

Application of Electrolyte Based Model on Ionic Liquids-Methane Hydrates Phase Boundary

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Abstract. In the current study, the phase behaviour of selected methane (CH₄) hydrate-Ionic Liquids (ILs) systems were predicted via Dickens and Quinby-Hunt model. The model chosen is an electrolyte-based model; therefore easily accommodate ILs that are molten salts. The experimental hydrate vapour liquid Equilibrium (HL_wVE) data of ILs was extracted from various literature sources for validation of the applied model. The overall predicted results suggested that the studied predictive model found in line with the experimental literature data for almost all the studied systems. The maximum deviation observed from the pyrrolidinium family of IL which also found to less than 0.67 K. Apparently it can be concluded that the selective model could applicable for accurate prediction of thermodynamic hydrate phase boundaries of methane hydrates in the presence of ILs. Since hydrate experimentations are very time-consuming, accurate thermodynamic predictions of hydrate phase are very crucial for exploring various hydrate-based technologies like flow assurance, natural gas recovery and gas storage and transportations.

1. Introduction

Gas hydrate formation is one of the foremost impedance faced by the offshore oil and gas exploration and production facilities. The problem is even getting harder since petroleum exploration is a move to more in-depth off-shores, which provide further thermodynamically favourable conditions leads to more close hydrate encounters. According to Xia et al. [1], nearly 70 per cent of all the flow assurance problems accounted for due to the hydrate formations. To avoid hydrate formations, oil and gas industry spends 100s of Million dollars (\$) without any permanent solutions [1,2].

Gas or clathrates hydrates are non-stoichiometric ice-type enclosure solids, produced when small gas molecule (guest) trapped inside the hydrogen bonded water structure (host) under thermodynamically favourable conditions. Gas hydrates stabilized, owing to the existence of an active hydrogen-bonded network of water in hydrate structure. Methane (CH₄), ethane (C₂H₆), carbon dioxide (CO₂) are among the typical hydrate formers [3]. Often, three types of conventional gas hydrate structures are found which recognised as structure I (sI), structure II (sII) and structure H (sH) hydrates which depend upon the thermodynamic conditions and the presence of guest molecules [4].

There are four conventional methods available for mitigation of gas hydrates, which includes thermal heating, depressurization, dehydration and chemical inhibition. In most of the scenarios, chemical inhibition is the only viable method available for hydrate mitigations [5]. There are three types of chemicals inserted as hydrate inhibitors; namely: Thermodynamic hydrate inhibitors (THIs), Kinetic hydrate inhibitors (KHIs) and Anti Agglomerates (AAs) [6,7]. THIs shifts the hydrate formation



conditions towards lower-temperature and higher-pressure regions. The conventional thermodynamic hydrate inhibitors include alcohols like ethylene glycol (EG), methanol besides traditional salts for example potassium chloride (KCl) and sodium chloride (NaCl) [8]. The unconventional THI include different chemicals, which are relatively more environmentally friendly in properties particularly with lower vapour pressure like ionic liquids [9–12].

Since hydrate experimentation is very complicated and time-consuming process; it is practically not possible to experimentally investigate the all the potential chemicals (ILs). Besides, the commercial hydrate prediction soft wares (such as CSMGem, PVTsim, etc.) are very limited and could only incorporate the commercial inhibitors (like methanol, EG or NaCl) which restrain their applications to the newer inhibitors (ILs). ILs are a molten salts having melting points less than 100 °C. The ILs are the combination of organic part (electropositive) cation and inorganic part anion (electronegative). The ILs could influence THI behaviour uniquely; they possess strong electrostatic force (coulombic charge) together with enhanced hydrogen-bonding ability with water molecules. For that reasons, ILs are efficiently able to act as dual-functional hydrate inhibitors. However, the most of the ILs studies mainly focused on THI impact only.

