

PARAMETER'S ESTIMATE IN WILSON EQUATION

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Abstract: The reliable solution of nonlinear parameter estimation problems is an important computation problem in chemical engineering. The present paper is devoted to an application of a nonlinear solving process to a system of transcendent equations. In such systems we may define the values of the parameters Λ_{12} and Λ_{21} to the Wilson equation on the base of the activity coefficients at infinite dilution. The Wilson equation was used in the mathematical model for prediction of mixture flash point temperature.

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1. Introduction

The flash point (FP) is one of the most important flammability characteristics of liquids and low-melting substances. The knowledge of the flash points is important for classification of materials according to the classes defined in each particular regulation [Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH); Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labeling and packaging of substances and mixtures] and has great practical significance in handling, transport, storage and packaging of these materials. The flash point is defined as the "lowest temperature (corrected to a pressure of 101.3 kPa) at which the application of an ignition source causes the vapors of a sample specimen to ignite under specified testing conditions [ASTM. Annual book of standards. Philadelphia, PA: American Society for Testing and Materials, (2002)]. Flash points of common pure chemical substances are widely reported, but very limited data are available for mixtures. Since the experimental measurement of flash point is expensive and time consuming therefore predictive theoretical methods are required to estimate the flash points of the both pure components and mixtures. Several prediction models are presented in the literature for the prediction of mixture flash point have reported a series of models, which could be used for predicting the flash points for ideal and non ideal solutions (see e.g., [1], [3], [5]-[9], [10], [12], [13]). The imperfectness of the liquid phase is accounted by liquid-phase activity coefficients by means of thermodynamic models. The activity coefficient is a dimensionless parameter that measures the deviation from ideality in a mixture. Values of these coefficients can be calculated by the Wilson equation, [14]. In the application of the Wilson equation for binary systems, for example, two energy parameters are required which are usually determined by using VLE data. If VLE data is unavailable, binary parameters can be estimated from activity coefficients at infinite dilution by solving the system of non-linear equations. In the present paper, the applicability of the estimation method was examined and discussed.

2. The Model Arising of Chemical Point of View

The basic assumption in Liaw et al. model (see e.g., [5]–[9]) is that the liquid phase is in equilibrium with the vapor, and the vapor phase is behaving as an ideal gas:

$$\sum \frac{x_i \gamma_i P_i^{sat}}{P_{i,fp}^{sat}} = 1, \quad (1)$$

where x_i , γ_i , P_i^{sat} and $P_{i,fp}^{sat}$ are the mole fraction, activity coefficient, vapour pressure at temperature T , and vapour pressure at the flash point temperature of the mixture

components, respectively. The temperature T that satisfies equation (1) implicitly is the flash point temperature of the mixture. The activity coefficient γ_i can be estimated by the use of the Wilson equation. The Wilson equations for binary systems containing two components indicated as **1** and **2** have the form

$$\begin{aligned}\ln \gamma_1 &= -\ln(x_1 + x_2\Lambda_{12}) + x_2\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) \\ \ln \gamma_2 &= -\ln(x_2 + x_1\Lambda_{21}) - x_1\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right),\end{aligned}\quad (2)$$

where γ_1 and γ_2 denote activity coefficients of the components **1** and **2**, respectively. The Wilson parameters Λ_{12} and Λ_{21} are expressed by

$$\Lambda_{12} = \frac{V_2}{V_1} \exp\left(\frac{-A_{12}}{RT}\right) \quad (3)$$

$$\Lambda_{21} = \frac{V_1}{V_2} \exp\left(\frac{-A_{21}}{RT}\right) \quad (4)$$

where V_1 and V_2 are the molar volumes [$\text{cm}^3 \cdot \text{mol}^{-1}$] of component **1** and component **2**; A_{21} , A_{12} - interaction energy parameters [$\text{cal} \cdot \text{mol}^{-1}$] between unlike molecules, in which $A_{12}(= \lambda_{12} - \lambda_{11})$ and $A_{21}(= \lambda_{21} - \lambda_{22})$ are the cross interaction energy parameters, independent of temperature and composition; R - universal gas constant [$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$]; T - temperature [K]. The activity coefficients at infinite dilution provide a good basis for the initial estimate of the parameters of the Wilson's equation for binary systems,

$$\begin{aligned}\ln \gamma_1^\infty &= -\ln \Lambda_{12} - \ln \Lambda_{21} + 1 \\ \ln \gamma_2^\infty &= -\ln \Lambda_{21} - \ln \Lambda_{12} + 1.\end{aligned}\quad (5)$$

