

Letter to the Editor

Comments on “isobaric (vapor + liquid) equilibria for three binary systems (toluene + anisole, *n*-butylbenzene + anisole, and guaiacol + anisole) at 101.33 kPa”



1. Introduction

Li et al. [1] have recently reported isobaric vapor–liquid equilibrium (VLE) data for the three binary systems toluene + anisole, *n*-butylbenzene + anisole, and guaiacol + anisole, and remarked that their data are thermodynamically consistent. The purpose of this communication is to show that this conclusion is doubtful, since Li et al. [1] have made mistakes in analyzing their data and have applied a doubtful test for determining consistency (the integral test of Herington [2]).

2. Fugacity coefficients and their effect on data treatment

At pressures near atmospheric the fugacity ϕ and effective fugacity $\hat{\phi}$ coefficients of the components may be approximated by a virial pressure-series for the compressibility factor Z , truncated after the second term:

$$Z = 1 + \frac{BP}{RT} \quad (1)$$

where $B = \sum \sum y_i y_j B_{ij}$ is the second virial coefficient of the mixture, B_{ij} is the virial coefficient of the interaction between i and j molecules, P is the pressure, T is the temperature, and R is the universal gas constant. According to Eq. (1), the fugacity coefficients may be calculated from the following relationships [3]:

$$\hat{\phi}_i = \exp \left[\frac{P}{RT} \left(2 \sum_{j=1}^n y_j B_{ij} - B \right) \right]$$

$$\phi_i = \lim_{y_i \rightarrow 1} \hat{\phi}_i = \exp \left[\frac{B_{ii}P}{RT} \right] \quad (2)$$

For the case of anisole, the second virial coefficients measured by Hales et al. [4] in the range of the VLE data reported by Li et al. [1] are reasonably smoothed by the Tsonopoulos' [5] correlation appropriately modified by the polar correction given by the dimensionless parameters $a = -1.740 \times 10^{-2}$ and $b = -4.074 \times 10^{-3}$. In addition, according to the values recommended in Landolt-Börnstein [6], the data of toluene may be fairly approximated by Tsonopoulos' [5] correlation without including polar corrections. To the best of our knowledge, no virial coefficient data have been reported for pure *n*-butylbenzene or guaiacol. However, considering the results commented for toluene and the predictions obtained from the group contribution method of McCann and

Danner [7], we can expect that the values of the second virial coefficient of *n*-butylbenzene be reliably predicted by the non-polar Tsonopoulos' [5] approach. The second virial coefficients of guaiacol have also been determined by the non-polar Tsonopoulos' [5] method; however, due to the lack of experimental results, it is not possible to assess the reliability of their prediction. In Supplementary material, the predictions obtained from polar and non-polar Tsonopoulos correlations for the second virial of the components are compared with available experimental data.

Activity coefficients γ_i may be calculated from the following relation [3]:

$$\gamma_i = \frac{y_i P \phi_i^0}{x_i P_i^0 v_i \phi_i^0} \quad (3)$$

where P_i^0 represents the pure component vapor pressure, ϕ_i^0 represents the pure component fugacity coefficient at the saturation pressure, and v_i represents the Poynting correction factor defined as:

$$v_i = \exp \left[\frac{\bar{v}_i^L (P - P_i^0)}{RT} \right] \quad (4)$$

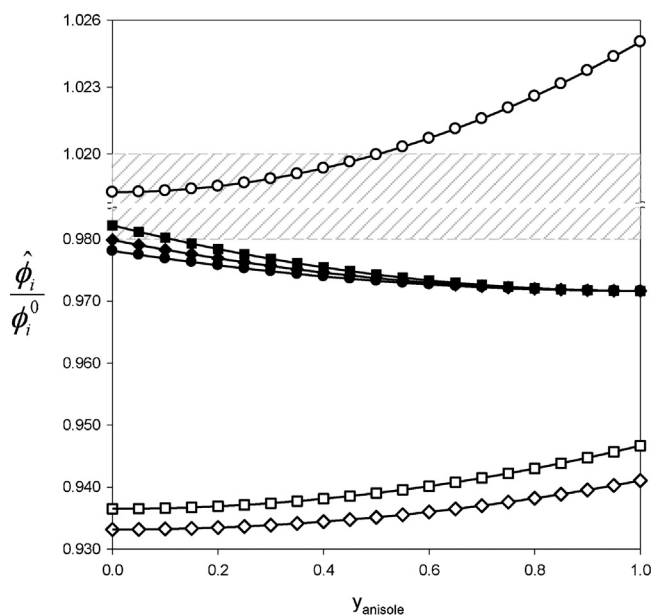


Fig. 1. Fugacity coefficient $\hat{\phi}_i/\phi_i^0$ ratio at 400 K and 101.33 kPa. Anisole in (●) toluene, (■) *n*-butylbenzene and (◆) guaiacol, (○) toluene, (□) *n*-butylbenzene, and (◇) guaiacol in anisole.