There are many families of ILs; like imidazolium, pyrrolidinium, morpholinium, ammonium etc. The gas hydrate-ILs research mainly focused on imidazolium-based ILs [7]. Relatively less literature has published over the different families of ILs.

Therefore, at this point, the emphasis of this study is to apply the electrolyte based (Dickens and Quinby-Hunt) model on the selected reported literature data of CH₄ hydrates. The model predictions (HL_wVE boundaries) are stretched on the different ILs-families to evaluate the applicability of the studied model. Therefore, this work is expected to efficiently predict the HL_wVE data of ILs-CH₄ system which ultimately save time, cost, and to support the appropriate selection of more efficient ILs for THI mitigation.

2. Methodology

2.1. Model Theory

Mainly most of the hydrate thermodynamic models determine the activity of additive in the aqueous phase. The THI behaviour induced due to the disturbance occurred in the activity of water. Therefore, to calculate the HL_wVE points of CH₄ hydrates in the presence of ILs, the electrolytes based model offered by Dickens and Quinby-Hunt [13] was used in this study. Since ILs are molten salts, hence the considered model excellently worked for electrolytes (salts) [14]. The applied model was the adaptation of the Pieroen [15] model; and earlier used for the electrolytes modelling like ionic liquid and amino acids solutions on the CH₄ hydrate phase boundary by Partoon et al. [16], Javanmardi et al. [17,18] and other researchers [6,19,20]. Recently, the existing model was also successfully applied on the CO₂ and CH₄ riched binary mixtures (30-70 and 70-30) of CH₄-CO₂ gases in the presence of ammonium based ionic liquids (AILs) [20,21]. The model has fundamentally established from the classical thermodynamic theory, which assumed that the amount of gas in the water phase is negligible, and vice versa. Also, the effect of ILs on CH₄ HL_wVE boundary was sole to decrease water activity (a_w), and at small temperature ranges, the hydrate enthalpy of dissociation (ΔH_d) remained constant. The derivation details had provided by Dickens and Quinby-Hunt [13] and Pieroen [15]. Based on this model, the effect of ILs on the methane hydrate dissociation temperature can be denoted as;

$$\ln a_w = \frac{\Delta H_d}{nR} \left[\frac{1}{T_w} - \frac{1}{T_{IL}} \right] \quad (1)$$

where,

$$\ln a_w = \frac{\Delta H_{FUS(i)}}{R} \left[\frac{1}{T_{f(i)}} - \frac{1}{T_f} \right] \quad (2)$$

where a_w denotes water activity, n was the methane hydrate hydration number (5.75 [22]), ΔH_d represented the dissociation enthalpy of methane (59.966 kJ/mol), R denoted as the universal gas constant, T_{IL} and T_w represented the hydrate formation temperatures in water + ILs solution and pure

water, respectively. CSMGem software was used to calculate the water- methane hydrate dissociation temperatures. $\Delta H_{FUS(i)}$ was the heat of fusion of ice (6.008 kJ/mol), $T_{f(i)}$ and T_f were the freezing point temperatures of water (273.15 K) and water + aqueous ILs solutions, respectively. T_f was calculated as suggested by Dickens and Quinby-Hunt [13] by using a cryoscopic constant for water as 1.853 K·kg/mol. Hence, merging Eq. (1) and (2), narrated the temperature offset of methane hydrate phase condition and the temperature of the ice-water equilibrium condition in any IL solution at constant pressure as follows;

$$\left[\frac{1}{T_w} - \frac{1}{T_{IL}} \right] = \frac{n\Delta H_{FUS(i)}}{\Delta H_d} \left[\frac{1}{T_{f(i)}} - \frac{1}{T_f} \right] \quad (3)$$

Therefore, Eq. (3) can be used to calculate T_{IL} , the hydrate formation temperature in the presence of ILs. The model predictions average absolute error (AAE) is calculated using Eq. (4).

$$AAE = \frac{1}{m} \sum_{i=1}^m |T_{Exp.} - T_{Cal.}|_i \quad (4)$$

2.2. Material

Table 1 provided the details of the selected (literature) ILs used in this work. These literature HL_wVE data have chosen for the model application since they covered the different types (families) of ILs. The typical concentration of ILs was selected as 10 wt%. Overall, modelling of 19 ILs-CH₄ systems (see Table 1) were performed in this work.

