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IDENTIFICATION OF THE BEST MODEL AND PARAMETERS FOR T-Y-X EQUILIBRIUM DATA OF ETHANOL-WATER MIXTURE

Bilel HADRICH, Nourhène BOUDHRIOUA and Nabil KECHAOU

Groupe de Génie des Procédés Agro-alimentaires - Unité de Recherche en Mécanique des
Fluides Appliquée et Modélisation - Ecole Nationale d'Ingénieurs de Sfax, BP '1173' 3038,
Sfax, Tunisia – Fax: 0021674275595

bilel.hadrich@enis.rnu.tn, nourhene.boudhrioua@fss.rnu.tn & nabil.kechaou@enis.rnu.tn

Abstract

Four empirical models are tested for fitting the T-y-x equilibrium data of ethanol-water mixture by minimizing the Root Mean Square (RMS) between equilibrium data and theoretical points. The total pressure of the correspondent data is 101.3 kPa. All models parameters are also identified. The NRTL model shows the best fit of equilibrium data with $\text{RMS} = 0.4 \%$.

Nomenclature

R	ideal gas constant	(J/mol K)
T	absolute temperature	(K)
x	ethanol mole fraction in liquid	(-)
y	ethanol mole fraction in vapour	(-)
γ	activity coefficient	(-)

I. Introduction

The bioethanol is considered as a very important renewable energy in this decade. It could be produced from natural sources (wheat, sugar cane, sugar beet, corn ...) by fermentation and purified by distillation. The calculation of distillation column (continuous and batch processes) is based on determination of its equilibrium-stage. This step could be obtained by graphic methods (McCabe and Thiele or Ponchon-Savarait) basing on equilibrium curve and operating lines. Usually, the equilibrium curve is presented in literature as equilibrium point such as presented in Table 1 [1]. Its fitting by mathematical models is a very important step for programming the graphic methods.

The equilibrium liquid-vapour of ethanol-water mixture presents some particularity. In fact it's considered as a non-ideal mixture and it presents an azeotrope in mole fraction of 89 % [1]. In this case the identification of the activity coefficients of ethanol and water is very important step in fitting equilibrium data.

Wilson, NRTL, van Laar and Margules are among the most empiric models used for identification of those activity coefficients [1, 2]. Each of them presents some particularities in their expressions.

The aim of this work is the identification of the best mathematical model fitting the T-y-x equilibrium data of ethanol-water mixture.

Table 1: Liquid-vapour equilibrium data for ethanol-water at atmospheric pressure

T (°C)	x	y
95.5	0.0190	0.1700
89.0	0.0721	0.3891
86.7	0.0966	0.4375
85.3	0.1238	0.4704
84.1	0.1661	0.5089
82.7	0.2337	0.5445
82.3	0.2608	0.5580
81.5	0.3273	0.5826
80.7	0.3965	0.6122
79.8	0.5079	0.6564
79.7	0.5198	0.6599
79.3	0.5732	0.6841
78.74	0.6763	0.7385
78.41	0.7472	0.7815
78.15	0.8943	0.8943

II. Mathematical Models

II.1. Thermodynamic data

The relative volatility of an ideal binary system is defined by:

$$\alpha_{ij} = \frac{P_i^0}{P_j^0} \quad (1)$$

where P_i^0 is the vapour pressure of the component i in the mixture. It could be determined by Antoine equation [1].

In the whole manuscript the index 1 is relative to ethanol and the index 2 is relative to water.

For the non-ideal system, relation 1 became:

$$\alpha_{ij} = \frac{\gamma_i \cdot P_i^0}{\gamma_j \cdot P_j^0} \quad (2)$$

where γ_i is the activity coefficient of the component i.

Those parameters could be obtained by identification, by using a number of mathematical models for different binary or complex systems. The determination of those parameters allows the fitting the equilibrium data.

II.2. Wilson model

The Wilson model presents the activity coefficients for binary system with the following relations [1]:

$$\ln(\gamma_1) = -\ln(x_1 + \Lambda_{12} \cdot x_2) + x_2 \cdot \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} \cdot x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} \cdot x_1} \right) \quad (3)$$

$$\ln(\gamma_2) = -\ln(x_2 + \Lambda_{21} \cdot x_1) - x_1 \cdot \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} \cdot x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} \cdot x_1} \right) \quad (4)$$

where

$$\Lambda_{12} = \frac{v_2}{v_1} \cdot \exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right) \quad (5)$$

$$\Lambda_{21} = \frac{v_1}{v_2} \cdot \exp\left(-\frac{\lambda_{21} - \lambda_{22}}{RT}\right) \quad (6)$$

where λ_{ij} : interaction energy between components i and j, $\lambda_{ij} = \lambda_{ji}$; v_i molar volume of pure-liquid component i (J/mol).

$(\lambda_{12} - \lambda_{11})$ et $(\lambda_{21} - \lambda_{22})$ are the adjustable model parameters.

