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Prediction of hydrate formation conditions in the solutions containing electrolyte and alcohol inhibitors and their mixtures using UNIQUAC-NRF models

Sara Moradi[a], Ali Haghtalab[b,*], Alireza Fazlali[a]

[a] Department of Chemical Engineering, Arak University, P.O. Box 38156-8-8849, Arak, Iran
[b] Department of Chemical Engineering, Tarbiat Modares University, P.O. Box 14115-143, Tehran, Iran

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ABSTRACT

In this work, the prediction of hydrate formation conditions in the presence of the thermodynamic inhibitors is presented. Using the van der Waals–Platteeuw model, computation of the L–S–G equilibrium is carried out for hydrate formation conditions in the presence of methanol and electrolytes using the local composition models of the UNIQUAC-NRF and Electrolyte-UNIQUAC-NRF for nonelectrolyte and electrolyte systems, respectively. The model is applied to calculate water activity coefficient for prediction of the hydrate formation pressure of methane, ethane, H_2S in the absence and presence of the electrolytes. The results of the present model are compared with the experiment and UNIFAC group contribution model. Also both UNIQUAC-NRF and UNIFAC activity coefficient models are used to predict the hydrate formation conditions in the presence of alcohols. The results show very good agreement with the experiment.

1. Introduction

Gas hydrates are crystalline molecular complexes which are formed through mixtures of water and low molecular weight gases. Following Sir Humphry Davy who discovered clathrate hydrate in 1810, in 1934 Hammer Schmidt considered blockage of gas transmission lines due to gas hydrate so that prevention of gas hydrate formation in pipes has been an essential step in the transportation of natural gas through piping network. The natural gas hydrate can be formed in temperatures higher than the freezing point temperature of water that leads to blockage of gas and oil transportation pipes. Therefore, the investigation to find an effective technique in prevention and elimination of gas hydrate formation has been paid significant attention. So far the different methods such as increasing temperature, decreasing the pressure and using thermodynamic or kinetic inhibitors have been used to prevent gas hydrate formation. Thermodynamic inhibitors such as alcohols, glycols and salts are those materials that cause to reduce hydrate formation temperature in a certain pressure.

The thermodynamic basis of gas hydrate formation modeling was studied by van der Waals and J.H. Platteeuw in 1959 [1]. Following the framework of vdw–platteeuw, in 1972 Parrish and Prausnitz [2] modified this model to estimation the hydrate formation condition of pure methane, ethane, propane and their binaries. So far many researchers have tried to simulate hydrate formation conditions in the presence of thermodynamic inhibitors. Among the most recent works are those of Anderson–Prausnitz approach [3] and Moshfeghian–Maddox model [4]. Although these methods have been used to produce somewhat accurate results at their range of applicability, however most of the proposed models may not be used out of their specific applications. For instance, the method of Anderson and Prausnitz [3] is usually applicable to calculate hydrate formation conditions in the solutions containing methanol. The method of Moshfeghian and Maddox [4] is useful to calculate hydrate formation conditions in natural gas streams. The gas hydrate inhibition effect of electrolyte solutions has been investigated and modeled by several workers such as Harvey and Prausnitz [5], Tohidi et al. [6], Clarke and Bishnoi [7] and Haghtalab et al. [8]. Following the previous works, Masoudi et al. [9] have presented a new thermodynamic model that is capable reliably to predicting the equilibrium conditions of multiphase systems including the hydrate formation of single and mixed electrolyte aqueous solutions over a wide range of pressure and temperature. Moreover, Masoudi et al. [10] modified their previous work for the solutions containing salts and alcohols such as ethylene glycol. Therefore, in this work to predicting hydrate formation conditions in the presence all kind of inhibitors, based on local composition concept, a different activity coefficient model such as the UNIQUAC-NRF model [11] is used. This activity coefficient model [11] is used to

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* Corresponding author. Tel.: +98 2182883313; fax: +98 2182884959.
E-mail addresses: ahaghtalab@hotmail.com, haghtala@modares.ac.ir (A. Haghtalab).

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calculate activity of water in solutions containing alcohol and electrolyte to predicting hydrate formation conditions.

2. Thermodynamic framework

Using the solid adsorption model of van der Waals and Platteeuw [1], the hydrate formation pressure is calculated through the approach was used by Parrish and Prausnitz [2]. This model is based on equality of the chemical potential differences between hydrate and water phases from empty hydrate phase so that fugacity in the vapor phase is calculated through mixing rules for gas mixtures. Thus, the following equations are usually used to calculate hydrate formation conditions [1,2]:

$$-RT\sum_{m}\vartheta_m \ln\left(1-\sum_{j}\theta_{mj}\right) = \frac{\Delta\mu_w(T_0,P_0)}{RT_0} - \int_{T_0}^{T}\frac{\Delta h_w^L}{RT^2}dT + \int_{P_0}^{P}\frac{\Delta V_w^L}{RT}dP - \ln(a_w) \qquad (1)$$

