

Influence of the mixing rule on the liquid-liquid equilibrium calculation

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ABSTRACT

Liquid-liquid equilibrium data were correlated with three mixing rules that incorporate excess Gibbs energy model into a equation of state: Wong-Sandler, Heidemann-Kokal and MHV2 methods. The Soave equation of state is employed to several binary mixtures, coupled with NRTL, UNIQUAC and UNIFAC models for excess Gibbs free energy. The best results for binary mixtures were obtained with NRTL and Wong-Sandler, then this combination was used to predict the ternary liquid-liquid equilibria.

1-INTRODUCTION

Correlations of liquid-liquid equilibria (LLE) can be carried out by employing either excess Gibbs free energy (G^E) models or equations of state (EOS). Although equation of state models have been employed in LLE calculations (Georgeton *et al.*, 1986; Suen *et al.*, 1989) the results indicated that conventional equations of state with Van der Waals mixing rules are not adequate to describe LLE behavior (Georgeton *et al.*, 1986).

Incorporation of G^E models into mixing rule expressions for the attractive term parameter of cubic EOS, has been receiving much attention for more than a decade, as it allows description of vapor-liquid equilibria in complex systems through a simple EOS (Vidal, 1978; Huron and Vidal, 1979; Gani *et al.*, 1989; Tochigi *et al.*, 1988; Sheng *et al.*, 1989; Holderbaum and Gmehling, 1991; Boukouvalas *et al.*, 1994). These mixing rules have been extensively discussed for vapor-liquid equilibrium calculations. There have been only scattered attempts to apply equations of state to LLE calculations. The most extensive of these studies was reported by Huang (Huang, 1991).

The purpose of the present work is to study the applicability of the three mixing rules: Wong-Sandler (Wong and Sandler, 1992), Heidemann-Kokal (Heidemann and Kokal, 1990) and MHV2 (Dahl and Michelsen, 1990) to LLE calculations. Several binary mixtures were examined including: water, carboxylic acid, ester, ether, phenol, ketone, alcohol, etc. By fixing the EOS and its pure parameters correlations, we investigate the best combination between mixing rule and G^E model applying this to ternary mixtures.

2-MIXING RULES

The SRK cubic EOS (Soave, 1972) has been used for all mixing rules investigated. Verotti and Costa (Verotti, 1994) concluded that, in the LLE prediction, the choice of the two parameters EOS was immaterial. The three different mixing rules are extensively described in the references. To investigate the quality of the predictions for these mixing rules, the results were compared with the ones carried out employing only excess Gibbs free energy models. The different mixing rules and nomenclature used are described in Table 1.

Table 1
Models used to compare mixing rules

Method	Mixing rule	G^E model
M1	-	NRTL
M2	-	UNIQUAC
M3	-	UNIQUAC ^a
M4	Wong-Sandler ^b	NRTL
M5	Wong-Sandler ^b	UNIQUAC
M6	Wong-Sandler ^b	UNIQUAC ^a
M7	MHV2	NRTL
M8	MHV2	UNIQUAC
M9	MHV2	UNIQUAC ^a
M10	Heidemann-Kokal	NRTL
M11	Heidemann-Kokal	UNIQUAC
M12	Heidemann-Kokal	UNIQUAC ^a

^a UNIQUAC parameters estimated from UNIFAC

^b k_{ij} (the mixing rule binary interaction parameter) = 0

In order to fit the model's parameters to experimental mutual solubility data, we choose two objective functions. In the first part of the program the objective function to be minimized is the sum of the square differences between the activities calculated under the experimental compositions, taken from a series of experimental data. The parameters optimized in this first adjustment are utilized in the second adjustment as first guess. The reason for the first step is the high sensibility between the calculated compositions and the binary parameters. The sum of the square differences between the compositions obtained from experimental data and from calculation is the objective of the next optimization. The simplex algorithm modified by Nelder and Mead (1965) is used for this optimization. The direct use of G^E model's parameters, as reported in the literature, coupled with these new mixing rules, cannot identify the two phases. Regarding to fit the model parameters to experimental data over a wide range of temperature, we assumed that the energy parameters are given by an inverse function of temperature. This temperature dependence with two parameters for each pair, in the form $A_{ij} = a_{ij}/T$, was used in G^E models for the mixing rules and also in the traditional LLE calculations applying traditional models, to attain higher accuracy.

