Thermodynamic Modeling Of Electrolytic Solutions of Ionic Liquids for Gas Hydrates Inhibition Applications

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\textbf{ABSTRACT}

The formation of hydrates in oil and gas transmission pipelines can cause blockage inside them and disrupt the normal flow. It may cause safety problems along with economic loss. To avoid these problems, it is necessary to have knowledge about gas hydrate formation. In this regard, hydrate liquid vapor equilibrium (HLVE) modeling can prove to be of significance as it predicts the phenomenon accurately. Dickens and Quimby-Hunt model is used to predict HLVE points. The experimental data has been obtained from open literature concerning inhibition of gas hydrates. The electrolytic binary solution mixtures of ionic liquids and quaternary ammonium salts (QAS) with commercial hydrate inhibitors have been taken into consideration. Methanol and mono ethylene glycol (MEG) are commercially used inhibitors. The gases forming hydrates include CO\textsubscript{2}, CH\textsubscript{4} and mixed gas (CO\textsubscript{2}/CH\textsubscript{4}/N\textsubscript{2}). The experimental results are compared with the results obtained through modeling. The results show the applicability of the model as in case of QAS+MEG solution mixture hydrates with CO\textsubscript{2}, it shows a good fit. The HLVE findings of EMIM-Cl+MEG mixture for CH\textsubscript{4} hydrates showed good results. The binary solution mixtures of NaCl+MEG, NaCl+MeOH and CaCl\textsubscript{2}+MeOH with tertiary gas mixture rich in CO\textsubscript{2} were also modeled. It is found that the selected model is suitable to be used in hydrate forming pressure conditions. It shows the suitability of the model and it can be further used in case of ionic compounds to predict hydrate inhibition behavior.

\textbf{Keywords:}

Gas hydrates; Hydrate Liquid Vapor Equilibrium (HLVE); Dickens and Quimby-Hunt model; Quaternary Ammonium Salts (QAS); Monoethylene glycol (MEG); Methanol

\section{1. Introduction}

Natural gas is the primary source of energy in modern world and the issue of CO\textsubscript{2} separation is of primary concern for flow assurance industry. The formation of methane and carbon dioxide hydrates in the transmission pipeline poses threat to normal operation and their formation must be avoided [1-3]. Gas hydrates are non-stoichiometric crystalline solids which appear like ice [4-6]. Their
formation is due to the interaction between gas of relatively low molecular weight and water [5,7-10]. Gas hydrates are formed at high pressure and low temperature conditions [11-13]. During the formation, gas molecules which are also known as guest molecules are trapped in water cages that act as a host [14-16]. These cages are created due to hydrogen bonding between gas and water molecules [17-19]. Gas hydrates are found in natural conditions as it can be found in permafrost regions, or at the bottom of the oceans [20-22]. At seabed conditions, high pressure and low temperature is achieved readily and frequently so hydrate formation is normal to occur [23]. Gas hydrates can also be formed in flow conditions in gas transportation pipelines and can cause safety problems because of the solid structure of hydrates which cause damage to these pipelines [9,24-26]. Therefore, the prevention for gas hydrates formation has been in the center of research to improve flow assurance strategies and avoid the problems caused by hydrates formation in pipelines. Several methods exist in this way, like heating, depressurization or dehydration, but the most used in industry is the chemical inhibition [18,27,28].

This inhibition is based on introducing a certain compound inside the pipeline. These compounds include anti-agglomerants, kinetic or thermodynamic hydrate inhibitors [9,29,30]. Currently, modeling is present in almost all scientific problems. In some areas like engineering, it is a part of the process conception. It could be very important in the future to know how this kind of system can be modeled. This work will be focused on thermodynamic inhibition modeling, and in particular on Dickens and Quinby-Hunt’s [31] model for gas hydrate. This model is activity-based model and studies the influence of the additives, like inhibitors, on the water activity [11,31]. The employed model is an extended form of the model used by Pieroen [32]. According to the literature, this model is used to describe Hydrate Liquid Vapor Equilibrium (HLVE) in electrolytic solutions [17,33]. It was also adapted for other types of solutions like Ionic Liquids or Amino Acid solutions or compounds which dissolve into solutions in polar heads [33].

