Comments & Replies

Comments on “Experimental Isobaric Vapor−Liquid Equilibrium Data for Binary Mixtures of Cyclic Ethers with (1-Methylethyl)benzene” (Gill, B. K.; Rattan, V. K.; Kapoor, S. *J. Chem. Eng. Data* 2008, *53*, 2041−2043)

Jaime Wisniak*,[†] **and Hugo Segura**[‡]

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel, and Departamento de Ingeniería Química, Universidad de Concepción, POB 160-C, Correo 3, Concepción, Chile

Gill et al.[1] have recently reported experimental vapor−liquid equilibrium (VLE) data for the binary mixtures of tetrahydrofuran (THF) and tetrahydropyran (THP) with (1-methylethyl)-benzene at 97.3 kPa and stated that they are thermodynamically consistent, according to the Herington and Black tests. The purpose of the present communication is to criticize their conclusions regarding the accuracy of the reported VLE data from two aspects.

(a) The Herington Test. The paper of Gill et al. is another example of the incorrect use of this criterion to qualify the thermodynamic quality of VLE data. First of all, the isobaric version of Herington’s test has been proven to be wrong, and thus it should not be used for testing the thermodynamic consistency of VLE data.[2−4] Second, the Herington test is based on an attempt to evaluate the right-hand side of the following equation, expressing the effect of the heat of mixing (ΔH) on the value of the ratio of the activity coefficients ($\log \gamma_1/\gamma_2$)

$$\int_0^1 \log(\gamma_1/\gamma_2)\mathrm{d}x_1 = \int_{T_2^0}^{T_1^0} (\Delta H/RT^2)\mathrm{d}T \qquad (1)$$

A plot of the right-hand side of the equation leads to the definition of parameter D, as follows

$$D \equiv 100\frac{||A_+|-|A_-||}{|A_+|+|A_-|} \qquad (2)$$

where A_+ and A_- represent the positive and negative areas of the plot ($\log \gamma_1/\gamma_2$) vs x_1. According to Herington[5] (eq 11 in ref 5), the right-hand side of eq 1 satisfies the following condition

$$\int_{T_2^0}^{T_1^0} (\Delta H/RT^2)\mathrm{d}T < 150\Delta T_{\max}/T_{\min} \equiv J \qquad (3)$$

where $\Delta T_{\max}$ and $T_{\min}$ represent the maximum difference in boiling point and the minimum boiling point temperature (both in Kelvin) present in the VLE of the system. Herington declares the data to be consistent if $|D| < J$ or $|D - J| < 10$ (eq 15 in ref 5) and not as used *incorrectly* by Gill et al., $(D - J) < 10$. The value of J, by its proper nature, increases as the difference in the boiling points of the pure components ($T_2^0 - T_1^0$) becomes larger, and hence, following Gill et al. would allow a larger error in the experimental data and still declare the data consistent because $(D - J)$ would become negative, as reported by Gill et al. for both the systems they studied. A correct application of the Herington criteria to the numbers reported by Gill et al. indicates that $|D - J| = 15.88$ for the system THF + (1-methylethyl)benzene, and hence their data are *not consistent* according to Herington.

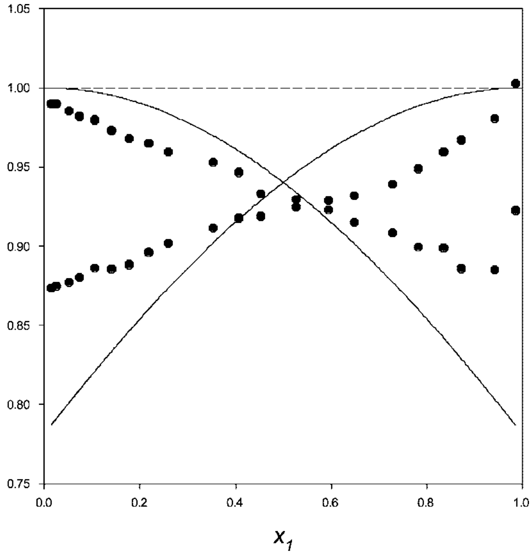

Figure 1. Activity coefficient plot for the system tetrahydrofuran (1) + (1-methylethyl)benzene (3) at 97.3 kPa. ●, Experimental data of Gill et al.;[1] −, Calculated using a 1-parameter Legendre polynomial.

