ	constant in terms of Debye–Hückel expression
α	non randomness factor
N_p	number of data points
Greek letters	
μ	chemical potential
ϕ	osmotic coefficient
γ	activity coefficient
$\beta^{(0)}$, $\beta(1)$, $C(\phi)$	constant parameters in Pitzer–Mayorga model
f^ϕ	Debye–Hückel expression
A_ϕ	Debye–Hückel constant
α	non-randomness parameter
β_{MX}^ϕ	Pitzer–Mayorga ionic interaction parameter
Subscripts	
w	water
s	solute
small	small size of cavities per water molecule in gas hydrate structure
large	large size of cavities per water molecule in gas hydrate structure
P_{wi}	equilibrium pressure for pure water system
P_{li}	equilibrium pressure for ILs system
ws	water–solute
sw	solute–water
st	hydrate suppression temperature
Superscripts	
H	hydrate
L	liquid
g	gas
MT	empty hydrate phase/lattice
v'_{small}	number of small cavities per water molecule in hydrate structure
v'_{large}	number of large cavities per water molecule in hydrate structure
+	cation
–	anion
sat	saturation condition
calc	calculated result
expt	experimental result

Ionic liquids (ILs) are called as ‘green’ electrolytes (salts), which show negligible vapor pressure, low melting point, non-flammability, high thermal stability and are liquids at room temperature [5]. These ILs are constituted of cations and anions. The cations are generally organic in nature, such as: imidazolium, pyridinium, phosphonium and tetraalkylammonium and the anions can be organic or inorganic nature such as: triflate (organic) or halides (inorganic), respectively [6]. These green electrolytes are designed for a particular application by tuning of different functional cation and anion groups [7]. The ILs in the presence

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