

The Correlation of Lower Flash Point data with Activity Coefficient Models

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Abstract : Two popular activity coefficient models, Wilson and NRTL equations have been used to correlate the published flash point data on the n-propanol + propionic acid and n-butanol + propionic acid systems through the optimization method. The results of these correlation were compared with the results calculated by Raoult's law. The optimization method were found to be better than those based on the Raoult's law. The optimization method based on the Wilson equation described the published data more effectively than was the case when the optimization method was based upon the NRTL equation.

Key words : flash point, correlation, wilson, NRTL, optimization method

1. Introduction

The flash point is defined as the lowest temperature at which a liquid produces enough vapour to ignite in presence of a source of ignition [1]. The flash point provides the knowledge necessary for understanding the fundamental physical and chemical processes of combustion. Moreover, it is of importance in practice for safety considerations in storage, processing, and handling of a given compound, and is one of major flammability characteristics used to assess the fire and explosion hazards of chemical compounds [2].

There are many methods for prediction of the flash point of binary solution in the literature.

Affens and McLaren [3] developed a predictive model for the flash points of binary hydrocarbon mixtures using Raoult's law. However, this model is not able to effectively predict the measured the flash point for a non-ideal solution.

Liaw et al. [4,5] developed a mathematical model for the flash points of highly non-ideal solutions using activity coefficient models, such as Wilson, NRTL and UNIQUAC models. Surely, the Liaw's model needs the binary interaction parameters of activity coefficient model to calculate the flash points. Without the binary interaction parameters, the Liaw's model cannot be able to predict the

flash points for the binary solutions.

Vidal et al. [6] evaluated prediction methods of the flash point behavior of binary solutions using quantum chemical calculation methods such as COSMO-RS and theoretical methods such as UNIFAC.

Kim and Lee [7] developed a prediction model based on the the partial least squares (PLS) of the multivariate statistical analysis methods for the flash point of binary liquid mixtures.

Ha et al. [8,9] predicted the flash points of the flammable binary solutions using the prediction models based on activity coefficient models.

The purpose of this study was to predict the lower flash points for the flammable binary mixtures. Two binary solutions, n-propanol + propionic acid and n-butanol + propionic acid were used. The experimental flash points of these binary solutions were obtained from the literature [10].

Two popular activity coefficient models, such as Wilson and NRTL equations [11], have been used to correlate the published flash points through the optimization method. The results of these correlation were compared with the results calculated by Raoult's law.

2. Mathematical Formulation for the Lower Flash Point Prediction

The Le Chatelier's rule [12] for the flammable vapor-air

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mixture of multicomponents is as follows :

$$\sum_{i=1}^N \frac{y_i}{LFL_i} = 1 \quad (1)$$

where y_i is the composition of a flammable substance i in the vapor phase, and LFL_i is the lower flammable limit (LFL) of the pure component i . From the definition of the flash point, the LFL_i is expressed relative to its saturated vapor pressure at flash point, $P_{i,fp}^{sat}$, as :

$$LFL_i = \frac{P_{i,fp}^{sat}}{P} \quad (2)$$

where P is the ambient pressure. The composition of flammable substance i in the vapor phase, y_i , can be derived from the vapor-liquid equilibrium (VLE).

For every component i in the mixture, the condition for equilibrium between a liquid phase and a vapor phase at the same T and P is given by :

$$y_i \Phi_i P = x_i \gamma_i f_i \quad (i = 1, 2, \dots, N) \quad (3)$$

At low pressure, the vapor phase can be approximated as an ideal gas, then the vapor phase solution's fugacity coefficient for component i is reduced to :

$$\Phi_i = 1 \quad (4)$$

and the fugacity of pure liquid i , at the temperature and pressure of the system can be simplified as :

$$f_i \cong P_i^{sat} \quad (5)$$

where P_i^{sat} is the vapor pressure of pure i at the system temperature. Therefore, the vapor-liquid equilibrium relation is reduced as :

$$y_i P = x_i \gamma_i P_i^{sat} \quad (6)$$

or

$$y_i = \frac{x_i \gamma_i P_i^{sat}}{P} \quad (7)$$

Substitution Eq. (2) and Eq. (7) into Eq. (1) results in :

$$\sum_{i=1}^N \frac{x_i \gamma_i P_i^{sat}}{P_{i,fp}^{sat}} = \frac{x_1 \gamma_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 \gamma_2 P_2^{sat}}{P_{2,fp}^{sat}} = 1 \quad (8)$$

The saturated vapor pressure variation with temperature for a pure substance i can be estimated by the Antoine equation [11] :

$$\log P_i^{sat} = A_i - \frac{B_i}{T + C_i} \quad (9)$$

where A_i , B_i and C_i are the Antoine coefficients and T is the temperature in degree Celsius ($^{\circ}\text{C}$). The Antoine coefficients, A_i , B_i and C_i , were adapted from the literature

Table 1. The Antoine coefficients of the components

| Components | Coefficients | | |
|----------------|--------------|---------|--------|
| | A | B | C |
| n-Propanol | 7.8477 | 1499.21 | 204.64 |
| n-Butanol | 7.4768 | 1362.39 | 178.77 |
| Propionic acid | 7.9906 | 1929.30 | 236.43 |

[13] and are listed in Table 1.