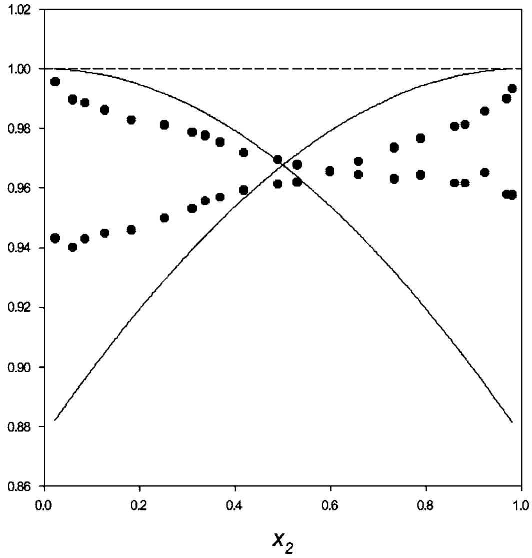

Figure 2. Activity coefficient plot for the system tetrahydropyran (2) + (1-methylethyl)benzene (3) at 97.3 kPa. ●, Experimental data of Gill et al.;[1] −, Calculated using a 1-parameter Legendre polynomial.

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* To whom correspondence should be addressed. Fax: (972)-8-647-2926. E-mail address: wisniak@bgu.ac.il.

[†] Ben-Gurion University of the Negev.

[‡] Universidad de Concepción.

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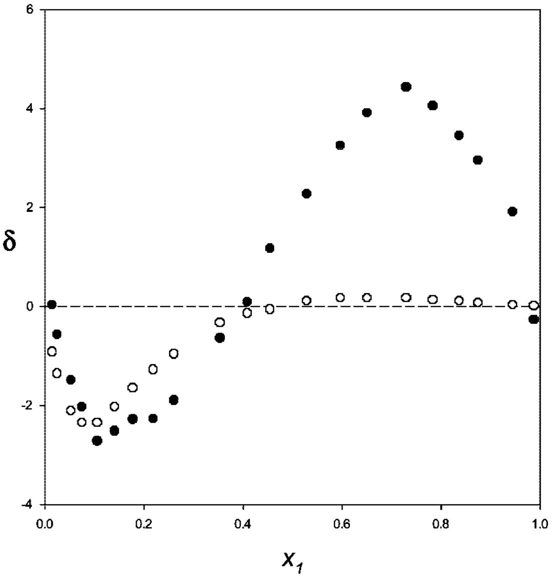

Figure 3. Punctual consistency residuals plot for the system tetrahydrofuran (1) + (1-methylethyl)benzene (3) at 97.3 kPa, as calculated from a 1-parameter Legendre polynomial. ●, Pressure residuals (kPa); ○, Vapor phase mole fraction residuals ($100 \cdot \delta y$).

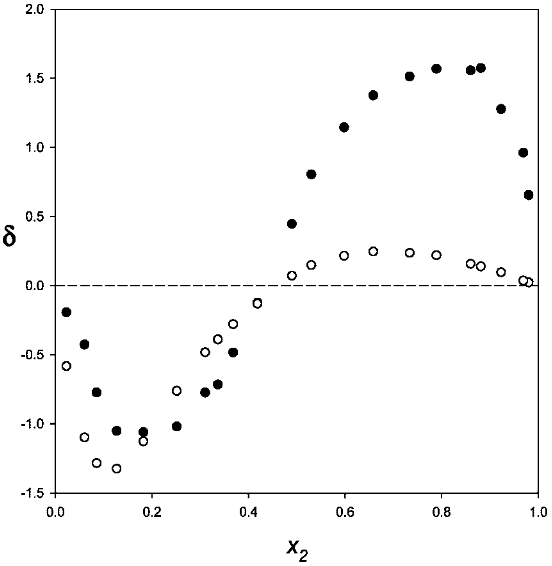

Figure 4. Punctual consistency residuals plot for the system tetrahydropyran (2) + (1-methylethyl)benzene (3) at 97.3 kPa, as calculated from a 1-parameter Legendre polynomial. ●, Pressure residuals (kPa); ○, Vapor phase mole fraction residuals ($100 \cdot \delta y$).