Several methods were developed for the measurement of activity coefficients at infinite dilution. The most important methods are: gas-liquid chromatography (GLC), non-steady-state gas-liquid chromatography, differential ebulliometry, static methods and the dilutor method. The simple experimental method for rapid determination of activity coefficients at infinite dilution is based on gas-liquid chromatography.

3. Mathematical Preliminaries

Consider the system (5) containing a pair of two transcendent equations. Consider a more general system

$$F(x_1, x_2, \dots, x_n) = 0, \quad (6)$$

where F is a vector function possessing components $F_i : \mathbb{R}^n \rightarrow \mathbb{R}^n$ ($i = 1, 2, \dots, n$), which are real scalar functions nonlinear, and depending on the unknowns x_1, x_2, \dots, x_n .

All known methods for solving such systems are based on the known Fixed Point Theorem (FPT); we refer the reader to several classical textbooks, [2, 11]. There are many cases with nonlinear equations, where the authors use the Newton’s method as well its modifications, [4]. Here we prefer to make use of the standard iterative techniques in vectorial form, [11]. Convert for this purpose the system (6) in an equivalent form

$$x_i = f(x_1, x_2, \dots, x_n) = 0, \quad i = 1, 2, \dots, n. \tag{7}$$

Practically there are infinitely many ways to represent the system under consideration in the form (7).

Example. We write the system (6) in the equivalent form (7) by

$$x_i = x_i - \sum_{k=1}^n \varphi_{ik} F_k(x_1, x_2, \dots, x_n) = 0, \quad i = 1, 2, \dots, n, \tag{8}$$

where the $n \times n$ -matrix $A = (\varphi_{ik})$ ($i = 1, 2, \dots, n$) possesses an inverse A^{-1} for $(x_1, x_2, \dots, x_n) \in \mathbb{R}^n$. Thus having in mind (8) we obtain an iterative technique represented in vector form

$$x^{(s)} = f(x^{(s-1)}), \quad s = 1, 2, \dots, \tag{9}$$

where $x^{(s)} \equiv (x_1^{(s)}, x_2^{(s)}, \dots, x_n^{(s)})$, $f \equiv (f_1, f_2, \dots, f_n)$.

4. Convergence of the Iterative Process

Let the constant vector $(\xi_1, \xi_2, \dots, \xi_n) \in \mathbb{R}^n$ be any root of the nonlinear system (6), and be defined a closed ball $\overline{B}_\varepsilon = \{y : \|y - \xi\| \leq \varepsilon\}$, where $\varepsilon > 0$ is a small positive number; $\|\cdot\|$ is the standard Euclidean "max"-norm. Introduce the metric

$$\rho(a, b) \equiv \|a - b\| = \max_{1 \leq i \leq n} |a_i - b_i|, \quad \forall a, b \in \mathbb{R}^n.$$

Assume that the following hypotheses hold:

H1. The vector-function f belongs to the class $C^1(\mathbb{R}^n, \mathbb{R}^n)$, and

$$\left| \frac{\partial f_j(y)}{\partial x_k} \right| \leq R_{jk} \quad (j, k = 1, 2, \dots, n), \quad \forall y \in \overline{B}_\varepsilon, \tag{10}$$

where $\sum_{k=1}^n R_{jk} < 1$.

Consider the vectorial map $f(x) = (f_1(x), f_2(x), \dots, f_n(x))$.