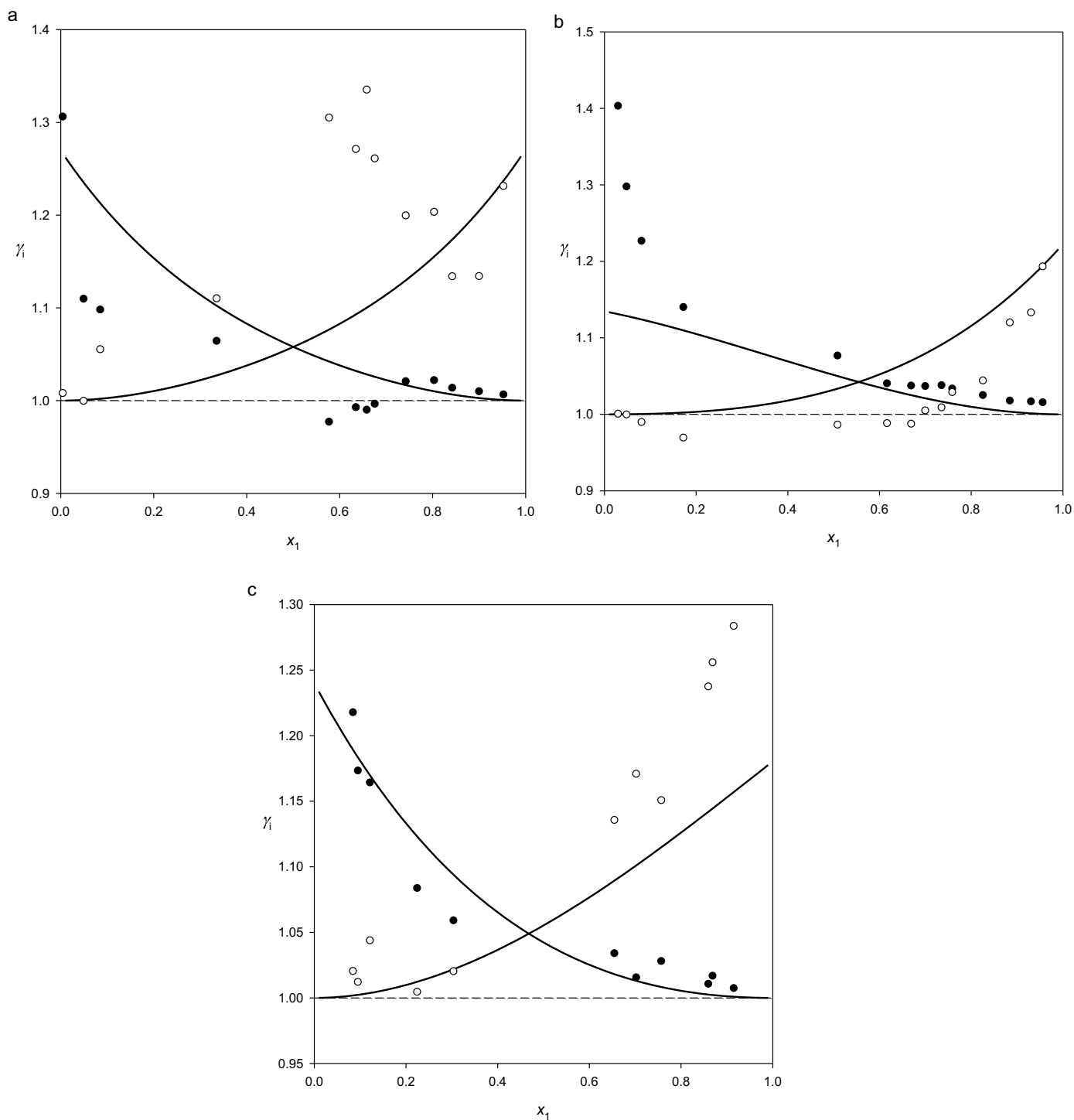


Fig. 2. (a) Activity coefficient plot for the system toluene(1) + anisole(2) at 101.33 kPa. (●, ○): γ_1, γ_2 calculated from experimental data VLE data, respectively. (—): predicted from the two-parameter Legendre polynomial used in point-to-point consistency analysis (see Table 1). (b) Activity coefficient plot for the system anisole(1) + *n*-butylbenzene (2) at 101.33 kPa. (●, ○): γ_1, γ_2 calculated from experimental data VLE data, respectively. (—): predicted from the two-parameter Legendre polynomial used in point-to-point consistency analysis (see Table 1). (c) Activity coefficient plot for the system anisole(1) + guaiacol(2) at 101.33 kPa. (●, ○): γ_1, γ_2 calculated from experimental data VLE data, respectively. (—): predicted from the two-parameter Legendre polynomial used in point-to-point consistency analysis (see Table 1).

In Eq. (4), \tilde{v}_i^L is the volume of liquid phase, which may be correctly estimated using Rackett's [8] correlation. Usually, Eq. (4) predicts an almost unitary value for v_i if $P < 5$ bar, as observed in the present case. Consequently, a reasonable estimation of the effect of fugacity corrections on the calculation of the activity coefficients is to analyze the trend of the $\hat{\phi}_i/\phi_i^0$ ratio. This has been done using the Tonopoulos [5] correlation at 400 K (a rough estimation of the

average temperature of the experimental determinations of Li et al. [1]) and atmospheric pressure. Critical data and acentric factors for pure components have been taken from Daubert and Danner [9]. Results are shown in Fig. 1, where the shaded area delimits the range inside which fugacity corrections are negligible (affecting γ_i calculations by less than 2%). We conclude that – contrary to the claim of Li et al. [1] – the use of the modified Raoult's law [10], i.e.,

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