3-RESULTS

LLE calculation results have been presented in this study on a representative sample of 47 binary mixtures. Table 2 lists a summary of binary systems, used to carry out LLE calculations. The name of all compounds have been maintained as given in the original source. In order to visu-

alize both the influence, G^E models and mixing rules, the binary systems are divided into 4 groups, according to the polarity of the components. Table 3 shows our LLE calculation in various binary mixtures by employing either the EOS/ G^E models or with the G^E model only.

Table 2
Summary of binary systems studied^a

system	NP ^b	system	NP ^b
W (weakly polar) - N (nonpolar)	24	acetic anhydride-carbon disulfide	6
1 1,2-propanediol-benzene	6	25 acetic acid, nitrile-hexane	5
2 furfural-cyclopentane	4	26 acetic acid-nonane	4
3 furfural-cyclohexane	6	27 formic acid, methyl ester-heptane	5
4 furfural-hexane	7	28 ethane, nitro-hexane	6
5 furfural-heptane	9	29 ethane, nitro-octane	8
W (weakly polar) - S (strongly polar)	30	acetic anhydride-cyclohexane	7
6 2-propanone-glycerol	6	31 water-propanal,2-methyl	4
7 2-butanone-glycerol	6	32 diethylene glycol-benzene	8
8 2-butanone-water	8	33 phenol-butane,2-methyl	5
9 acetic acid,ethyl ester-water	9	34 phenol-pentane	4
10 propanoic acid, methyl ester-water	7	S (strongly polar) - S(strongly polar)	
11 ether, diethyl-water	9	35 methane, trichloro-water	8
12 furfural-water	6	36 methane, dichloro-water	5
13 3-pentanone-water	7	37 methane, nitro-glycerol	6
S (strongly polar) - N (nonpolar)	38	methane, nitro-1-butanol	4
14 heptane, perfluor-CCl ₄	4	39 acetic acid, nitrile-1-dodecanol	4
15 water-CCl ₄	5	40 ethane,1,1-dichloro-water	5
16 formic acid-benzene	7	41 ethane,1,2-dichloro-water	9
17 methane, nitro-carbon disulfide	5	42 ethane, nitro-1-decanol	5
18 methane, nitro-cyclohexane	9	43 ethane, nitro-water	8
19 methane, nitro-nonane	9	44 acetic anhydride-water	6
20 methanol-carbon disulfide	6	45 1-butanol-water	8
21 methanol-cyclohexane	6	46 2-butanol-water	6
22 methanol-heptane	5	47 1-butanol,3-methyl-water	6
23 acetic acid, nitrile-carbon disulfide	6		

^a Data sources: Experimental data are taken from Sorensen et al. (1979)

^b NP: number of experimental points

We have tested these mixing rules using five ternary systems with liquid-liquid equilibria, the selected systems are shown in Table 4. As it was necessary, the binary interaction parameters are regressed by minimizing the sum of the square difference between the compositions obtained from experiment and from calculation of one phase, keeping the composition of the other one as independent variable. The best combination, Wong-Sandler with NRTL model, is applied for ternary calculations and the results are listed on Table 4. The ability of an equation of state to directly utilize existing parameter tables for G^E models is investigated when we use these best method with the NRTL parameters estimated from UNIFAC. We included on Table 4 the results for this method (M4), as well as the original NRTL with parameters estimated from UNIFAC.

Table 3
Mean deviation (mole percent) between experimental and calculated compositions

