Comprehensive Comparison and Evaluation of the WS, MHV2, Twu and CWSM Mixing Rules

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Three mixing rules, the Wong-Sandler (WS), MHV2, and Twu et al. (1991), are widely used for their predictive and correlative capability for VLE of highly non-ideal systems. Recently, a new mixing rule, the combined WS-Michelsen (CWSM) mixing rule has been proposed by the authors (Qu and Wang, 1995). It has been proved that the CWSM mixing rule is a good improvement over the WS mixing rule in complete predictions of VLE using the EoS/UNIFAC method. In this presentation, comprehensive comparison and evaluation have been conducted in terms of the PR EOS and experimental data for nonpolar-nonpolar, polar-polar and polar-nonpolar systems (see Table 1):

(1) Using the four mixing rules incorporated with the Wilson, UNIQUAC, NRTL activity coefficient models, VLE data at low and high pressures have been correlated. Correlated accuracies for the four mixing rules have been compared in Table 2.

(2) The WS, MHV2, CWSM mixing rules have been used to predict VLE at high pressures from the data at low pressures. Their predictive results have been compared in Table 3. In conclusion, of simplicity, the CWSM mixing rule presents the same quality correlation and better predictive results, in particular for asymmetric polar-nonpolar systems.

References:

Twu, C. H. et al., Fluid Phase Equilibria, 69: 33-50 (1991).

Qu, Y. and W. Wang, A predictive equation of state/UNIFAC method for vapor-liquid equilibria, submitted to Fluid Phase Equilibria, March, 1995.

Table 1 Source of High-Pressure Experimential Data

System	n.d.*	Temp.(K)	Press.(Bar)	Ref.
1. Nonpolar - Nonpolar System				
A C2H6 - C6H6	80	273.15 - 533.15	20.684 - 82.736	[11]
B C3H8 - n-C6H14	40	333.15 - 493.15	0.763 - 41.368	[12]
C 1-C4H8 - n-C4H10	33	310.93 - 338.71	3.551 - 8.693	[13]
D n-C4H10 - nC7H16	41	355.37 - 538.71	6.895 - 39.645	[14]
E n-C5H12 - n-C7H16	28	403.75 - 526.45	10.132 - 30.610	[15]
2. Polar - Polar System				
F CH3OH - H2O	47	373.15 - 523.15	1.041 - 68.552	[16]
G C2H5OH - H2O	63	423.15 - 623.15	5.586 - 189.793	[17]
H 2-C3H5OH - H2O	93	298.15 - 355.54	0.032 - 9.170	[18]
I C3H6CO - H2O	91	298.15 - 523.15	0.067 - 67.586	[19]
3. Nonpolar - Polar System				
J C3H8 - C2H5OH	97	325.00 - 500.00	0.323 - 62.742	[20]
K n-C5H12 - CH3OH	34	372.70 - 422.60	3.471 - 25.276	[21]
L n-C5H12 - C2H6CO	33	372.70 - 422.60	3.661 - 16.358	[22]
M C6H6 - CH3OH	93	298.15 - 337.85	0.233 - 4.178	[23]
N n-C6H14 - CH3OH	30	333.15 - 333.15	0.760 - 1.497	[24]
4. Multicomponents System				
O C3H6CO - CH3OH - H2O	110	373.15 - 523.15	1.234 - 81.634	[25]
P n-C5H12 - CH3OH - C3H6CO	36	372.70 - 372.70	5.378 - 8.236	[26]

* n.d. is the nember of data points.

Table 2. Correlated results for four mixing rules

Sys.	G^E model	Mixing Rule							
		WS		MHV2		TWU		CWSM	
		DP/P (%)	DY x100	DP/P (%)	DY x100	DP/P (%)	DY x100	DP/P (%)	DY x100
1. Nonpolar - Nonpolar System									
A	UNIQUAC	2.81	4.70	2.54	0.89	1.44	0.74[a]	1.55	0.53
	NRTL	2.33	0.63	2.74	0.87			1.68	0.53
	Wilson	3.05	0.74	2.36	0.89			1.49	0.54

Continued Table 2.