This model is suitable to use as it predicts the phase behavior of the ionic compounds accurately. The significance of this model has been mentioned in literature also as it takes into account the freezing point depression of the employed chemicals at varying temperature and pressure conditions in presence of electrolytes and water activity [31,34-36]. The main issue is about the complexity of these binary mixed systems because of the interactions. Moreover, several pure components can have some secondary negative effects like corrosion, partial solubility and environmentally un-benign behavior. In this way, mixed solutions might play an important role in the future flow assurance applications. Here, the average absolute error between experiments and modeling results is calculated to evaluate the suitability of the model.

2. Methodology

2.1 Model for Pure Inhibitor

The model which is taken into consideration has previously been used for pure inhibitor compounds. Preceding literatures show that ionic liquids and quaternary ammonium salts (QAS) which are imidazolium, piperidenium and ammonium based have been employed in THI and KHI applications. Literature data is available for the use of some ionic liquids and QASs including TEAB, TMAB, TMACl, TMAOH, EMPip-Br, EMPip-BF₄ and BMIM-BF₄ in presence of CO₂ for hydrate inhibition. Among imdazolium based ionic liquids, Nasir et al., [37] worked on EMIM-Cl in mixture with monoethylene glycol (MEG) for inhibition of methane hydrates. These compounds have mostly been employed in THI applications. The modeling shows that the experimental results fit with the model. Bavoh et al., [30] worked in case of amino acids such as L-Valine, L-Threonine, L-Asparagine
and L-Phenylalanine for methane hydrates. The main objective is to find out whether the model is suitable to be used for mixed inhibitor solutions.

2.2 Experimental Data from Literature

The experimental data needed for comparison with the model is obtained from the literature for CO₂, CH₄ and CO₂/CH₄ hydrates. For each group of data, there is different gas compositions. The first set of data is obtained from the work of Nasir et al., [37]. It involves inhibition effects of EMIM-Cl+MEG aqueous solutions with different concentrations of 10wt%, 20wt% and 30wt% in pure methane in between the the pressure range of 10 to 20 MPa. The other set of data is obtained from the work of Richard and Adidharma [38]. This work is concerned with the aqueous salt solutions. These solutions are composed of water, Methanol (MeOH) or MEG, and salts like Sodium chloride (NaCl) and Calcium chloride (CaCl₂). In this work, experimental data of three mixture solutions are used (10wt% NaCl + 20wt% MeOH / 10wt% CaCl₂ + 20wt% MeOH / 10wt% NaCl + 20wt% MEG). Another particularity of this work is related to gas composition because it involves CO₂/CH₄ gas mixtures. The composition of gas mixture used involves Carbon dioxide (CO₂), Nitrogen (N₂) and Methane (CH₄) (70.35/3.09/26.55 %). The last group of data involves Quaternary Ammonium based Salts (QAS) like Tetramethylammonium Bromide (TMAB) and Tetraethylammonium Bromide (TEAB). The experimental data for these components are available from the work of Qasim et al., [17] wherein CO₂ hydrate mitigation is studied. In their work, TEAB and TMAB are mixed with MEG at different concentrations of 1, 5 and 10 wt%. In this work, the modeling results are compared with 5 and 10 wt% solution mixtures.

2.3 Model Theory

The model used was developed by Dickens and Quinby-Hunt [31]. This model is a modification of the Pieroen [32] model which is adapted for non-electrolytic solutions. This model was also adapted for hydrates in ionic liquid solutions and aqueous salts by Keshavarz et al., [39], Partoon et al., [40], and Bavoh et al., [41]. Their findings showed that this model is also appropriate with amino acid solutions for pure CO₂ gas. So, it can be concluded that this model can be used for hydrates modeling with pure ionic liquids, aqueous salts and amino acids.

The main objective of the inhibitor considered is the reduction in water activity in the system. Moreover, it postulates that the amount of gas in water and the amount of water in gas are negligible. There are two ways to describe this reduction. These involve hydrate formation temperature in pure water with an inhibitor and with the dissociation enthalpy of the hydrate. The effects of the inhibition are expressed in Eq. (1).

