Comments

Comments on “Vapor−Liquid Equilibria Data for Methanol, Ethanol, Methyl Acetate, Ethyl Acetate, and *o*-Xylene at 101.3 kPa” (Costa López, J.; Garvín, A.; España, F. J. *J. Chem. Eng. Data* 1995, *40,* 1067−1071)[†]

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A recent publication by Costa López et al. reports vapor−liquid equilibrium data for different systems involving *o*-xylene at 101.3 kPa (Costa López et al., 1995). I believe that the data are incorrect and that the thermodynamic analysis is inappropriate, for the following reasons.

1. The activity coefficients of the four binary systems reported show an unusual behavior: They are less than unity at the dilute end and increase to values above 1 at the concentrated end. The system ethyl acetate + *o*-xylene (Table 4 in the reference) is even more unusual, it shows negative deviations for *o*-xylene in the full concentration range while the deviations for ethyl acetate are at first negative and then positive. This behavior is against the Gibbs−Duhem equation even when we consider that that data are isobaric. No explanation is given for this phenomena.

2. The authors indicate that they have fitted their data using different thermodynamic models. I have used their constants to try to recover their original data with little success (Figure 1 and Tables 1 and 2). For example, the authors report the Wilson parameters for the system methanol + *o*-xylene as $A_{12} = 0.2154$ and $A_{21} = 0.2208$ and indicate that the mean average deviation (MAD) is 0.0098 for the vapor composition. This conclusion is incorrect, as shown in Table 1. The authors should have reported the MAD value together with the maximum deviation since averages, by their definition, hide the range of values of the variable. In addition, the models are activity coefficient descriptors not vapor composition predictors, hence, the authors should have also indicated the description capability of each model.

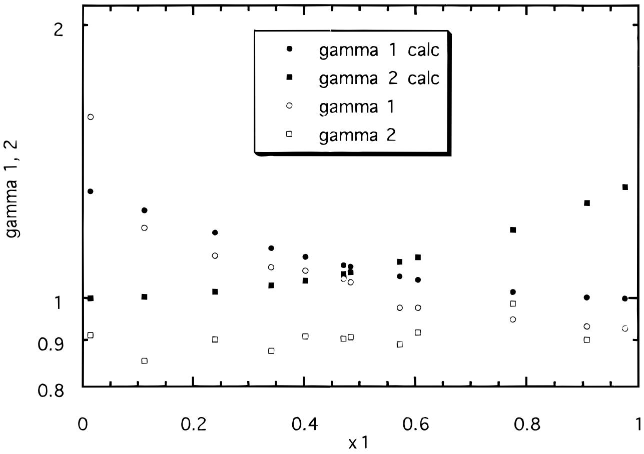

Figure 1. Data recovery: Wilson model (ethyl acetate + *o*-xylene).

Table 1. Methanol(1) + *o*-Xylene (2): Data Recovery (Costa López et al., 1995)[a]

Wilson

A_{12} 0.2154
A_{21} 0.2208

x_1	x_2	β	$\gamma_{1\text{calc}}$	$\gamma_{2\text{calc}}$	$\gamma_{1\text{expt}}$	$\gamma_{2\text{expt}}$	% dev$_1$	% dev$_2$
0.9878	0.0122	−0.741 241 7	1.0006	9.0299	0.9518	10.894	5.1	17.1
0.9833	0.0167	−0.72 608 6	1.0011	8.7338	0.9498	10.413	5.4	16.1
0.9767	0.0233	−0.704 610 9	1.0020	8.3284	0.9526	9.7604	5.2	14.7
0.967	0.033	−0.674 565 6	1.0040	7.7885	0.9538	9.0097	5.3	13.6
0.9334	0.0666	−0.582 420 5	1.0150	6.3157	0.9618	6.8145	5.5	7.3
0.8684	0.1316	−0.442 665 1	1.0520	4.5424	1.0063	4.5934	4.5	1.1
0.8424	0.1576	−0.396 811 1	1.0719	4.0655	1.0101	4.0504	6.1	0.4
0.833	0.167	−0.381 312 6	1.0798	3.9150	1.0097	3.4837	6.9	12.4
0.7674	0.2326	−0.285 710 9	1.1446	3.0971	1.0639	2.8157	7.6	10.0
0.4933	0.5067	−0.001 118 3	1.6590	1.6253	1.5806	1.3417	5.0	21.1
0.2176	0.7824	0.291 963 52	3.2544	1.1300	3.1715	0.8564	2.6	32.0
0.0249	0.9751	0.691 674 59	8.3553	1.0024	8.4648	0.6974	1.3	43.7
							5.0[b]	15.8[b]