The vapor pressure of pure substance i at its flash point $P_{i,fp}^{sat}$, as presented in Eq. (8), can be estimated by substituting $T_{i,fp}$, the flash point of component i , into the Antoine equation.

Under an ideal solution assumption, the activity coefficients of the liquid phase are equal to unity. Therefore Eq. (8) was reduced to Raoult's law, this being decribed as :

$$\sum_{i=1}^N \frac{x_i P_i^{sat}}{P_{i,fp}^{sat}} = \frac{x_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 P_2^{sat}}{P_{2,fp}^{sat}} = 1 \quad (10)$$

The temperature, which satisfies Eq. (10), is determined to be the lower flash point of the binary mixtures.

3. The optimization of the binary interaction parameters

The Wilson and NRTL equations are used to correlate the published experimental data for two binary solutions, these equations being decribed as :

Wilson equation :

$$\begin{aligned} \ln \gamma_1 &= -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_1} \right) \\ \ln \gamma_2 &= -\ln(x_2 + \Lambda_{21}x_1) + x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right) \end{aligned} \quad (11)$$

where Λ is as following

$$\Lambda_{ij} = \frac{v_j}{v_i} e^{\frac{\lambda_{ij} - \lambda_{ji}}{RT}}$$

NRTL equation :

$$\ln \gamma_i = \frac{\sum_{j=1}^m \tau_{ji} G_{ji} x_j}{\sum_{l=1}^m G_{li} x_l} + \sum_{j=1}^m \frac{x_j G_{ij}}{\sum_{l=1}^m G_{li} x_l} \left(\tau_{ij} - \frac{\sum_{r=1}^m x_r \tau_{rj} G_{rj}}{\sum_{l=1}^m G_{lj} x_l} \right) \quad (12)$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (\alpha_{ji} = \alpha_{ij})$$

The objective function was used to minimize the differ-

Table 2. The optimized binary parameters of the Wilson and NRTL equations for each binary system

| Systems | Parameters | Wilson | | NRTL | |
|-----------------------------------|------------|-----------------|-----------------|-----------------|-----------------|
| | | A ₁₂ | A ₂₁ | A ₁₂ | A ₁₂ |
| n-propanol(1) + propionic acid(2) | | 4160.9097 | -706.2283 | -841.6081 | 1682.4017 |
| n-butanol(1) + propionic acid(2) | | -840.3949 | 364.2248 | 10.8824 | -582.8816 |

ence between the experimental and calculated flash points, this being described as :

$$F = \sum_{j=1}^N ABS(T_j^{exp} - T_j^{cal}) \quad (13)$$

where, N is the number of experimental data, ABS is absolute value, T_j^{exp} is the experimental lower flash point of component j, and T_j^{cal} is the calculated lower flash point of component j which satisfies Eq. (8), is determined to be the lower flash point of the binary mixtures.

The values of the binary interaction parameters that minimized this objective function (F) were sought, using both the Wilson and NRTL equations.

Using the SIMPLEX [14] method, the binary interaction parameters of the Wilson and NRTL equations,

$$\text{Wilson : } A_{12} (= \lambda_{12} - \lambda_{11}), A_{21} (= \lambda_{21} - \lambda_{22})$$

$$\text{NRTL : } A_{12} (= g_{12} - g_{11}), A_{21} (= g_{21} - g_{22})$$

were calculated.

4. Results

In this study, the optimized binary interaction parameters are shown in Table 2, and the calculated values using the optimization method and the Raoult's law for the systems are presented in Table 3~4 and Fig. 1~2. Concentrations of component i are given in mole fraction, x_i . As

Table 3. The published experimental and the calculated flash points for n-propanol(x_1) + propionic acid(x_2) system

| Mole fractions | | Flash points (°C) | | | |
|----------------|-------|-------------------|--------------|--------|-------|
| x_1 | x_2 | Exp. | Raoult's law | Wilson | NRTL |
| 1.000 | 0.000 | 21.0 | - | - | - |
| 0.910 | 0.090 | 21.0 | 22.14 | 22.21 | 22.27 |
| 0.710 | 0.290 | 25.0 | 25.11 | 25.49 | 25.85 |
| 0.510 | 0.490 | 30.0 | 28.92 | 29.82 | 30.45 |
| 0.301 | 0.699 | 36.0 | 34.37 | 35.68 | 36.00 |
| 0.109 | 0.891 | 42.0 | 42.51 | 41.99 | 41.88 |
| 0.045 | 0.955 | 44.0 | 46.48 | 44.14 | 45.18 |
| 0.000 | 1.000 | 50.0 | - | - | - |
| A.A.D. | | - | 1.14 | 0.39 | 0.65 |