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

(1)

where \(a_w\) is the water activity, \(\Delta H_d\) is the enthalpy of dissociation of gas hydrate which is considered constant over small temperature ranges, \(n\) is the hydration number of hydrates, \(R\) is the universal gas constant, \(T_w\) is the hydrate formation temperature in pure water and \(T_{inhibitor}\) is the hydrate formation temperature in the mixture water + inhibitor. The temperature \(T_w\) can be calculated by hydrate prediction model in the literature as described by Sloan and Koh [7] or by the commercial hydrate predicting software CSMGem. In this work, the value of \(T_w\) is determined by CSMGem. This software deals with the prediction of thermodynamically stable hydrates structures and cage occupancy at given pressure, temperature and composition. It does so by minimizing Gibbs free
energy of the specified system. The influence of inhibitor on hydrate formation is described by the Eq. (2). According to Eq. (2) the influence on water activity is described by freezing points with and without inhibitor, and by the fusion enthalpy of ice.

\[
\ln(a_w) = \frac{\Delta H_{\text{fus},i}}{R} \left[ \frac{1}{T_{f,i}} - \frac{1}{T_f} \right]
\]

Where \( \Delta H_{\text{fus},i} \) is the fusion enthalpy of ice, \( R \) is the universal gas constant, \( T_{f,i} \) is the freezing point temperature of ice \((273.15 \text{ K})\), and \( T_f \) is the freezing point temperature of aqueous inhibitor solution.

In this case, \( T_f \) is calculated using the following Eq. (3)

\[
T_f = T_{f,i} - \Delta T_f
\]

Where, \( \Delta T_f \) is the depression freezing temperature between pure water freezing point temperature of ice and freezing point temperature of aqueous solution of the inhibitor. \( \Delta T_f \) is expressed as Eq. (4)

\[
\Delta T_f = K_f \cdot I \cdot \text{mol}
\]

Where \( K_f \) is the cryoscopic constant for water which is 1,853 K.kg/mol, \( I \) is the number of ion(s) of the inhibitor when it is dissociated in solution, \( \text{mol} \) represents molality of the inhibition solution and \( \Delta T_f \) the depression freezing temperature.

By combining of the Eq. (1) and Eq. (2), the hydrate formation temperature in presence of inhibitor can be expressed as Eq. (5)

\[
\left[ \frac{1}{T_w} - \frac{1}{T_{\text{inhibitor}}} \right] = \frac{n \Delta H_{\text{fus},i}}{\Delta H_d} \left[ \frac{1}{T_{f,i}} - \frac{1}{T_f} \right]
\]

From Eq. (5), \( T_{\text{inhibitor}} \) can be calculated with all the other known parameters. This is the temperature predicted by the model which could be compared with experimental temperature.

2.4 Dissociation Enthalpy

For \( T_{\text{inhibitor}} \) calculation, dissociation enthalpy \( \Delta H_d \) should be known. In order to determine dissociation enthalpy, following equation is used as mentioned in Eq. (6)

\[
\frac{d \ln(P)}{d \left( \frac{1}{T} \right)} = -\frac{\Delta H_d}{ZR}
\]

Where \( P \) and \( T \) are experimental pressure and temperature respectively, \( Z \) is the compressibility factor which is calculated for each pressure value using Peng-Robinson (PR) equation of state and \( R \) is the universal gas constant. Eq. (6) is rearranged as follows and written as Eq. (7)

\[
\Delta H_d = -ZR \frac{d \ln(P)}{d \left( \frac{1}{T} \right)}
\]

When experimental Pressure is plotted with a semi-logarithmic scale in function of the inverse of experimental temperature, a constant negative slope can be observed. This slope is previously calculated from experimental data before the calculation of dissociation enthalpy.
The average absolute error (AAE) for the model prediction is calculated following Eq. (8) and Eq. (9)

$$AAE(K) = \frac{1}{m} \sum_{i=1}^{m} |T_{Exp} - T_{Calc}|_i$$

(8)

$$AAE(\%) = \frac{100}{m} \sum_{i=1}^{m} \left| \frac{T_{Exp} - T_{Calc}}{T_{Exp}} \right|_i$$

(9)

2.5 Modeling

The model presented in the previous section is used in a computer program using Fortran 90. Figure 1 shows the organization of the program.

![Fig. 1. Flowchart of the calculation](image)

The generated code provides the value of inhibition temperature, $T_{inhibitor}$. If the depression in freezing temperature is known then it proceeds and dissociation enthalpy is calculated directly without the calculation of depression in temperature. Otherwise, it calculates freezing point temperature before the dissociation enthalpy calculation.

3. Results and Discussion

The work investigates the suitability of Dickens and Quinby-Hunt model for the conditions of binary mixture of inhibitors in aqueous solution. These binary mixtures involve the combination of ionic liquids or Quaternary Ammonium Salts (QAS) with a commercial inhibitor. The commercial inhibitors include MEG or methanol. At first, binary mixtures of QAS+MEG are taken into considerations which are used in inhibition application of CO$_2$ hydrates.
Concerning the QAS, experimental data for CO₂ hydrates are reported in the Table 1 given below.