$$\theta_{mj} = \frac{C_{mj}(T)f_j(T,P)}{1+\sum_j C_{mj}f_j(T,P)} \qquad (2)$$

$$C_{mj} = \frac{4\pi}{kT}\int_0^{R-a}\exp\left(-\frac{w(r)}{kT}\right)r^2dr \qquad (3)$$

where θ_{mj} denotes the fractional filling of cavity m by guest molecule j and ϑ_m stands for cavity number per water molecules in the hydrate structure. $f_j(T,P)$ is the fugacity of gas species j in the vapor phase that is calculated through a cubic equation of state such as SRK and the van der Waals mixing rule. C_{mj} is Langmuir's constant of gas j in a type m cavity that is calculated through the Kihara model as a potential function for spherical molecules forming the hydrate phase. $\mu_W(T_0, P_0)$ is the reference chemical potential at 273.15 K and zero pressure. The activity of water is calculated as bellow [4]

$$a_w = \gamma_w x_w \qquad (4)$$

where a_w and γ_w are the activity and the activity coefficient of water, respectively. The mole fraction of water is obtained as

$$x_w = 1-\sum x_k = 1-\sum\frac{f_k}{H_{kw}\exp(P\bar{v}^\infty/RT)} \qquad (5)$$

$$-\ln(H_{kw}(T)) = H_k^{[1]} + \frac{H_k^{[2]}}{T} + H_k^{[3]}\ln T + H_k^{[4]}T \qquad (6)$$

where H_{kw} is the Henry's constant and $\bar{v}^\infty$ is the infinite partial molar volume. The values of the coefficients in Eq. (6) are given by Sloan [12] and the infinite partial molar volume is given by Nguyen [12]. For solubility of gases in the presence of methanol the following relation is used [13].

$$\ln\ x_i = A + C\ln T + DT + Ex_{Met} + Fx_{Met}^2 + G\ln x_{Met} \qquad (7)$$

In the presence of alcohols as inhibitor, to calculate the activity of water in the liquid phase the local composition models of UNIQUAC-NRF [11] and E-UNIQUAC-NRF [14] are used for non-electrolytes and electrolytes, respectively. The detailed descriptions of these models are given in Appendix A.

Table 1
The interaction parameters of the UNIQUAC-NRF model for the water–methanol system. The data is given in [15].

u_{11} [a]	u_{22}	u_{12}	u_{21}
418.2269	787.7899	652.8832	396.7584

[a] 1 and 2 refer to methanol and water molecules, respectively.

3. Results and discussion

3.1. The parameters of UNIQUAC-NRF model for the water–methanol system

The UNIQUAC-NRF activity coefficient model [11] is based on the Wilson-type local composition model so that the random reference state is used for the central cells in contrast to the other local composition model such as UNIQUAC, NRTL in which the pure state are used. The adjustable parameters of this model are presented as

$$\tau_{ij} = \exp\left(\frac{-a_{ij}}{T}\right);\quad a_{ij} = \left(\frac{u_{ij}-u_{jj}}{R}\right) \qquad (8)$$

where u_{ij} and u_{ij} are used as the adjustable parameters for interaction energy between unlike or like components in this work. These parameters are calculated through optimization of the bubble pressure and dew temperature equilibrium data of water and methanol systems in different temperature and pressure [15]. Calculation of the water–hydrocarbon equilibrium systems is omitted here because of low solubility of hydrocarbons in water. Table 1 shows the optimized interaction energy parameters for the binary water–methanol system. To compare the results of the present work with the other models we use UNIFAC group contribution model as a predictive model in this work. Table 2 presents the results of prediction of the hydrate pressure formation for methane, propane and their mixtures. As one can see the results are in very good agreement with the experiment. Table 3 presents the results of the hydrate formation conditions for methane, ethane and their mixtures with methanol using UNIFAC, UNIQUAC and UNIQUAC-NRF models. As shown in Table 3, for all gases except methane, the UNIQUAC-NRF model presents very good agreement with experiment; vice versa UNIFAC and UNIQUAC models give good results only for methane and ethane, respectively. Thus, one may conclude that the UNIQUAC-NRF model yields overall better results. Fig. 1 shows the results of the hydrate formation pressure of methane, propane and hydrogen sulfide in the presence of %10 methanol. As it can be seen in Fig. 1, the results of prediction present a very good agreement with the experiment.

Table 2
The results of the pressure hydrate formation for methane, propane and their mixtures using UNIQUAC-NRF [17].

System	%AAD[a]
CH_4	0.82
C_3H_8	0.87
CH_4(%89/26) + N_2	1.51
CH_4 (%36.2) + C_3H_8	1.41
CH_4(%71/2) + C_3H_8	2.37
CH_4(%88/3) + C_3H_8	2.78
CH_4(%95/2) + C_3H_8	3.07

[a] $AAD\% = \frac{100}{N_p}\sum_{i=1}^{N_p}\frac{|P^{exp}-P^{cal}|}{P^{exp}}$.