[a] $\ln \gamma_1 = -\ln(x_1 + A_{12}x_2) + x_2\beta$, $\ln \gamma_2 = -\ln(x_2 + A_{21}x_1) - x_1\beta$. $\beta = A_{12}/(x_1 + A_{12}x_2) - A_{21}/(A_{21}x_1 + x_2)$. [b] MAD.

Table 2. Ethyl Acetate (1) + *o*-Xylene (2): Data Recovery (Costa López et al., 1995)[a]

Van Laar

A 0.2781
B 0.2979

x_1	x_2	$\gamma_{1\text{calc}}$	$\gamma_{2\text{calc}}$	$\gamma_{1\text{expt}}$	$\gamma_{2\text{expt}}$
0.9761	0.0239	1.0002	1.3269	0.9267	0.3826
0.908	0.092	1.0027	1.2743	0.9313	0.9003
0.7762	0.2238	1.0156	1.1899	0.9477	0.9867
0.6054	0.3946	1.0481	1.1088	0.9756	0.917
0.5724	0.4276	1.0565	1.0963	0.9759	0.8897
0.4843	0.5157	1.0822	1.0672	1.0409	0.9059
0.4712	0.5288	1.0864	1.0634	1.0495	0.9025
0.4024	0.5976	1.1105	1.0454	1.0715	0.9081
0.3412	0.6588	1.1347	1.0321	1.0809	0.8755
0.2397	0.7603	1.1806	1.0155	1.1128	0.9009
0.1116	0.8884	1.2496	1.0033	1.195	0.8534
0.0139	0.9861	1.3112	1.0001	1.5848	0.9113

[a] $\ln \gamma_1 = A/(1 + Ax_1/Bx_2)^2$, $\ln \gamma_2 = B/(1 + Bx_2/Ax_1)^2$.

3. The authors have used the Herington and the $L-W$ tests to check the thermodynamic consistency of their data. First, the Herington test has been shown to be inappropriate for this purpose (Wisniak, 1994), second, the $L-W$ test (Wisniak, 1993) has the advantage of being simultaneously a point−point and area test. The important element is the point-to-point test (sufficient); no reference is made to it. The area test is a necessary but not a sufficient condition for consistency.

4. I believe that the error source is an experimental one. The systems analyzed are characterized by a large difference in boiling point between the components. In this

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[†] The authors of this paper have not availed themselves of the opportunity to respond to this Comment.

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situation the phase separator will easily behave like an additional plate, with its surface achieving the dew point of the mixture. Hence, the composition of the two phases will not be related with the temperature reported (each variable is measured at a different location). The authors have indicated that they have tried to solve the problems presented by Othmer apparatus; apparently, this was not enough. In addition, alcohol + hydrocarbon systems are characterized by association effects; these were not considered (or their possibility mentioned) in the analysis of the data.

5. Some minor problems are that the constants in Table 6 are not in SI units and that it is not indicated whether the adjustable parameters of the different models are on a log or ln basis.

Literature Cited

Costa López, J.; Garvín, A.; España, F. J. Vapor−Liquid Equilibrium Data for Methanol, Ethanol, Methyl Acetate, and *o*-Xylene at 101.3 kPa. *J. Chem. Eng. Data* **1995**, *40*, 1067−1071.

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