**Table 1**
Experimental HLVE points for QAS+MEG mixtures at 5 and 10 wt% for CO₂ hydrates [17]

| Mixture                | Temperature (K) | Pressure (MPa) |
|------------------------|-----------------|----------------|
| 5 wt% TMAB + MEG (1:1) |                 |                |
| 274.6                  | 2               |
| 277.3                  | 2.5             |
| 280.9                  | 3               |
| 281.9                  | 3.5             |
| 10 wt% TMAB + MEG (1:1)|                 |                |
| 274                    | 2               |
| 276.5                  | 2.5             |
| 280.2                  | 3               |
| 281.2                  | 3.5             |
| 5 wt% TEAB + MEG (1:1) |                 |                |
| 275                    | 2               |
| 277.7                  | 2.5             |
| 281.3                  | 3               |
| 282.3                  | 3.5             |
| 10 wt% TEAB + MEG (1:1)|                 |                |
| 274.35                 | 2               |
| 277                    | 2.5             |
| 280.5                  | 3               |
| 281.5                  | 3.5             |

Figure 2 shows the curves for TMAB + MEG mixtures plotted according to the values as mentioned in Table 1. The graph shows the comparison of values obtained through model versus experimental in case of CO₂ hydrates.
Figure 3 shows the comparison of experimental and model values for TEAB+MEG mixtures for CO₂ hydrates.

Table 2 shows the AAE for TMAB-MEG and TEAB-MEG mixtures as follows.

| Mixture                     | Pressure (MPa) | $T_{\text{inhibitor}}$ (K) | AAE (%) |
|-----------------------------|----------------|---------------------------|---------|
| 5 wt% TMAB + MEG (1:1)      | 2              | 276.46                    | 0.263   |
|                             | 2.5            | 278.17                    | 0.402   |
|                             | 3              | 279.48                    | 0.349   |
|                             | 3.5            | 280.51                    | 0.356   |
| 10 wt% TMAB + MEG (1:1)     | 2              | 275.87                    | 0.299   |
|                             | 2.5            | 277.55                    | 0.433   |
|                             | 3              | 278.81                    | 0.419   |
|                             | 3.5            | 279.78                    | 0.461   |
| 5 wt% TEAB + MEG (1:1)      | 2              | 276.50                    | 0.248   |
|                             | 2.5            | 278.21                    | 0.440   |
|                             | 3              | 279.53                    | 0.278   |
|                             | 3.5            | 280.55                    | 0.29    |
| 10 wt% TEAB + MEG (1:1)     | 2              | 275.96                    | 0.256   |
|                             | 2.5            | 277.63                    | 0.411   |
|                             | 3              | 278.91                    | 0.291   |
|                             | 3.5            | 279.88                    | 0.295   |
From Figure 3 and Figure 4, it can be noticed that at the concentrations of 5 and 10 wt%, modeling curves for TMAB and TEAB shifted slightly towards right from experimental curves. As discussed previously, the model does not consider the interactions between the two components of the mixture (QAS and MEG), so this explains the minimal shifting of the curves. The shifting on the right is caused by a metastable area. Metastable region is the area which lies between the hydrate formation and dissociation curve. On this basis, it is interpreted that the model did not take into account metastable area. AAE values in K and in percentage are expressed in Table 3 mentioned below.

| Mixture                      | AAE (K) | AAE (%) |
|------------------------------|---------|---------|
| 5 wt% TMAB + MEG (1:1)       | 0.952   | 0.343   |
| 10 wt% TMAB + MEG (1:1)      | 1.117   | 0.403   |
| 5 wt% TEAB + MEG (1:1)       | 0.876   | 0.315   |
| 10 wt% TEAB + MEG (1:1)      | 0.934   | 0.337   |

The AAE analysis confirmed previously obtained results. The AAE mentioned in Table 3 is close to 1 K for all the solution mixtures. The AAE calculated in percentage is well below 1% for all solutions, so the model can be considered as fitting with the experimental data.

