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Review

A review of Barker's activity coefficient method and VLE data reduction

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ABSTRACT

The method of Barker is a popular scheme for determination of activity coefficients from total pressure measurements. A comprehensive review of this method is presented in this study. While discussing this technique various aspects of (vapor + liquid) equilibrium (VLE) data reduction process including types of algorithms applied, roles of saturated vapor pressures and equilibrium vapor compositions data, and types of objective functions used are analyzed. Activity coefficient or liquid state models frequently used in VLE data reduction are shown and their comparisons are investigated. More so, advantages and limitations of Barker's method are demonstrated.

Contents

1. Introduction

Barker's [1] method is an attractive P–x data reduction procedure and this is a one-step analytical fitting technique that makes direct use of the measured data [2]. This uses an arbitrary model for the molar excess Gibbs free energy, G^E (here expressed by g) and then obtains the constants of that model from the isothermal P–x data. Alternatively, it can also be applied to isobaric T–x data [3]. Primarily it was developed for non-electrolyte hydrocarbon mixtures; however, it is now being applied to electrolytes as well. This can be carried out without numerical problems for electrolytic systems and temperatures higher than the critical temperature [4]. Won and Prausnitz [5] extended this method to binary systems containing one supercritical component. The general applicability and advantages of Barker's method for the reduction of isothermal vapor/liquid equilibrium data are sufficiently demonstrated by the authors in reference [2]. The main advantage of Barker's method is that experimental difficulties in measuring y (vapor compositions) can be avoided since all values of y are obtained through data regressions. This method is useful in such cases where the gaschromotographic analysis of the vapor phase composition is not accurate enough [6]. However, the greatest limitation of Barker's method is that the g model must be chosen. The quality of the results will significantly depend on the chosen g model. In this article computational techniques applied in Barker's method will be investigated and some comparisons of g models used in this method for different (vapor + liquid) equilibrium (VLE) systems will be discussed.

2. Algorithms, roles of p_i^{sat}, y, and objective functions

Several algorithms are proposed for data reduction using Barker's method. From thermodynamics, the total pressure P for a binary system is given as

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$$P = x_1\gamma_1 p_1^{/} + x_2\gamma_2 p_2^{/}. \tag{1}$$

The symbols $p_1^{/}$ and $p_2^{/}$ are the “corrected” vapor pressures of component 1 and 2, respectively. These are defined by

$$p_1^{/} = P_1^{sat}\exp\left[\frac{(V_1^L - B_{11})(P - p_1^{sat})}{RT} - \frac{P\delta_{12}y_2^2}{RT}\right],$$
$$p_2^{/} = P_2^{sat}\exp\left[\frac{(V_2^L - B_{22})(P - p_2^{sat})}{RT} - \frac{P\delta_{12}y_1^2}{RT}\right]. \tag{2}$$

Here, P_1^{sat} and P_2^{sat} are the vapor pressure of the pure components, x and y are liquid and vapor molar fractions respectively, γ_1 and γ_2 are activity coefficients, V_1^L and V_2^L are liquid molar volumes, B_{11}, B_{22}, and B_{12} are second virial coefficients in the equations of state of the pure and mixed vapors, and $\delta_{12} = 2B_{12} - B_{11} - B_{22}$. R is the universal gas constant. Barker [1] himself used the following activity coefficient functions for equation (1):

$$\begin{aligned}\ln\gamma_1 &= C_0 l_1 + C_1 m_1 + C_2 n_1 + \cdots,\\ \ln\gamma_2 &= C_0 l_2 + C_1 m_2 + C_2 n_2 + \cdots,\end{aligned} \tag{3}$$

where

$$\begin{aligned} l_1 &= x_2^2, \quad m_1 = -x_2^2(1 - 4x_1), \quad n_1 = x_2^2(1 - 8x_1 + 12x_1^2),\\ l_2 &= x_1^2, \quad m_2 = -x_1^2(1 - 4x_2), \quad n_2 = x_1^2(1 - 8x_2 + 12x_2^2).\end{aligned} \tag{4}$$

The constants C_0, C_1, C_2 were determined by successive approximations. To initiate calculations C_1 and C_2 were set to zero and C_0 was given by

$$C_0 = 4\ln\left(\frac{2P^*}{p_1^{sat} + p_2^{sat}}\right). \tag{5}$$

P^* was the pressure for equimolar mixture estimated graphically. Using this value of C_0, approximate vapor concentrations were calculated and were sufficient enough to be used in the small correction term $\frac{P\delta_{12}y_2^2}{RT}$ in equation (2). Subsequently $p_1^{/}$ and $p_2^{/}$ were calculated from equation (2) followed by calculating a new P from equation (1). The residuals $r = P_{\text{exp}} - P_{\text{new}}$, and derivatives of dP/dC_0, dP/dC_1, dP/dC_2were predicted by

$$\begin{aligned} dP/dC_0 &= l_1\gamma_1 p_1^{/} + l_2\gamma_2 p_2^{/},\\ dP/dC_1 &= m_1\gamma_1 p_1^{/} + m_2\gamma_2 p_2^{/},\\ dP/dC_2 &= n_1\gamma_1 p_1^{/} + n_2\gamma_2 p_2^{/}.\end{aligned} \tag{6}$$

The changes ∂C_0, ∂C_1, ∂C_2 in C_0, C_1, C_2 would most nearly reduce the pressure residuals to zero by fitting least squares to the equation

$$(dP/dC_0)\partial C_0 + (dP/dC_1)\partial C_1 + (dP/dC_2)\partial C_2 = r. \tag{7}$$

Improved C_0, C_1, C_2 would be obtained upon adding ∂C_0, ∂C_1, ∂C_2 in C_0, C_1, and C_2, respectively. This process would be repeated until C_0, C_1, C_2 did not change significantly.