system	M1	M2	M4	M5	M7	M8	M10	M11
1	1.62	1.23	1.59	1.07	3.00	2.70	1.70	1.30
2	0.38	0.37	0.79	0.74	0.50	0.50	0.30	0.30
3	1.23	1.50	0.79	1.09	2.10	2.30	1.30	1.60
4	0.26	0.56	0.21	0.70	0.90	1.20	0.10	0.60
5	1.79	2.09	0.89	1.39	2.60	2.80	1.50	2.10
average	1.06	1.15	0.85	1.00	1.82	1.90	0.98	1.18
6	0.66	1.05	1.02	0.93	7.10	7.60	7.20	8.20
7	1.63	1.61	1.73	1.74	9.70	8.90	3.00	1.30
8	3.49	4.32	3.86	4.90	8.70	3.90	3.90	4.60
9	0.95	0.69	0.72	0.94	1.20	0.40	0.50	0.80
10	1.98	1.01	1.12	1.00	2.10	1.10	1.30	0.70
11	0.61	0.75	1.26	1.67	0.60	0.90	0.60	1.20
12	3.30	2.31	1.63	1.11	3.60	3.10	2.00	2.00
13	3.25	0.73	2.07	0.54	2.60	0.70	1.60	0.30
average	1.98	1.56	1.68	1.60	4.45	3.33	2.51	2.39
14	2.25	0.79	0.27	0.81	2.10	0.70	2.00	0.60
15	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00
16	1.17	0.77	2.54	3.39	1.00	0.70	0.70	0.60
17	1.56	1.70	1.03	1.67	1.50	1.60	1.50	1.60
18	2.50	2.44	0.62	1.16	2.40	2.40	2.40	2.40
19	2.87	1.68	1.45	1.76	2.90	1.70	2.70	1.60
20	1.45	1.37	0.44	1.99	1.50	1.50	1.40	1.30
21	1.51	1.96	1.33	2.19	1.60	2.10	1.50	1.90
22	3.08	3.03	1.99	3.14	3.10	3.20	1.80	2.20
23	2.23	2.27	2.44	2.76	2.10	2.20	2.20	2.20
24	2.52	1.64	1.66	0.23	3.40	2.90	2.50	1.60
25	0.63	0.68	1.18	1.32	0.60	0.70	0.60	0.60
26	1.77	1.18	0.76	0.67	1.70	1.10	5.10	5.40
27	3.55	3.17	1.63	0.41	3.80	3.50	2.70	2.50
28	3.04	3.26	2.28	2.57	3.50	3.70	2.90	3.20
29	3.24	3.32	1.74	1.69	3.60	3.70	3.00	3.20
30	2.53	2.57	1.79	1.81	3.30	3.30	2.50	2.60
31	0.34	0.63	0.92	1.21	0.20	0.40	0.50	0.80
32	1.33	2.67	0.96	2.39	3.40	3.00	0.80	1.60
33	0.98	1.70	2.04	2.72	3.40	3.70	1.10	1.70
34	2.16	2.69	2.96	3.52	3.80	4.10	0.90	1.10
average	1.94	1.88	1.43	1.78	2.33	2.20	1.85	1.84
35	0.05	0.06	0.11	0.15	0.00	0.00	0.00	0.00
36	0.07	0.06	0.09	0.10	0.00	0.00	0.00	0.00
37	1.52	1.26	1.72	1.30	4.70	7.90	1.80	1.30
38	2.53	2.44	2.02	1.82	2.70	2.70	2.10	2.00

Table 3 (continued).
Mean deviation (mole percent) between experimental and calculated compositions

system	M1	M2	M4	M5	M7	M8	M10	M11
39	6.51	3.91	3.53	0.76	5.10	4.80	2.70	2.00
40	0.03	0.02	0.03	0.05	0.00	0.00	0.00	0.00
41	0.14	0.07	0.09	0.17	0.10	0.00	0.10	0.00
42	4.11	3.47	3.22	1.66	4.90	4.60	2.60	2.50
43	4.60	3.39	1.81	2.10	3.50	2.80	2.70	2.00
44	1.50	2.06	1.68	2.25	1.00	1.50	1.60	2.10
45	3.19	1.53	2.31	1.79	3.50	0.00	3.00	2.30
46	1.89	1.88	2.18	3.25	1.30	1.70	2.40	3.20
47	0.76	1.37	0.40	0.70	1.00	0.20	0.10	3.00
average	2.07	1.65	1.48	1.24	2.14	2.02	1.47	1.57
overall	1.89	1.68	1.42	1.52	2.58	2.31	1.76	1.79

Table 4
Mean deviation (mole percent) in composition of ternary systems^a

system	NP ^b	M1	M4	M1+UNIF	M4+UNIF
water-ethanol-benzene	16	0.19	0.21	8.51	7.93
water-acetic acid-CCl ₄	11	0.24	0.24	14.38	26.69
isobutanol-propanal-water	8	0.11	0.18	19.97	22.20
nC ₆ -methylcyclopentane-aniline	8	0.10	0.10	3.58	4.43
benzene-propionic acid-water	11	0.26	0.26	18.92	7.86

^aData source: experimental data are taken from Sorensen *et al.* (1979)