3. Results and Discussions

The proposed electrolyte model had used to predict the influence of ILs on the HL_wVE conditions for CH₄ hydrates. The authors would like to mention that the considered model had been successfully used for different electrolyte system in the literature to predict the dissociation temperature within the acceptable deviation range (Line). However, for validation purpose the model had also applied for common salts system, i.e., NaCl+CH₄ and KCl+CH₄ by the literature reported data of Mohammadi *et al.* [27]. For the modelling, the constants and model parameters have kept uniform with recently published article of Nashed *et al.* [19]. The model predicted results were found in acceptable agreement with the salts literature data as evident in the following Figure 1 and Table 2.

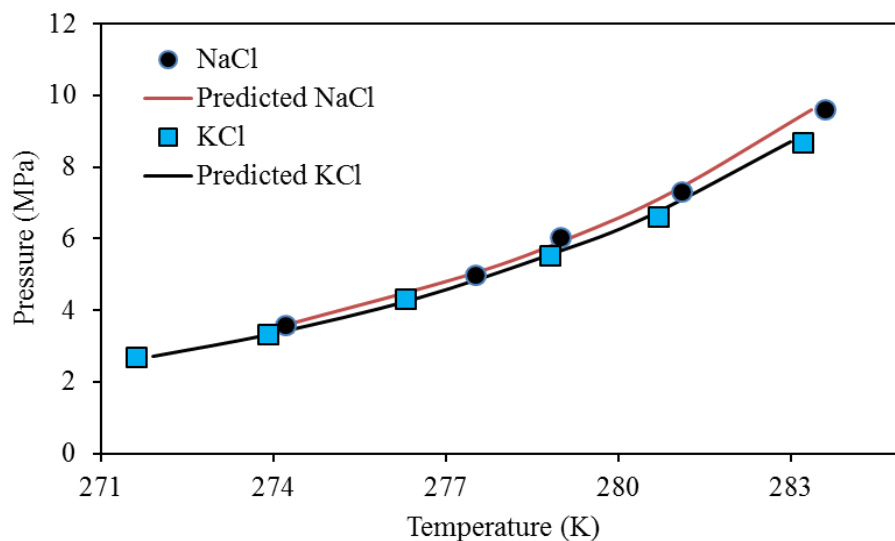


Figure 1: Experimental and Model predicted HL_wVE data for 5 wt% salts (NaCl and KCl) solutions for validation.

Table 1. Details of the reported aqueous ILs solutions used (10 wt%) in this work.