II.3. NRTL model

In this case, the activity coefficients are presented by relations 7 and 8 [3]:

$$\ln(\gamma_1) = x_2^2 \cdot \left(\tau_{21} \cdot \left(\frac{G_{21}}{x_1 + x_2 \cdot G_{21}} \right)^2 + \tau_{12} \cdot \frac{G_{12}}{(x_2 + x_1 \cdot G_{12})^2} \right) \quad (7)$$

$$\ln(\gamma_2) = x_1^2 \cdot \left(\tau_{12} \cdot \left(\frac{G_{12}}{x_2 + x_1 \cdot G_{12}} \right)^2 + \tau_{21} \cdot \frac{G_{21}}{(x_1 + x_2 \cdot G_{21})^2} \right) \quad (8)$$

where $G_{ij} = \exp(-0,3 \cdot \tau_{ij})$, $\tau_{ij} = \frac{g_{ij}}{RT}$.

The binary interaction parameters to determinate are g_{12} and g_{21} and they are different to zero but $g_{11} = g_{22} = 0$. So, g_{12} and g_{21} must be optimized to fit the equilibrium data.

II.4. Van Laar model

Relations 9 and 10 present the activity coefficients as follows [1]:

$$\ln(\gamma_1) = A_{12} \cdot \left(\frac{A_{21} \cdot x_2}{A_{12} \cdot x_1 + A_{21} \cdot x_2} \right)^2 \quad (9)$$

$$\ln(\gamma_2) = A_{21} \cdot \left(\frac{A_{12} \cdot x_1}{A_{12} \cdot x_1 + A_{21} \cdot x_2} \right)^2 \quad (10)$$

A_{ij} is the adjustable parameters of van Laar model.

II.5. Margules model

The activity coefficients are presented by the following relations [1]:

$$\ln(\gamma_1) = (\bar{A}_{12} + 2 \cdot (\bar{A}_{21} - \bar{A}_{12}) \cdot x_1) \cdot x_2^2 \quad (11)$$

$$\ln(\gamma_2) = (\bar{A}_{21} + 2 \cdot (\bar{A}_{12} - \bar{A}_{21}) \cdot x_2) \cdot x_1^2 \quad (12)$$

\bar{A}_{ij} is the adjustable parameters of Margules model.

III. Statistical analysis

The models parameters were determined by minimizing the Root Mean Square (RMS) which expresses the difference between equilibrium and predicted equilibrium curves. The root mean square was calculated as following:

$$RMS = 100 \times \sqrt{\frac{\sum_{i=1}^N \left(\frac{y_{i,cal} - y_{i,eq}}{y_{i,cal}} \right)^2 + \left(\frac{T_{i,cal} - T_{i,eq}}{T_{i,cal}} \right)^2}{N-1}} \quad (13)$$

where $y_{i,eq}$ and $y_{i,cal}$ were respectively equilibrium and predicted ethanol mole fraction in vapour ; $T_{i,eq}$ and $T_{i,cal}$ were respectively equilibrium and predicted temperature saturation and N is the number of points.

The model which gives the minimum RMS will be considered as the best one and showing the best fit of the equilibrium data. The tolerance is fixed at 10^{-4} .

A program was carried out with Matlab®, to optimize and to determinate the models parameters.

IV. Results and discussion

Table 2 shows the predicted parameters and the RMS values for all tested models.

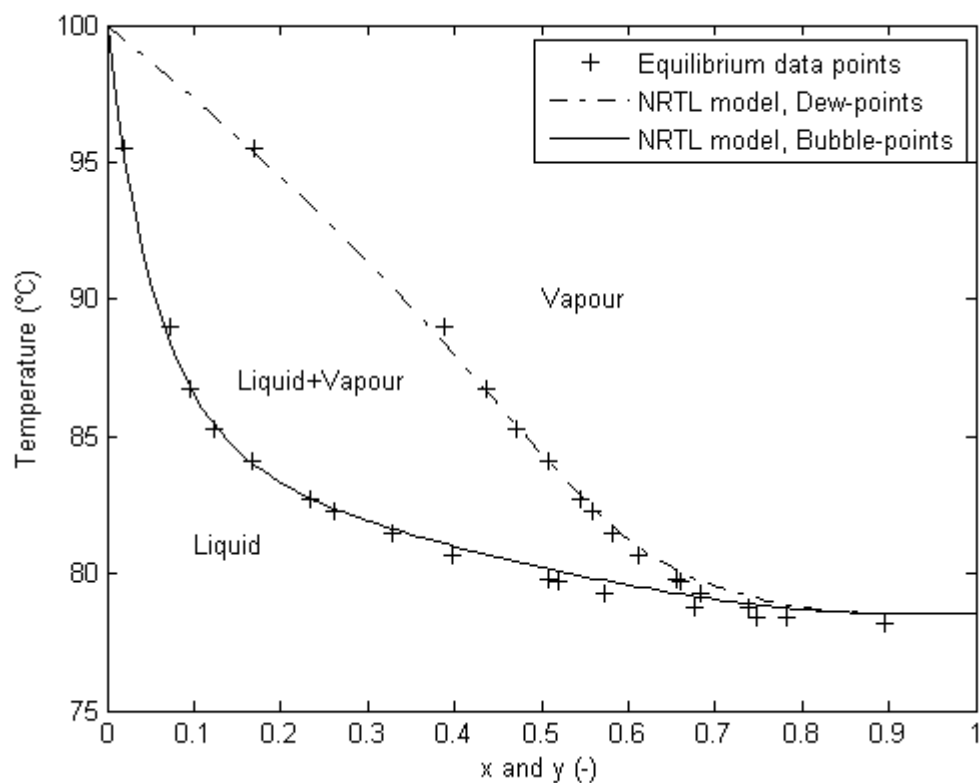
Table 2: Parameters and RMS values obtained for the tested models