The results comprising the inhibition performance of ionic liquid along with MEG are discussed. Experimental data from Richard and Adidharma [38] for methane hydrates were used to plot experimental curves for pure methane gas and EMIM-Cl+MEG aqueous solutions. Experimental results obtained from literature are presented in Table 4.

| Mixtures                      | Temperature (K) | Pressure (MPa) |
|------------------------------|-----------------|----------------|
| 10 wt% EMIM-Cl + MEG (1:1)   | 284.9           | 10             |
|                              | 288.0           | 14.8           |
|                              | 289.7           | 19.7           |
| 20 wt% EMIM-Cl + MEG (1:1)   | 281.9           | 9.7            |
|                              | 285.6           | 14.8           |
|                              | 287.2           | 19.8           |
| 30 wt% EMIM-Cl + MEG (1:1)   | 279.6           | 9.9            |
|                              | 281.6           | 14.9           |
|                              | 284.0           | 19.8           |

Figure 4 shows the comparison between experimental and modeling values in case of EMIM-Cl+MEG mixtures for CH₄ hydrates. The experimental data from literature is represented in full lines which are grouped in Table 4 and the modeling curves are shown by dashed lines.
Fig. 4. Experimental and modeling equilibrium curves of EMIM-Cl+MEG mixtures for CH₄ hydrates at 10, 20 and 30 wt%

Table 5 mentioned below shows the modeling temperature and the AAE (in percentage) for each pressure value as shown in Figure 5.

| Mixture                  | Pressure (MPa) | \(T_{\text{inhibitor}}\) (K) | IE (%) |
|--------------------------|----------------|-------------------------------|--------|
| 10 wt% EMIM-Cl + MEG (1:1) | 10             | 284.54                        | 0.125  |
|                          | 14.8           | 287.75                        | 0.088  |
|                          | 19.7           | 290.02                        | 0.109  |
| 20 wt% EMIM-Cl + MEG (1:1) | 9.7            | 282.31                        | 0.147  |
|                          | 14.8           | 285.65                        | 0.016  |
|                          | 19.8           | 287.94                        | 0.259  |
| 30 wt% EMIM-Cl + MEG (1:1) | 9.9            | 281.22                        | 0.578  |
|                          | 14.9           | 284.29                        | 0.956  |
|                          | 19.8           | 286.58                        | 0.908  |

It can be noticed that for each value of pressure, AAE is below 1%. It shows that experimental and modeling predicted temperatures are close even at pressure of 20 MPa.

The values for Average Absolute Error (AAE) are reported in terms of temperature difference and in percentage in Table 6 as follows.

| Mixture                  | AAE (K) | AAE (%) |
|--------------------------|---------|---------|
| 10 wt% EMIM-Cl + MEG (1:1) | 0.308   | 0.107   |
| 20 wt% EMIM-Cl + MEG (1:1) | 0.401   | 0.141   |
| 30 wt% EMIM-Cl + MEG (1:1) | 2.295   | 0.814   |
It is also observed that for 10 and 20 wt% mixtures taken into consideration difference among temperature depression values obtained through model and experiments is less than 1 K. At 30 wt% it is above than 1 K. Additionally, the AAE in terms of percentage is less than 1% for the three solutions. The highest error among experimental and modeling values is found for 30 wt% solution of EMIM-Cl+MEG. It is due to the quantity of inhibitors mixed in the aqueous solution. The amount of EMIM-Cl in 30 wt% solution is more as compared to 10 and 20 wt% mixture solutions. Interactions between EMIM-Cl and MEG could not be taken into account by the model but the low error percentage, even at high pressure. Even if interactions are more important because of the gas mixture and the inhibitor mixture at these pressure values, which shows that this model can be used to represent this type of system.

Experimental data of electrolyte aqueous + MEG/methanol solutions from Nasir et al., [37] are grouped in the Table 7. These data concern mixtures with electrolytic salt (NaCl or CaCl$_2$) and MeOH for mixed gas hydrates. This gas mixture is composed of 70% CO$_2$, 26.551% CH$_4$ and 3.096% N$_2$. So, it is a predominantly CO$_2$ rich gas mixture. Table 7 is given as:

| Mixture                      | Temperature (K) | Pressure (MPa) |
|------------------------------|-----------------|----------------|
| 10 wt% NaCl + 20 wt% MeOH    | 264.95          | 2.84           |
|                               | 266.75          | 3.94           |
|                               | 268.55          | 5.32           |
|                               | 269.65          | 6.12           |
| 10 wt% CaCl$_2$ + 20 wt% MeOH| 272.65          | 3.67           |
|                               | 274.15          | 5.33           |
|                               | 274.95          | 6.45           |
|                               | 275.75          | 7.10           |
| 10 wt% NaCl + 20 wt% MEG      | 268.35          | 3.01           |
|                               | 270.75          | 4.32           |
|                               | 272.35          | 5.58           |
|                               | 273.95          | 6.45           |

These results for NaCl+MeOH and CaCl$_2$+MeOH solution mixtures are plotted in Figure 5.