S. No.	Name of ILs	Symbol	Author
1	1-[2-Hydroxyethyl]-3-methylimidazolium chloride	[OH-EMIM][Cl]	Sabil et al. [23]
2	1-[2-Hydroxyethyl]-3-methylimidazolium bromide	[OH-EMIM][Br]	Sabil et al. [23]
3	1-butyl-3-methylimidazolium bromide	[BMIM][Br]	Sabil et al. [23]
4	1-butyl-3-methylimidazolium chloride	[BMIM][Cl]	Sabil et al. [23]
5	1-butyl-3-methylimidazolium perchlorate	[BMIM][ClO ₄]	Sabil et al. [23]
6	1-butyl-3-methylimidazolium dicyanamide	[BMIM][N(CN) ₂]	Sabil et al. [23]
7	1-butyl-3-methylimidazolium hydrogen sulfate	[BMIM][HSO ₄]	Sabil et al. [23]
	1-butyl-3-methylimidazolium trifluoromethane sul on a	[BMIM][CF ₃ SO ₃]	Sabil et al. [23]
9	1-butyl-3-methylimidazolium methylsulfate	[BMIM][CH ₃ SO ₄]	Sabil et al. [23]
10	1-ethyl-3-methylimidazolium chloride	[EMIM][Cl]	Xiao et al. [24]
11	1-ethyl-3-methylimidazolium bromide	[EMIM][Br]	Xiao et al. [24]
12	1-propyl-3-methylimidazolium iodide	[PMIM][I]	Xiao et al. [24]
13	1-butyl-3-methylimidazolium chloride	[BMIM][Cl]	Xiao et al. [24]
14	1-butyl-3-methylimidazolium bromide	[BMIM][Br]	Xiao et al. [24]
15	1-butyl-3-methylimidazolium iodide	[BMIM][I]	Xiao et al. [24]
16	1-[2-hydroxyethyl]-1- methylpyrrolidinium tetrafluoroborate	[HEMP][BF ₄]	Kim et al. [25]
17	1-butyl-1-methylpyrrolidinium tetrafluoroborate	[BMP][BF ₄]	Kim et al. [25]
18	1-ethyl-1-methylimidazolium tetrafluoroborate	[EMIM][BF ₄]	Kim et al. [25]
19	Tetramethylammonium hydroxide	TMAOH	Khan et al. [26]

Table 2: Experimental and Model predicted HLwVE data analysis for 5 wt% salts (NaCl and KCl) solutions.

System	Temperature range (K)	No. data point	AAE (K)	R ²
5 wt% aqueous salts solutions				
NaCl	274.2-283.3	5	0.13	0.998
KCl	271.9-283.0	6	0.15	0.999

It can be evident from the Figure 1 and Table 2 that the considered model was perfectly applicable for salt solution, therefore; it effectively be applied on other electrolytes solutions such as ILs solutions. Moreover, Figure 2 presented the experimental and predicted HLwVE data points of 10 wt% IL-CH₄ systems from literature. Additionally, Table 3 tabulated the model predicted range, AAD and correlation (R²) values of each considered ILs.