Theorem. ([11]) *Suppose that **H1** hold, then f should be contraction mapping. Indeed we note that*

$$\begin{aligned} \|f(y) - f(z)\| &= \max_{1 \leq i \leq n} |f_i(y) - f_i(z)| = \max_{1 \leq j \leq n} \left| \sum_{k=1}^n \frac{\partial f_j(\eta_j)}{\partial x_k} (y_k - z_k) \right| \leq \\ &\leq \|y - z\| \max_{1 \leq j \leq n} \left| \sum_{k=1}^n \frac{\partial f_j(\eta_j)}{\partial x_k} (y_k - z_k) \right|, \end{aligned}$$

whereupon obtain

$$\|f(y) - f(z)\| = \max_{1 \leq j \leq n} R_{jk} \|y - z\| = \lambda \|y - z\| \quad (0 < \lambda < 1). \tag{11}$$

Thus in accordance with the classical theory it turns out that:

Corollary. *Under the same condition as it is in the Theorem stated above the function f is a contracting map on the ball \overline{B}_ε .*

Therefore, it leads to the convergent iterative process (9) with arbitrary initial approximation $x^{(0)}$ satisfying $\|x^{(0)} - \xi\| \leq \varepsilon$.

Furthermore, we choose the Newton's method to solve the nonlinear system (1), [11].

5. The Numeric Method

Consider the Jacobi matrix $F' \equiv \left(\frac{\partial F_i}{\partial x_j} \right)$ ($i, j = 1, 2, \dots, n$), and the system of two transcendent equations (5) with two unknowns X and Y . In order to calculate easier rewrite the system in the following form:

$$\begin{aligned} 1 - X - \ln Y &= \ln \alpha \\ 1 - Y - \ln X &= \ln \beta \end{aligned} \tag{12}$$

where have let

$$\alpha = \gamma_1^\infty > 1, \quad \beta = \gamma_2^\infty > 1, \quad X = \Lambda_{21} > 0, \quad Y = \Lambda_{12} > 0.$$

Then we are able to choose the method stated above. Then we are able to choose the method stated above.

6. Numerical Results

We note that the hypothesis **H1** hold. Given the data containing activity coefficients γ_1^∞ and γ_2^∞ corresponding to certain temperature. Thus having in mind the notes stated above, after solving the system (12) we obtain the quantities $X = \Lambda_{21}$ and $Y = \Lambda_{12}$ (Table 1):

	$^{\circ}C$	γ_1^{∞}	γ_2^{∞}	$X = \Lambda_{21}$	$Y = \Lambda_{12}$
Acetone-Acetonitrile	45	1.05	1.04	1.17555	0.79
Acetone-Methylacetate	50	1.32	1.18	1.35254	0.5325
Benzene-n-heptane	30	1.35	1.82	0.37353	1.38592
Chloroform-Methanol	50	2	9.4	0.08275	1.2512
Acetone-Methanol	40	2.01	1.98	0.70266	0.66979
Chloroform-Methanol	40	2.53	9.21	0.11306	0.95956
	45	2.43	9.71	0.10194	1.01022
	55	2.39	9.24	0.10574	1.02323
Ethanol-Benzene	45	10.6	4.45	0.52486	0.15172
Water-2-propanol	35	2.18	2.78	0.12871	0.27017
	40	2.18	2.82	0.12349	0.27158
	45	2.16	2.86	0.11781	0.27864
	50	2.15	2.90	0.11271	0.28288
Water-Methanol	20	1.35	0.46	1.45599	0.27017
	25	1.36	0.49	1.40274	0.17157
	30	1.15	0.69	0.99033	0.31971
Water-Ethanol	25	2.01	1.66	0.40542	0.24282
	30	1.99	1.80	0.34540	0.26305

Table 1

7. Conclusion

By using the statement to the Theorem cited above and formula (5) we obtain numerically the pairs of parameters $X = \Lambda_{21}$ and $Y = \Lambda_{12}$. Note that the parameters are temperature dependent, which the reader may see in formulae (3), (4). The temperature independent binary interaction parameters A_{12} and A_{21} , which at the same time are input data in the mathematical model for the mixture flash point prediction, may be calculated easily by the same formulae (3), (4).

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