The curves of 10 wt% NaCl+MeOH, CaCl$_2$+MeOH, NaCl+MEG mixtures of gas mixture hydrates represented in Figure 5 show that at relatively moderate or low pressures of around 5 MPa, modeling results are quite close to experimental results. The curve showing equilibrium points for pure water are obtained using CSMGem through which $T_{inhibitor}$ can further be determined. The exact values of hydrate formation temperatures and the Average Absolute Error (AAE) in percentage are given in Table 8 as follows. Like the preceding cases, an absolute error under 1% is acceptable and the model fits well with the experimental data.
The percentage absolute error in Table 8 confirms the results obtained in Figure 5. It is evident that up to 5MPa, the AAE lies under 1% for all the solutions. For all the mixtures, the values for AAE are presented in Table 9 mentioned below.

### Table 8

| Mixture                  | Pressure (MPa) | $T_{inhibitor}$ (K) | AAE (%) |
|--------------------------|----------------|---------------------|---------|
| 10 wt% NaCl + 20 wt% MeOH| 2.84           | 266.14              | 0.448   |
|                          | 3.94           | 267.06              | 0.116   |
|                          | 5.32           | 266.22              | 0.868   |
|                          | 6.12           | 264.18              | 2.027   |
| 10 wt% CaCl₂ + 20 wt% MeOH| 3.67           | 271.82              | 0.306   |
|                          | 5.33           | 272.67              | 0.540   |
|                          | 6.45           | 271.78              | 1.152   |
|                          | 7.10           | 270.15              | 2.030   |
| 10 wt% NaCl + 20 wt% MEG  | 3.01           | 269.57              | 0.454   |
|                          | 4.32           | 270.92              | 0.062   |
|                          | 5.58           | 270.64              | 0.629   |
|                          | 6.45           | 269.02              | 1.800   |

### Table 9

| Mixture                  | AAE (K) | AAE (%) |
|--------------------------|---------|---------|
| 10 wt% NaCl + 20 wt% MeOH| 2.322   | 0.870   |
| 10 wt% CaCl₂ + 20 wt% MeOH| 5.221 | 1.900   |
| 10 wt% NaCl + 20 wt% MEG  | 4.675   | 1.726   |
For the above-mentioned solutions, the difference between experimental and modeling equilibrium temperature is high. The AAE in terms of difference in equilibrium temperature obtained for the 10wt% NaCl + 20wt% MeOH solution is 2.322 K but AAE in terms of percentage is found to be 0.870%. For the two other mixtures, the equilibrium temperature difference between experimental and modeling results is 5.221 for 10wt% CaCl$_2$ + 20wt% MeOH and 4.675 for the 10 wt% NaCl + 20 wt% MEG. The error in terms of percentage is 1.90% and 1.726% respectively which is greater than 1%. That can be explained by the interactions between the molecules of the inhibitors which are probably significant but not considered by the model. This may also be related with the usage of gas mixture as the model predicts equilibrium temperature for pure gases more accurately. The interaction between gas molecules may be an important factor, in particular at high pressure where interactions play a more significant role. At high pressure, the model does not fit well with the experimental values.

4. Conclusion

The comparison of experimental and modeling results for thermodynamic hydrate inhibition effect of different electrolytic solution mixtures have been presented. The equilibrium temperature for different solution is calculated using Dickens and Quinby-Hunt model. Preceding researches have reported about it. Its applicability has been reported in case of quaternary ammonium salts. The model accurately estimated thermodynamic hydrate inhibition temperature for mixture of TMAB and TEAB with ethylene glycol up to the pressure of 3.5 MPa concerning CO$_2$ hydrates. In case of ionic liquids such as EMIM-Cl mixed in aqueous solutions with MEG, the results predicted by model fitted well with the experimental results at different concentrations. The prediction results were better at low concentrations. The difference among experimental and modeling results at high concentration can be attributed to lesser number of interactions between EMIM-Cl and MEG. In case of binary systems involving NaCl+MEG, NaCl+MeOH and CaCl$_2$+MeOH mixtures, the fitness of model is more accurate at relatively lower temperatures. Overall, the usage of Dickens and Quinby-Hunt model is found to be suitable for predicting hydrate liquid vapor equilibrium (HLVE) of binary solution mixtures.

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