^bNumber of experimental points

4-CONCLUSIONS

The following comments summarize our observations on the performance of these mixing rules: good predictions can be achieved with all three mixing rules with the M4 method yielding better results, although almost the same results are obtained with the M5 method, as Table 3 indicate. In analyzing the results according the degree of complexity, as Table 3 demonstrate, the best results for each class of systems are:

weakly polar - nonpolar	- M4 method
strongly polar - weakly polar	- M2 method
strongly polar - nonpolar	- M4 method
strongly polar - strongly polar	- M5 method

Surprisingly the MHV2 mixing rule based on a structure similar to Heidemann-Kokal does not perform as it might been expected, from this similarity, giving poorer results. When we compare these mixing rules with the original G^E models, Wong-Sandler is better than UNIQUAC and NRTL, and Heidemann-Kokal is better than NRTL.

Figure 1 shows a plot of experimental and calculated compositions for both phases for all 47 binary systems, using the M4 method.

Considering the G^E models utilized coupled with EOS, NRTL performs better than UNIQUAC in three mixing rules, but disregarding the temperature dependence of the parameters, the accuracies reported are reversed.

Substantial improvement can be obtained if the binary interaction parameters are considered temperature dependents, as can be shown on comparing the mean deviation (mole percent) between the experimental and calculated compositions, for all system, using original NRTL and UNIQUAC as described by Verotti and Costa (1994):

	constant	f(T)
NRTL	2.74	1.89
UNIQUAC	2.84	1.68

The purely predictive character, with UNIQUAC model parameters obtained from UNIFAC fails badly and for several systems (approximately 30 %) were impossible to identify two phases, it was not possible to obtain convergence with the mixing rules and also with original method that utilizes only G^E models (Table 5). For multicomponent systems, the applied method was the one identified as M4. The reason for this choice was the best performance for binary systems. Similar behavior is observed with the M1 method, presented in Table 4. Once more the parameters obtained by UNIFAC method gave poorer predictions.

A respectable increase in elapsed CPU time was detected with the use of EOS/ G^E models. These methods were also the most sensitive to initial values of the binary interaction parameters. Wong-Sandler mixing rule provided the fastest convergence during the calculation of the binary interaction parameters, with the Heidemann-Kokal being the slowest in convergence out of the three mixing rules. Furthermore the best stability in the parameters estimated was observed with the Wong-Sandler rule.

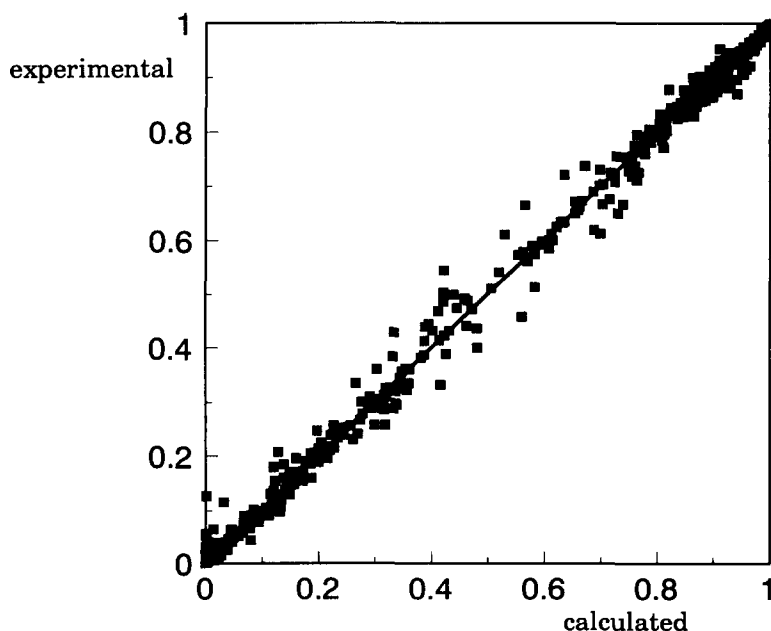


Figure 1. Experimental and calculated compositions (M4 method)

Table 5
Performance of the mixing rules using UNIFAC model

	deviation ^a	systems that converged
M3	10.78	33
M6	9.89	30
M9	11.94	34
M12	10.99	34

^aMean deviation (mole percent) in compositions

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