MBWR EOS를 사용한 LNG혼합물의 상평형

손 주 영 · 이 태 종
경북대학교 화학공학과

Vapor-liquid equilibrium of LNG by means of the MBWR

Juyoung Son and Taejong Lee
Department of Chemical Engineering, Kyungpook National University

1. 서 론

정확한 상평형 예측은 공정 설계의 효율성과 성공적인 공정모사에 직접적인 영향을 미친다. 상태 방정식을 이용한 LNG혼합물의 물성예측을 위해 Mixing Rule의 적용이 매우 중요하다. 혼합물의 물성 계산에 대한 중요성을 인식하여 LNG 혼합물의 VLE물성 예측을 향상 시키기위해 Non-cubic 상태방정식에 사용하는 Mixing Rule을 개선 해야하므로 LNG 성분을 Non-cubic 상태방정식으로 열역학적 물성을 예측할때 서로 다른 Mixing Rule을 사용해 비교하였다.

2. 이 론

2.1 Modified van der Waals one fluid Mixing Rule

Conformal Solution Theory(CST)를 적용한 BWRS 상태방정식은 아래와 같다.[3,4,5]

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

$$B_i = a_i + \gamma b_i$$

a_i : isotropic part,

b_i : anisotropic part

γ : orientation parameter which describes molecule's non-spherisity

σ_x : characteristic distance parameter

ε_x : characteristic energy parameter

위 식에서 사용된 Generalized parameter를Table 1.에 나타내었다.

Table 1. Generalized Parameters of MBWR EOS[3]

Parameter subscript	Bi=ai + bi(CST MR)	
	ai	bi
1	1.45907	0.32872
2	4.98813	-2.64339
3	2.20704	11.3293
4	4.86121	
5	4.59331	2.79979
6	5.06707	10.3901
7	11.4871	10.373
8	9.22469	20.5388
9	0.094264	2.7601
10	1.48858	-3.11349
11	0.015273	0.18915
12	3.51486	0.9426

* Modified van der Waals one fluid Mixing

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

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

$$\varepsilon_{\alpha\beta} = \zeta_{\alpha\beta} \sqrt{\varepsilon_{\alpha\alpha} \varepsilon_{\beta\beta}} \qquad \gamma_{\alpha\beta} = \frac{1}{2}(\gamma_{\alpha\alpha} + \gamma_{\beta\beta})$$

2.2 Improved Bishnoi-Robinson Mixing Rule

[MBWR 상태방정식]

$$P = \rho RT + \left(B_0RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4}\right)\rho^2$$
$$+ \left(bRT - a - \frac{d}{T}\right)\rho^3 + \alpha\left(a + \frac{d}{T}\right)\rho^6$$
$$+ \frac{c\rho^3}{T^2}(1 + \gamma\rho^2)\exp(-\gamma\rho^2)$$

* Improved Bishnoi-Robinson Mixing Rule

$$B_0 = \sum_i x_i B_{0i} \qquad A_0 = \sum_i \sum_j x_i x_j A_{0i}^{1/2} A_{0j}^{1/2}(1 - k_{ij})$$

$$C_0 = \sum_i \sum_j x_i x_j A_{0i}^{1/2} C_{0j}^{1/2}(1 - k_{ij})^3 \qquad \gamma = \left[\sum_i x_i \gamma_i^{1/2}\right]^2$$

$$b = \left[\sum_i x_i b_i^{1/3}\right]^3 \qquad a = \left[\sum_i x_i a_i^{1/3}\right]^3$$

$$\alpha = \left[\sum_i x_i \alpha_i^{1/3}\right]^3 \qquad c = \left[\sum_i x_i c_i^{1/3}\right]^3$$

$$d = \left[\sum_i x_i d_i^{1/3}\right]^3 \qquad D_0 = \sum_i \sum_j x_i x_j D_{0i}^{1/2} D_{0j}^{1/2}(1 - k_{ij})^4$$

$$E_0 = \sum_i \sum_j x_i x_j E_{0i}^{1/2} E_{0j}^{1/2}(1 - k_{ij})^5$$

3. 결 과

Table 2. A comparison of Modified van der Waals one fluid Mixing Rule and Improved Bishnoi-Robinson Mixing Rule

SYSTEM	A.A.D%	
	Modified van der Waals one fluid Mixing Rule(X1)	Improved Bishnoi-Robinson Mixing Rule(X1)
C1-NC4	9.2	11.8
C1-NC5	8.49	8.51
C1-NC6	16.3	12.7
C1-NC7	23.5	31.5
average	14.37	16.13

$$AAD\% = 100 \times \frac{1}{N} \Sigma \left\{ \left| \left(\frac{Lit. - Cal.}{Lit.} \right) \right| \right\}$$

본 연구에서는 LNG혼합물의 물성예측을 위하여 먼저, MBWR 상태방정식에

사용하는 Improved Bishnoi-Robinson Mixing Rule와 BWRS 상태방정식에 사용하는 Modified van der Waals one fluid Mixing Rule로 LNG 이성분계 혼합물의 기액평형물성을 예측해 보았다. Modified van der Waals one fluid Mixing Rule이 평균적으로 14.37로 Improved Bishnoi-Robinson Mixing Rule의 16.13보다 A.A.D%가 더 작아 예측 능력이 더 우수 하였다.

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