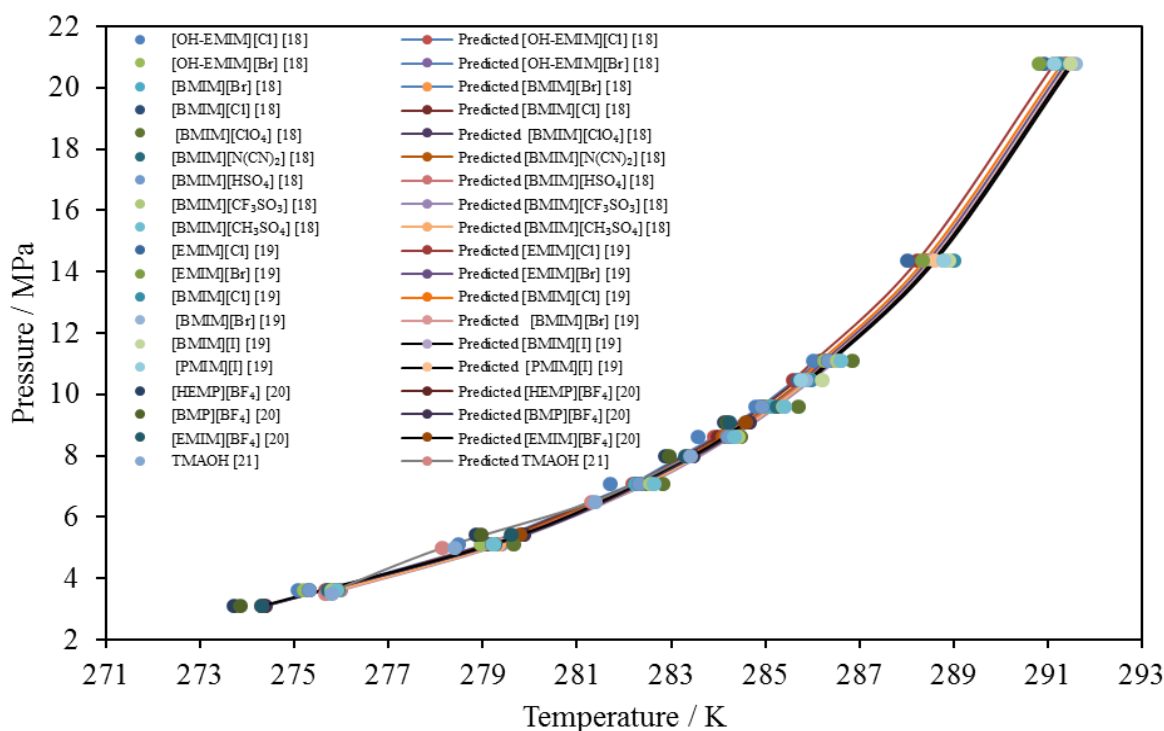


Figure 2. Experimental and Model predicted HL_{wVE} data for 10 wt% aqueous ILs solution.

Table 3. Predicted methane HL_{wVE} points in the presence aqueous ILs solutions

ILs	No. data point	Temperature range (K)	AAE (K)	R ²
[OH-EMIM][Cl]	06	279.77-287.45	0.24	0.996
[OH-EMIM][Br]	06	278.91-286.65	0.23	0.997
[BMIM][Br]	06	278.72-285.59	0.55	0.997
[BMIM][Cl]	06	279.91-286.77	0.3	0.995
[BMIM][ClO ₄]	06	279.37-286.62	0.18	0.998
[BMIM][N(CN) ₂]	06	275.82-286.32	0.15	0.999
[BMIM][HSO ₄]	06	275.90-286.41	0.19	0.998
[BMIM][CF ₃ SO ₃]	06	276.00-286.51	0.11	0.999
[BMIM][CH ₃ SO ₄]	06	275.93-286.44	0.13	0.999
[EMIM][Cl]	03	285.59-291.14	0.18	0.998
[EMIM][Br]	03	285.80-291.35	0.26	0.999
[PMIM][I]	03	285.96-291.53	0.25	0.989
[BMIM][Cl]	03	285.73-291.29	0.30	0.987
[BMIM][Br]	03	285.89-291.45	0.14	0.998
[BMIM][I]	03	285.90-291.47	0.21	0.998
[HEMP][BF ₄]	04	274.34-284.63	0.67	0.998
[BMP][BF ₄]	04	274.37-284.67	0.60	0.998
[EMIM-BF ₄]	04	274.29-284.58	0.14	0.999
TMAOH	04	275.65-283.38	0.13	0.999

Consulting to the Figure 2, it is evident that the model predicted data found in good agreement with the experimental literature data. It was clearly observed from the Table 3 that only pyrrolidinium based

ILs, i.e., [HEMP][BF₄] and [BMP][BF₄] slightly deviated with AAE values of 0.667 and 0.660, respectively. Furthermore, good correlations obtained with most of the R² values < 0.99 (with 95 % confidence level) were observed among the model predicted and experimental HL_wVE points. This validates the applicability of the studied model on the CH₄ hydrate and thus endorses the application of the electrolyte model for the prediction of the behaviour of the different ILs for other gas hydrate formers too.

4. Conclusions

In this work, the electrolyte-based model is applied to CH₄-ILs hydrate systems. Dickens and Quinby-Hunt Model predicted HL_wVE data revealed that the used model found in acceptable agreement with the experimental literature data of CH₄ hydrates in the presence of aqueous ILs solutions. Generally, for most of the ILs, the AAE values are found to be less than 0.25 K; while maximum AAE value (0.67) obtained for pyrrolidinium based IL ([HEMP][BF₄]) perhaps due to their higher alkyl chain length and molecular weights. Therefore, the suggesting model can be efficiently applied as a tool to predict new ILs with the aim to accomplish the desired THI inhibition for the petroleum industry.

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