Prausnitz *et al.* [7] showed a slightly different approach. In their techniques y_1 and y_2 are set equal to zero in equation (2). Then experimental P–x data are regressed to estimate the parameters of appropriate activity co-efficient models (expressions of γ_1 and γ_2). Once the parameters are obtained, new y_1 and y_2 can be found by solving the following non-linear equation (8). This process should be iterative until a consistent y_1 and y_2 reached

$$\begin{aligned}\ln\gamma_1 &= \ln\left(\frac{Py_1}{x_1 p_1^{sat}}\right) - \frac{(B_{11} - V_1^L)(P - p_1^{sat})}{RT} + \frac{P_1 y_2^2\delta_{12}}{RT},\\ \ln\gamma_2 &= \ln\left(\frac{Py_2}{x_2 p_2^{sat}}\right) - \frac{(B_{22} - V_2^L)(P - p_2^{sat})}{RT} + \frac{P_2 y_1^2\delta_{12}}{RT}.\end{aligned} \tag{8}$$

Abbot and Van Ness [2] showed regression of following P–x relation by

$$P = \frac{x_1 p_1^{sat}}{\Phi_1}\exp\left(g + x_2\frac{dg}{dx_1}\right) + \frac{x_2 p_2^{sat}}{\Phi_2}\exp\left(g - x_1\frac{dg}{dx_1}\right), \tag{9}$$

where

$$g \equiv G^E/RT = x_1\ln\gamma_1 + x_2\ln\gamma_2, \tag{10}$$

$$\gamma_1 = \frac{y_1 P}{x_1 p_1^{sat}}\Phi_1 \tag{11}$$

and

$$\Phi_1 = \exp\left(\frac{(B_{11} - V_1^L)(P - p_1^{sat})}{RT} + \frac{Py_2^2\delta_{12}}{RT}\right). \tag{12}$$

Here equations (9)–(12) are the algebraic manipulations of equations (1), (2), and (8). Equation (12) or the symbol Φ in equation (9) is accounted for vapor pressure corrections. Similar to the previous case, the calculation starts by a guessed value of y in equation (12). Equation (9) is minimized through the regression of a set of values for the parameters in the correlating expression for g to find P_{cal}. First and second terms of this equation represent Py_1 and Py_2, respectively. Therefore new y values can be estimated from corresponding terms by division of P_{cal}. This process is continued until a steady y values are obtained. They [2] provided an alternative procedure basing the correlation on just P–x data through application of equation (9). However, single values of p_1^{sat} and p_2^{sat} are required whereas each data set has its own values for the pure component vapor pressures. To overcome this, they obtained an additional equation (equation (13)) to correct all reported values of P

$$\frac{\nabla P}{P} = y_1\frac{\nabla p_1^{sat}}{p_1^{sat}} + y_2\frac{\nabla p_2^{sat}}{p_2^{sat}}. \tag{13}$$

The corrected P values are then used along with the average values of p_1^{sat} and p_2^{sat} in equation (9). The parameters determined by regression are finalized only when the entire data set (including p_1^{sat} and p_2^{sat}) is validated in accord with equation (13).

Equation (1) can be re-written as follows for component i:

$$P = \sum_i (x_i\gamma_i p_i^{sat}/\Phi_i). \tag{14}$$

Here p_i^{sat} of the pure components appear explicitly as physical constants, presumably known at the temperature at which P–x data are considered. Moreover, p_i^{sat} are properly measured as part of the P–x data set and they should be included in the regression process like all other data points. As x_i approaches 1.0, the p_i^{sat} values are no more significant than other values of P and are equally subject to experimental error and to smoothing during data reduction. Their special significance enters only through the right terms in equation (14) interacting with all data points of the regression set. The authors in reference [8] suggested to accommodate these roles of p_i^{sat} by treating them both as data points and as adjustable parameters; thus measured values of P for $x_i = 1.0$ are included in the data set, however, are not identified initially with p_i^{sat}. Rather, the values of p_i^{sat} are determined by regression along with the parameters of the expression of g. According to them, these values of p_i^{sat} become the smoothed values of P for $x_i = 1.0$ in any comparison of correlated results with experimental data. This extended Barker’s method can be recommended as a procedure of complete P–x data set reduction, however, application of this technique is not guaranteed as a means of correcting for the neglect of researchers to provide vigilant measurements of p_i^{sat} values, taken in the same apparatus and with the same materials as all other reported P–x data.

Kuschel *et al.* [9] elaborately discussed the role of vapor composition (y) in VLE data reduction. The superiority of the g values is most striking in systems having large relative volatility values. Inclusion of y values of these systems into the data reduction results in considerable deterioration of the calculated g values.