Model	Parameters' model		Activity coefficient		RMS (%)
Wilson	$\lambda_{12} - \lambda_{11} = 1242.5$	$\lambda_{21} - \lambda_{22} = 4096.8$	$\gamma_1 = 1.0085$	$\gamma_2 = 2.3933$	1.323
NRTL	$g_{12} = -633$	$g_{21} = 5823.1$	$\gamma_1 = 1$	$\gamma_2 = 2.4090$	0.403
Van Laar	$A_{12} = 1.6939$	$A_{21} = 0.9076$	$\gamma_1 = 1.0060$	$\gamma_2 = 2.2315$	0.745
Margules	$\bar{A}_{12} = 1.6432$	$\bar{A}_{21} = 0.6923$	$\gamma_1 = 0.9994$	$\gamma_2 = 2.0431$	1.246

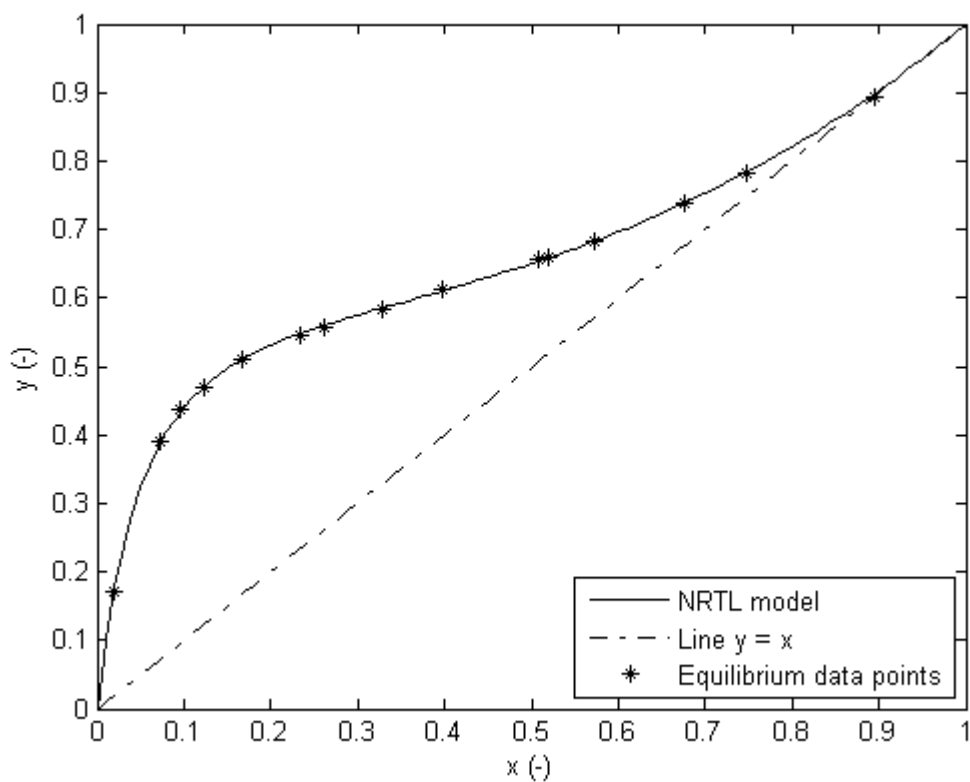
It's clear that the NRTL and van Laar models show the best fit. Having the smallest RMS, the NRTL model is retained to fit the T-y-x equilibrium data of ethanol-water mixture. This result was obtained and confirmed by [3].

It is important to remark that all activity coefficients are very comparable for all models. So it could be considered that the suggested program was validated and it's very important to optimize this type of model.

Figures 1 (a and b) shows the quality of fitting of equilibrium data (at atmospheric pressure) by NRTL model for two types of results: $T = (x,y)$ (figure 1.a) and $y = f(x)$ (figure 1.b).



(a)



(b)

Figure 1: Equilibrium and predicted (by NRTL model) equilibrium liquid-vapour of ethanol-water mixture at atmospheric pressure

V. Conclusion

The fitting of liquid-vapour equilibrium of ethanol-water mixture at atmospheric pressure was investigated. Four models were tested. NRTL model is the best one fitting equilibrium data.

It's important to say that this work is very important step to program the graphic methods valid for calculation of distillation column (batch and continuous).

VI. References

- [1] Seader J. D., Sirola J. J. and Bernicki S. D. Perry's Chemical Engineers' Handbook, chapter 13 - Distillation, pages 13-1-13-108. The McGraw-Hill Companies, Inc., 7ième edition, 1997.
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