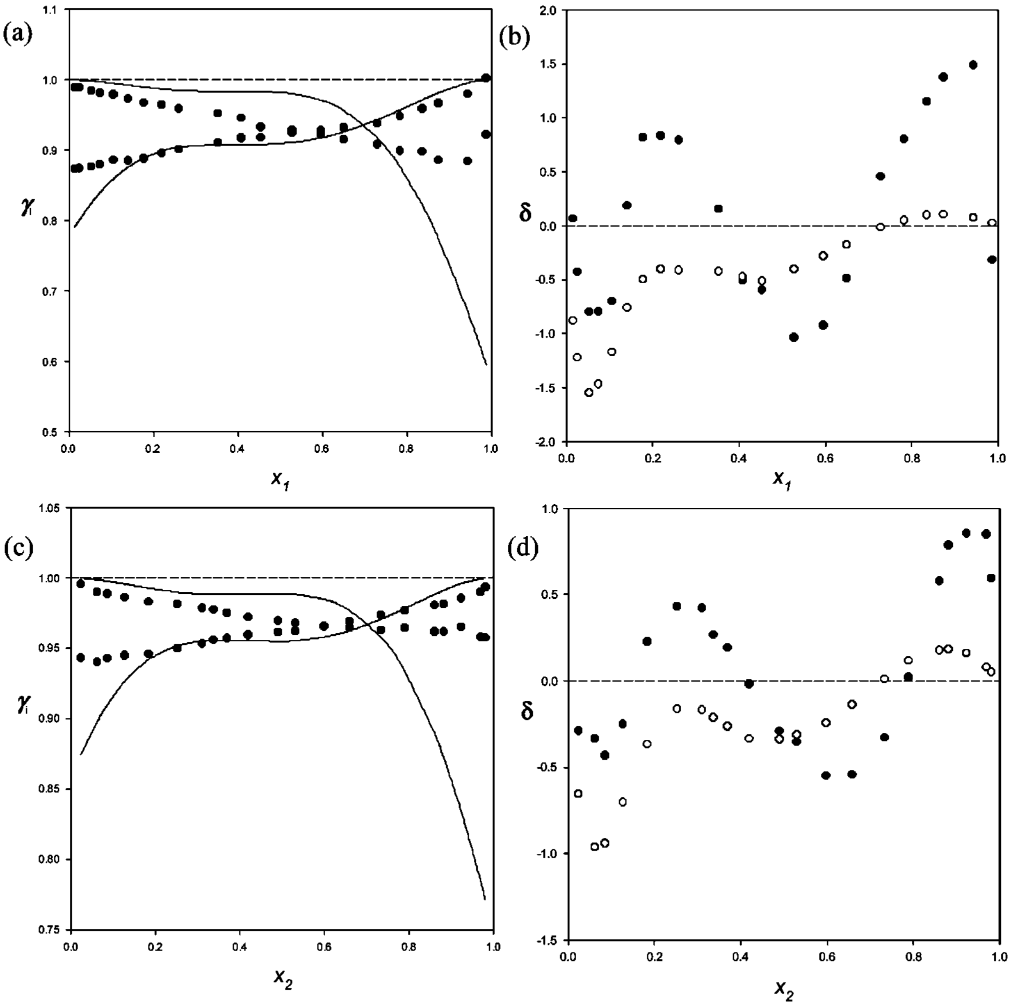

Figure 5. Consistency data treatment based on a statistically significant fit of the experimental bubble pressures at 97.3 kPa (3-parameter Legendre polynomial): (a) Activity coefficients for tetrahydrofuran (1) + (1-methylethyl)benzene (3). ●, Experimental data of Gill et al.;[1] −, Calculated. (b) Residuals for the system tetrahydrofuran (1) + (1-methylethyl)benzene (3). ●, Pressure residuals (kPa); ○, Vapor phase mole fraction residuals ($100 \cdot \delta y$). (c) Activity coefficients for tetrahydropyran (2) + (1-methylethyl)benzene (3) at 97.3 kPa. ●, Experimental data of Gill et al.;[1] −, Calculated. (d) Residuals for the system tetrahydropyran (2) + (1-methylethyl)benzene (3). ●, Pressure residuals (kPa); ○, Vapor phase mole fraction residuals ($100 \cdot \delta y$).

(b) Thermodynamic Consistency of the Data Reported by Gill et al. A plot of the activity coefficients reported in the paper (Figures 1 and 2) indicates that the activity coefficients do not approach $x_i = 1.0$ with a constant nil slope. It is probable that either the parameters of the Antoine equations used are not accurate for treating the data or experimental inaccuracy may be present due to the large difference in boiling points of the components. In the latter situation, care must be taken to avoid the separation section of the equipment to act as an additional distillation plate.

To analyze the punctual consistency, we have followed the protocol suggested in ref 4: proper quality of the data requires a good simultaneous adjustment of the equilibrium pressure of the phases, of the activity coefficients, and of the molar fractions of the vapor. Although the Fredenslund et al.[6] criterion for thermodynamic consistency is satisfied in every case, when there is a reasonable fitting of the trend of experimental activity coefficients (using, for example, a 1-parameter Legendre series), pressure residuals do not scatter randomly about the zero line (Figures 3 and 4). In addition, when there is a good fit of the residues of the equilibrium pressure, then an unreliable fit of the activity coefficients is obtained (as shown in Figure 5). Finally, it is important to mention that no statistically significant consistency fit is able to match the experimental uncertainty of 0.27 kPa declared by Gill et al.[1] The above analysis does not change if a higher-order Legendre series is employed.

According to our experience with the VLE of binary systems composed by ethers and aromatic compounds,[7−9] they may be treated by means of the Porter symmetric model. Although it seems that the systems studied by Gill et al. tend to behave symmetrically (as clearly shown by the trend of the experimental activity coefficients in Figures 1 and 2), the inadequate quality of the data does not support this assumption.

Literature Cited

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