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Thermodynamic Modeling of Ethanol-Water Azeotrope: A Comparative Study of Wilson, NRTL, UNIFAC and UNIQAUC Models

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ABSTRACT

The ethanol–water mixture forms a minimum boiling azeotrope at 89.52 mol% ethanol and 78.15°C. This azeotropic composition cannot be separated by conventional distillation techniques. However, advanced separation methods such as pressure-swing distillation, extractive distillation, azeotropic distillation, and salt-assisted distillation can be employed. These techniques can be effectively simulated using Aspen Plus^{TM} software. Selecting an appropriate thermodynamic model is crucial before performing such simulations. Therefore, a comparative study was conducted using the Wilson, **N**on **R**andom **T**wo **L**iquid (NRTL), **Uni**versal **Qua**si-**C**hemical (UNIQUAC) and **UNIQUAC** **F**unctional **A**ctivity **C**oefficients (UNIFAC), models for the ethanol–water binary system, based on T–x–y and x–y experimental data The Root Mean Square Deviation (RMSD) values between the predicted vapor mole fraction of ethanol and temperature with experimental data at the same liquid mole fraction of ethanol were analyzed. Among the models, the NRTL model showed the best agreement, with RMSD(y) = 0.0106 and RMSD(T) = 0.002. Therefore, it was concluded that the NRTL thermodynamic model is the most suitable for further simulation work.

Keywords: Aspen plus Software, NRTL, UNIQUAC, UNIFAC, Wilson, RMSD

1. INTRODUCTION

The production of ethanol has exhibited a marked increase over the years, predominantly in response to the escalating global demand for energy. A significant proportion of global fuel ethanol is generated through the fermentation of carbohydrates contained in the starches of diverse grains, including corn, sorghum, and barley, alongside the sugars obtained from sugar cane and sugar beets. To achieve high-purity ethanol, it is imperative to eliminate the extraneous water content via distillation. Nevertheless, the ethanol-water binary mixture poses a significant challenge due to the establishment of an azeotropic composition, which constrains the efficacy of traditional distillation techniques in realizing complete separation (Raosaheb, 2015). The ethanol-water azeotropic system has been the subject of extensive investigation over recent decades, attributable to its industrial significance and the complexities associated with its separation characteristics. The ethanol-water binary mixture establishes an azeotropic composition at a temperature of 78.15℃, characterized by an ethanol mole fraction of 89.52%. Consequently, the liquid phase exhibits deviations from ideal behavior, rendering the application of ideal equilibrium relations inapplicable. Prominent thermodynamic models, such as Wilson, NRTL, and UNIQUAC, have been comprehensively applied to analyze the vapor-liquid equilibrium (VLE) behavior of this particular system. Pioneering foundational studies, including [12], which introduced the UNIFAC group-contribution methodology, and [13], which presented a modified equation of state, have established the essential framework for effectively modeling non-ideal mixtures.

Marco Guevara, 2018 [5] studied the thermodynamic modeling using the polar-SRK equation of state and Redlich-Kister consistency test for new binary interaction parameters of ethanol-water system using atmospheric pressures and azeotropic data. Ternary liquid-liquid equilibrium data for water-ethanol system through experimental procedures were developed and tested with NRTL and UNIQUAC liquid activity coefficient models, n-pentane was identified as the most effective entrainer for ethanol-water separation, achieving a root mean square deviation of 0.00038 when analyzed with the NRTL model [6]. Zhang et. al, (2015) established reliable activity coefficient model for the water-ethanol-glycerol, with an emphasis on the application in ethanol dehydration by extractive distillation [7].