Table 4. The published experimental and the calculated flash points for n-butanol(x_1) + propionic acid(x_2) system

| Mole fractions | | Flash points (°C) | | | |
|----------------|-------|-------------------|--------------|--------|-------|
| x_1 | x_2 | Exp. | Raoult's law | Wilson | NRTL |
| 1.000 | 0.000 | 31.0 | - | - | - |
| 0.949 | 0.051 | 31.0 | 31.49 | 31.82 | 31.72 |
| 0.909 | 0.091 | 35.0 | 31.89 | 32.60 | 32.38 |
| 0.698 | 0.302 | 38.0 | 34.26 | 37.55 | 36.79 |
| 0.507 | 0.493 | 40.0 | 36.93 | 41.94 | 41.38 |
| 0.296 | 0.704 | 46.0 | 40.84 | 46.00 | 46.00 |
| 0.107 | 0.893 | 49.0 | 45.88 | 48.78 | 48.95 |
| 0.000 | 1.000 | 50.0 | - | - | - |
| A.A.D. | | - | 3.12 | 0.97 | 1.00 |

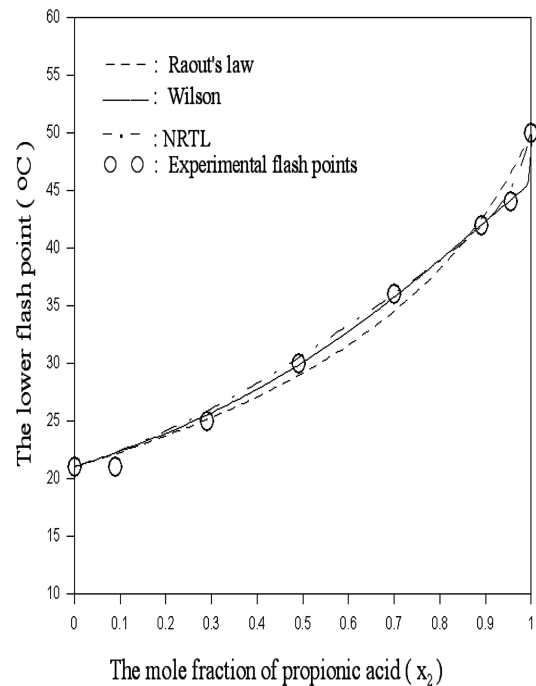


Fig. 1. The comparison of the lower flash point prediction curves with the published experimental data for n-propanol(x_1) + propionic acid(x_2) system.

shown in Figures, the lower flash points of the systems plotted as a function of mole fraction. And included in Table 3~4 is the A.A.D.(average absolute deviation) defined [15] as follows :

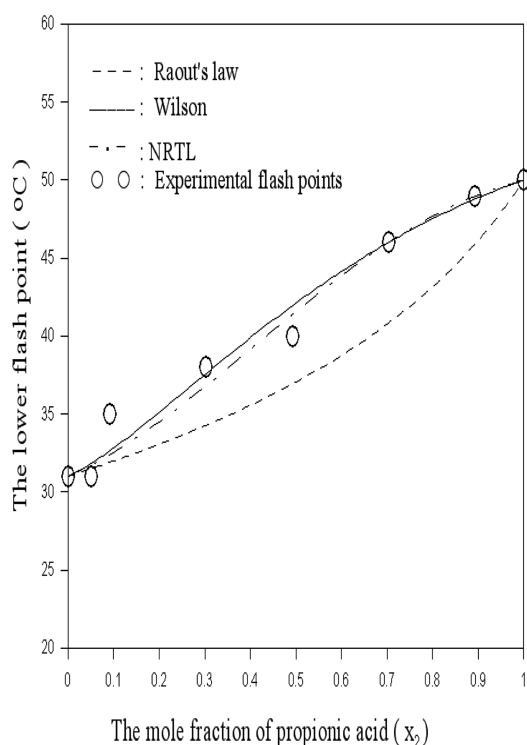


Fig. 2. The comparison of the lower flash point prediction curves with the published experimental data for n-butanol(x_1) + propionic acid(x_2) system.

$$A.A.D. = \sum_{i=1}^N \frac{|T_i^{\text{exp}} - T_i^{\text{cal}}|}{N} \quad (13)$$

where the A.A.D. is a measure of agreement between the experimental values and the calculated values, the T_i^{exp} is the experimental lower flash point of component i , and T_i^{cal} is the estimated lower flash point of component i .

As can be seen from the A.A.D. in tables, the reported flash points are generally in bad agreement with the predicted values based on the Raoult's law and in good agreement with the predicted values based on the optimization method using the Wilson and NRTL equations.

Table 3~4 also depict the results of comparing the predicted values provided by the optimized binary interaction parameters in the Wilson and NRTL equations for estimating the corresponding activity coefficients. The NRTL equation is a little more accurate than the Wilson equation, as can be seen from the A.A.D. in tables.

5. Conclusion

The published flash points for the two binary solutions, n-propanol + propionic acid and n-butanol + propionic acid, were correlated by the optimization method. The optimization method using the Wilson and NRTL equations

were compared with the Raoult's law. The calculated values based on the optimization method were found to be better than those based on the Raoult's law. The NRTL equation is a little more accurate than the Wilson equation, as can be seen from the A.A.D.

The prediction method in this study can thus be applied to incorporate inherently safer design for chemical process, such as the determination of the safe storage conditions for combustible solutions.

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