다른 Mixing Rules를 사용한 Modified-BWR 상태 방정식의 황화수소를 포함한 LNG 혼합물에 대한 열역학 물성 예측 비교

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Comparison of thermodynamic properties prediction of Modified-BWR equations of state for hydrogen surfide mixtures with hydrocarbon in LNG

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1. 서론

본 연구에서는 물성 예측에 사용되는 대표적인 Non-cubic식인 Modified Benedict-Webb-Rubin(MBWR)상태 방정식에 다른 Mixing Rules를 적용하였을 때, 그 각각의 열역학적 물성 예측 능력을 비교하였다. MBWR 상태방정식에 Bishinoi & Robinson Mixing Rules(BRMR)를 적용하였으며, 또 다른 방법으로, Conformal Solution Theory에 의거한, Modified van der Waals one fluid Mixing Rule(CSTMR)을 사용하여 물성을 예측한 후 두 결과를 비교하였다. [1, 2, 6]

2. 이론

1) Bishnoi-Robinson Mixing Rules

Modified Benedict-Webb-Rubin 상태 방정식은 아래와 같다.

$$P = \rho RT + (B_oRT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4})\rho^2 + (bRT - a - \frac{d}{T})\rho^3 + \alpha(a + \frac{d}{T})\rho^6 + \frac{c\rho^3}{T^2}(1 + \gamma\rho^2)\exp(-\gamma\rho^2)$$

11개의 순수물질 parameter는 다음 식으로 계산된다. (Han&Starling Correlation)

$$\rho_{ci} B_{oi} = A_1 + B_1 \omega_i \qquad (\rho_{ci} A_{oi})/(R T_{ci}) = A_2 + B_2 \omega_i$$

$$(\rho_{ci}^2 C_{oi})/(R T_{ci}^3) = A_3 + B_3 \omega_i \qquad \rho_{ci}^2 \gamma_i = A_4 + B_4 \omega_i$$

$$\rho_{ci}^2 b_i = A_5 + B_5 \omega_i \qquad (\rho_{ci}^2 a_i)/(R T_{ci}^3) = A_6 + B_6 \omega_i$$

$$\rho_{ci}^3 a_i = A_7 + B_7 \omega_i \qquad (\rho_{ci}^2 c_i)/(R T_{ci}^3) = A_8 + B_8 \omega_i$$

$$(\rho_{ci} D_{oi})/(R T_{ci}^4) = A_9 + B_9 \omega_i \qquad (\rho_{ci}^2 d_i)/(R T_{ci}^2) = A_{10} + B_{10} \omega_i$$

$$(\rho_{ci} E_{oi})/(R T_{ci}^5) = A_{11} + B_{11} \omega_i \exp(-3.8 \omega_i)$$

The Bishinoi-Robinson Mixing Rules

$$B_{oij} = \sum_{i=1}^{n} x_i B_{oi}$$

$$A_o = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j A_{oi}^{\frac{1}{2}} A_{oj}^{\frac{1}{2}} (1-k_{ij})$$

$$C_o = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j C_{oi}^{\frac{1}{2}} C_{oj}^{\frac{1}{2}} (1-k_{ij})^3 \qquad \gamma = \left[\sum_{i=1}^{n} x_i \gamma_i^{\frac{1}{2}} \right]^2$$

$$b = \left[\sum_{i=1}^{n} x_i b_i^{\frac{1}{3}} \right]^3 \qquad a = \left[\sum_{i=1}^{n} x_i a_i^{\frac{1}{3}} \right]^3$$

$$\alpha = \left[\sum_{i=1}^{n} x_i \alpha_i^{\frac{1}{3}} \right]^3 \qquad c = \left[\sum_{i=1}^{n} x_i c_i^{\frac{1}{3}} \right]^3$$

$$D_o = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j D_{oi}^{\frac{1}{2}} D_{oj}^{\frac{1}{2}} (1-k_{ij})^4 \qquad d = \left[\sum_{i=1}^{n} x_i d_i^{\frac{1}{3}} \right]^3$$

$$E_o = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j E_{oi}^{\frac{1}{2}} E_{oj}^{\frac{1}{2}} (1-k_{ij})^4$$

2) Dimensionless reduced form of Modified-BWR EOS for which conformal solution theory applied.