The Non-Random Two-Liquid (NRTL) model is frequently used for modeling VLE in ethanol-water systems. It has been applied to systems involving additional components like sulfur dioxide, where it demonstrated high accuracy in predicting phase behavior across various temperatures [1]. The experimental data on vapor-liquid equilibria (VLE) for ethanol-water binary system at pressures 100, 1500, and 2000 kPa were presented and the findings contribute to the understanding of phase behavior in ethanol-water mixtures [3]

Simulation tools like Aspen Plus continue to be instrumental for designing and optimizing separation processes involving ethanol–water azeotropes. Studies integrating accurate thermodynamic modeling with process simulation have demonstrated significant improvements in process efficiency and cost-effectiveness, particularly in extractive and pressure-swing distillation techniques. A Comparative study of NRTL, UNIQUAC, UNIFAC, Wilson thermodynamic models for ethanol-water azeotropic mixture has not been done on Aspen Plus simulation software with Root Mean Square Deviation analysis.

This study focuses on evaluating the performance of Wilson, NRTL, UNIFAC and UNIQUAC models in representing the ethanol–water system using Aspen Plus^{TM} V11.1, with a particular emphasis on fitting experimental **T–x–y** and **x–y** data. The model showing the best agreement with experimental data is selected for further simulation of advanced distillation techniques in Aspen Plus.

2. METERIALS AND METHODS

2.1. Materials

In this work, Ethanol (C_2H_5OH) and water (H_2O) were used from Aspen Plus data base. The properties were shown in the following table. 2.1.

Table 2.1. Property Table of ethanol and water

Property	Ethanol (C_2H_5OH)	Water (H_2O)
Molecular Formula	C_2H_5OH	H_2O
Molar Mass	46.07 g/mol	18.02 g/mol
Appearance	Colorless liquid	Colorless liquid
Odor	Characteristic (alcohol-like)	Odorless
Boiling Point	78.4°C	100 °C
Polarity	Polar	Highly polar
Hydrogen Bonding	Yes	Strong hydrogen bonding

2.2. Methods

2.2.1. Aspen Plus Software

Aspen Plus^{TM} V11.1 Platform has been used in this work for thermodynamic model testing of ethanol and water azeotrope.

2.2.2. Thermodynamic modeling

The **Non-Random Two-Liquid (NRTL)** model is a widely used activity coefficient model designed to predict the behavior of non-ideal liquid mixtures. It considers the non-randomness in the spatial arrangement of molecules and accounts for local composition effects. It uses binary energy interaction parameters to describe the excess Gibbs energy, making it suitable for accurately predicting vapor-liquid equilibria, especially in systems that form azeotropes.

The **UNIQUAC (Universal Quasi-Chemical)** model is a semi-theoretical model that divides the activity coefficient into two parts: a combinatorial part that accounts for size and shape differences between molecules, and a residual part that accounts for energy interactions. This model is more physically grounded than purely empirical models and is capable of representing a wide range of non-ideal mixtures. UNIQUAC is often used when detailed molecular structure information is available, and it provides good accuracy in predicting phase equilibria for both polar and nonpolar systems.

The **UNIFAC (UNIQUAC Functional-group Activity Coefficient)** model extends the UNIQUAC framework by using a group contribution approach. Instead of requiring binary interaction data for every specific mixture, UNIFAC estimates activity coefficients based on the interactions between functional groups (such as -OH, -CH_3, etc.). This predictive capability makes it highly valuable for systems where experimental data is scarce. It is widely applied in chemical process simulation and design, especially when screening large numbers of potential solvent or mixture combinations.

The **Wilson model** is an empirical model used for predicting the non-ideal behavior of completely miscible liquid mixtures. It is based on the concept of local compositions and energy interactions between different species. The model assumes that there are no immiscibility issues and that molecular interactions can be represented by binary energy parameters.

The above four thermodynamic activity coefficient models were evaluated using Aspen Plus simulations to analyze the vapor-liquid equilibrium behavior of the ethanol-water system and were compared against experimental data to identify the best-fitting models.

2.2.3. Root Mean Square Deviation (RMSD)

The Root Mean Square Deviation (RMSD) is a statistical measure used to evaluate the accuracy of predicted values from a model compared to actual experimental data. In the context of vapor-liquid equilibrium (VLE) studies, such as the ethanol-water system, RMSD quantifies how well a thermodynamic model (e.g., NRTL, UNIQUAC, UNIFAC, Wilson) predicts the vapor phase composition (mole fraction of ethanol) at given liquid compositions.

$$RMSD = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(y_i^{\exp} - y_i^{\mathrm{mod}\,el}\right)^2} \qquad (1)$$

where y_i^{exp} is experimental value of vapor phase ethanol mole fraction, y_i^{model} is corresponding value predicted by the thermodynamic modeling and N is number of data points.