B	UNIQUAC	1.29	1.86	1.01	1.89	1.12	1.95	1.11	1.98
C	UNIQUAC	0.60	0.28	0.70	0.38	0.62	0.32	0.69	0.36
D	UNIQUAC	1.89	1.34	1.96	1.37	2.05	2.24	2.20	1.65
E	UNIQUAC	0.47	0.66	0.41	0.96	0.46	0.95	0.42	1.23
2. Polar - Polar System									
F	UNIQUAC	1.02	1.01	1.63	1.12	0.99	1.08[b]	1.52	1.21
	NRTL	1.08	1.21	1.05	1.03			1.07	1.15
	Wilson	1.41	1.23	1.75	1.10			1.76	1.11
G	UNIQUAC	0.94	0.39	1.40	0.67	1.01	0.56	1.22	0.60
H	UNIQUAC	1.80	1.20	1.75	1.12	2.42	1.26	1.77	1.24
I	UNIQUAC	1.78	1.21	2.33	0.99	3.23	1.29	1.97	1.02
3. Nonpolar - Polar System									
J	UNIQUAC	4.42	3.24	7.45	2.06	2.75	1.79[c]	4.72	1.96
	NRTL	4.37	2.28	7.17	2.00			4.49	1.88
	Wilson	5.39	2.01	7.37	1.99			4.65	1.90
K	UNIQUAC	1.04	1.18	1.77	1.05	4.66	2.24	1.39	1.75
L	UNIQUAC	0.40	0.60	1.08	0.75	1.33	1.05	0.39	0.61
M	UNIQUAC	0.84	0.84	1.71	1.04	4.96	2.63	1.25	1.11
N	UNIQUAC	0.60	0.75	5.31	3.49	6.97	4.18	3.46	2.07
Grand Average		1.73	1.34	2.33	1.32	2.43	1.59	2.05	1.44

a For nonpolar-nonpolar systes two parameters k_{12}, k_{21} are needed.

b For polar-polar systems three parameters k_{12}, k_{21}, $\beta_{12}(\beta_{12}=\beta_{21})$ are needed.

c For polar-nonpolar systems four parameters k_{12}, k_{21}, β_{12}, β_{21} are needed.

Table 3. Predicated results for four mixing rules

Sys. G^E model	Mixing Rule							
	WS		MHV2		TWU		CWSM	
	DP/P (%)	DY x100	DP/P (%)	DY x100	DP/P (%)	DY x100	DP/P (%)	DY x100
1. Polar - Polar System								
F UNIQUAC[27][a]	2.10	1.41	1.74	1.18	1.03	1.11 [16][b]	1.57	1.30
NRTL [27]	2.67	1.55	3.69	1.74			2.43	1.25
Wilson [27]	3.37	1.69	4.94	2.18			3.22	1.41
G UNIQUAC[28]	2.33	1.53	2.00	0.86	1.59	0.75 [17]	1.39	0.70
NRTL [28]	4.74	2.30	6.55	2.41			2.52	1.13
Wilson [28]	2.41	1.46	4.70	2.20			4.72	1.89
I UNIQUAC[29]	3.48	1.07	3.46	1.43	3.73	1.40 [18]	5.96	1.51
NRTL [29]	4.07	1.31	3.35	1.63			5.62	1.21
Wilson [29]	4.91	1.03	2.12	0.88			6.50	1.18
2. Nonpolar - Polar System								
L UNIQUAC[30]	3.23	1.85	5.70	2.42	1.23	0.57 [22][c]	2.76	0.79
M UNIQUAC[31]	12.22	5.03	18.60	7.68	6.00	3.09 [23]	5.12	3.28
N UNIQUAC[32]	25.39	9.74	37.73	11.19	6.58	4.18 [24]	7.58	3.43
3. Multicomponent System								
O UNIQUAC	1.61	1.98	3.50	1.63	2.84	2.09	1.53	1.71
P UNIQUAC	9.32	2.45	22.95	4.82	3.17	1.11	12.20	2.94
Grand Average	5.85	2.46	8.65	3.02	3.27	1.79	4.51	1.70

a,b The numbers in the parentheses indicate the reference number, where the parameters of G^E model, and the VLE data at low pressure are gotten, respectively.

c β_{12} and β_{21} are needed.