$$Z = 1 + \rho^* \left[B_1 - \frac{B_2}{T^*} - \frac{B_3}{T^{*3}} + \frac{B_9}{T^{*4}} - \frac{B_{11}}{T^{*5}} \right] + \rho^{*2} \left[B_5 - \frac{B_6}{T^*} - \frac{B_{10}}{T^{*2}} \right]$$
$$+ \rho^{*5} \left[\frac{B_7}{T^*} + \frac{B_{12}}{T^{*2}} \right] + \frac{B_8 \rho^{*2}}{T^{*3}} \left[(1 + B_4 \rho^{*2}) \exp(-B_4 \rho^{*2}) \right]$$

$B_i = a_i + \gamma b_i$

a_i : isotropic part,

b_i : anisotropic part

γ : orientation parameter which describes molecule's non sphericity

σ_x : characteristic distance parameter,

ε_x : characteristic energy parameter

Modified van der Waals one fluid Mixing Rules.

$$\sigma_x^3 = \sum_\alpha \sum_\beta x_\alpha x_\beta \sigma_{\alpha\beta}^3$$

$$\varepsilon_x \sigma_x^3 = \sum_\alpha \sum_\beta x_\alpha x_\beta \varepsilon_{\alpha\beta} \sigma_{\alpha\beta}^3$$

$$\gamma_x \varepsilon_x^2 \sigma_x^3 = \sum_\alpha \sum_\beta x_\alpha x_\beta \gamma_{\alpha\beta} \varepsilon_{\alpha\beta}^2 \sigma_{\alpha\beta}^3$$

$$\sigma_{\alpha\beta} = \xi_{\alpha\beta} \sqrt{\sigma_{\alpha\alpha} \sigma_{\beta\beta}}$$

$$\varepsilon_{\alpha\beta} = \zeta_{\alpha\beta} \sqrt{\varepsilon_{\alpha\alpha} \varepsilon_{\beta\beta}}$$

$$\gamma_{\alpha\beta} = \frac{1}{2}(\gamma_{\alpha\alpha} + \gamma_{\beta\beta})$$

Table1. Generalized Parameters of Modified-BWR with use of Bishinoi-Ribinson MR and CST MR

Parameter subscript	Ai +Bi(BS MR)		Bi=ai +bi(CST MR)	
	Ai	Bi	ai	bi
1	0.443690	0.115449	1.45907	0.32872
2	1.28438	-0.920731	4.98813	-2.64339
3	0.356306	1.70871	2.20704	11.3293
4	0.544979	-0.270896	4.86121	
5	0.528639	0.349261	4.59331	2.79979
6	0.4884011	0.754130	5.06707	10.3901
7	0.0705233	-0.044448	11.4871	10.373
8	0.504087	1.32245	9.22469	20.5388
9	0.0307452	0.179433	0.094264	2.7601
10	0.0732828	0.463492	1.48858	-3.11349
11	0.006450	-0.022143	0.015273	0.18915
12			3.51486	0.9426

3. 결론

CST에 의거한 M-vdW 1F Mixing Rule을 사용하면 전반적으로 황화수소가 포함된 이성분계의 물성을 BR MR에 비해 정확히 예측할 수 있다. 특히 C_2H_8/H_2S 이성분계의 x_i의 경우 20%이상의 오차가 6%미만으로 줄어들었고, iC_4H_{15}/H_2S 이성분계의 경우에도 17%의 오차가 4.1%로 줄어들었다. LNG 계를 좀더 잘 묘사할 수 있는 Mixing Rules의 연구가 뒤따라야 할 것이다.

Table 2. Comparison of prediction for hydrocarbon/hydro-sulfide systems.

Binary Systems	EOS	A.A.D.(%) Density	No. of Data points	A.A.D.(%) VLE (x_i)	No. of Data points
CH_4/H_2S	CST MR	0.9	12	0.7	4
	BR MR	0.94	12	3.2	4
C_2H_8/H_2S	CST MR	2.3	16	5.6	8
	BR MR	5.6	16	21.7	8
$C3H_{12}/H_2S$	CST MR	1.9	12	3.1	12
	BR MR	2.4	12	7.4	12
iC_4H_{15}/H_2S	CST MR	4.2	6	4.1	8
	BR MR	4.7	6	17.0	8

4. 참 고 문 헌

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