3. RESULTS AND DISCUSSION

The predicted VLE data from these models were compared with the reported experimental data [10]. Specifically, the vapor-phase compositions and equilibrium temperatures were evaluated against the available experimental values.

Table. 3.1. T- x-y experimental Vapor Liquid Equilibrium data [10]

xEtoh	xw	yEtoh	yw	T,℃
0	1	0	1	100
0.019	0.981	0.17	0.83	95.5
0.0721	0.9279	0.3891	0.6109	89
0.099	0.9034	0.4375	0.5625	86.7
0.1238	0.8762	0.4704	0.5296	85.3
0.1661	0.8339	0.5089	0.4911	84.1
0.2337	0.7663	0.5445	0.4555	82.7
0.2608	0.7392	0.558	0.442	82.3
0.3273	0.6727	0.5826	0.4174	81.5
0.3965	0.6035	0.6122	0.3878	80.7
0.5198	0.4802	0.6599	0.3401	79.7
0.5732	0.4268	0.6841	0.3159	79.3
0.6763	0.3237	0.7385	0.2615	78.74
0.7472	0.2528	0.7815	0.2185	78.41
0.8943	**0.1057**	**0.8943**	**0.1057**	**78.15**
1	0	1	0	78.3

Table. 3.1. shows the experimental temperature and equilibrium mole fractions of ethanol and water, indicating the azeotropic composition at 0.8943 mole fraction ethanol at 78.15 C.

Table 3.2: x-y values for different thermodynamic models of ethanol-water mixture (Aspen Plus Simulation)

[NRTL] x (Ethanol)	[NRTL] y (Ethanol)	[UNIFAC] x (Ethanol)	[UNIFAC] y (Ethanol)	[UNIQUAC] x (Ethanol)	[UNIQUAC] y (Ethanol)	[Wilson] x (Ethanol)	[Wilson] y (Ethanol)
0	0	0	0	0	0	0	0
0.0625	0.35489	0.0625	0.3813	0.0625	0.354987	0.0625	0.366305
0.125	0.473062	0.125	0.474374	0.125	0.471291	0.125	0.468581
0.1875	0.529561	0.1875	0.517713	0.1875	0.528334	0.1875	0.519591
0.25	0.563771	0.25	0.547089	0.25	0.56382	0.25	0.55384
0.3125	0.589021	0.3125	0.572447	0.3125	0.590388	0.3125	0.58149
0.375	0.611027	0.375	0.597378	0.375	0.613461	0.375	0.6066
0.4375	0.632676	0.4375	0.623388	0.4375	0.635803	0.4375	0.631185
0.5	0.655648	0.5	0.651191	0.5	0.659044	0.5	0.656466
0.5625	0.681068	0.5625	0.681178	0.5625	0.684306	0.5625	0.683345
0.625	0.709804	0.625	0.713632	0.625	0.712494	0.625	0.712625
0.6875	0.742633	0.6875	0.748848	0.6875	0.744461	0.6875	0.745138
0.75	0.780343	0.75	0.787245	0.75	0.781116	0.75	0.781843
0.8125	0.823796	0.8125	0.829523	0.8125	0.823505	0.8125	0.823906
0.875	0.875	0.875	0.876948	0.875	0.87292	0.875	0.872832
0.9375	0.932215	0.9375	0.932012	0.9375	0.931021	0.9375	0.930622
1	1	1	1	1	1	1	1

Table 3.2. represents the equilibrium x-y (mole fractions of ethanol) values for NRTL, UNIFAC, UNIQUAC and Wilson thermodynamic models in Aspen Plus Simulation. It was observed that NRTL model values were almost nearer to the experimental finding values when compared with that values obtained from other models

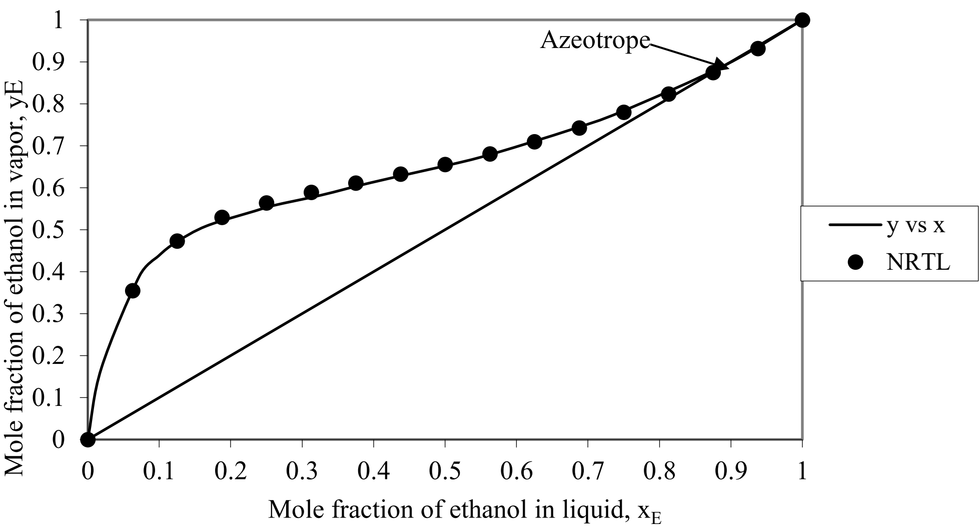

Fig. 3.1. Experimental and NRTL Model

The above graph 3.1. Shows the comparison between experimental x-y values with predicted values from the NRTL model and RMSD values for vapor mole fraction of ethanol and temperatures at a given x values were evaluated as 0.0106, 0.0201 respectively.

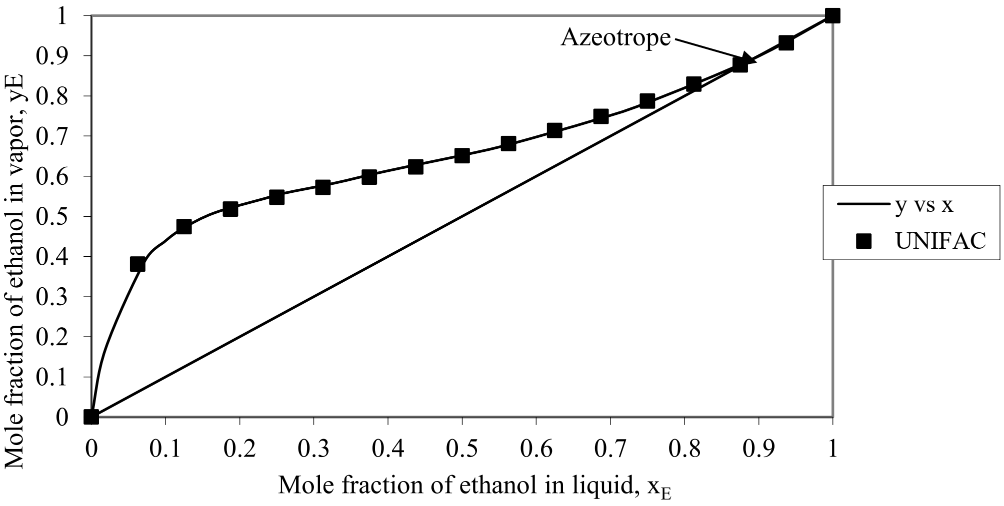

Fig. 3.2. Experimental and UNIFAC Model

The above graph 3.2 shows the comparison between experimental x-y values with the predicted values from the UNIFAC model and RMD values for vapor mole fraction of ethanol and temperatures at given x values were evaluated as 0.226 and 0.256 respectively.

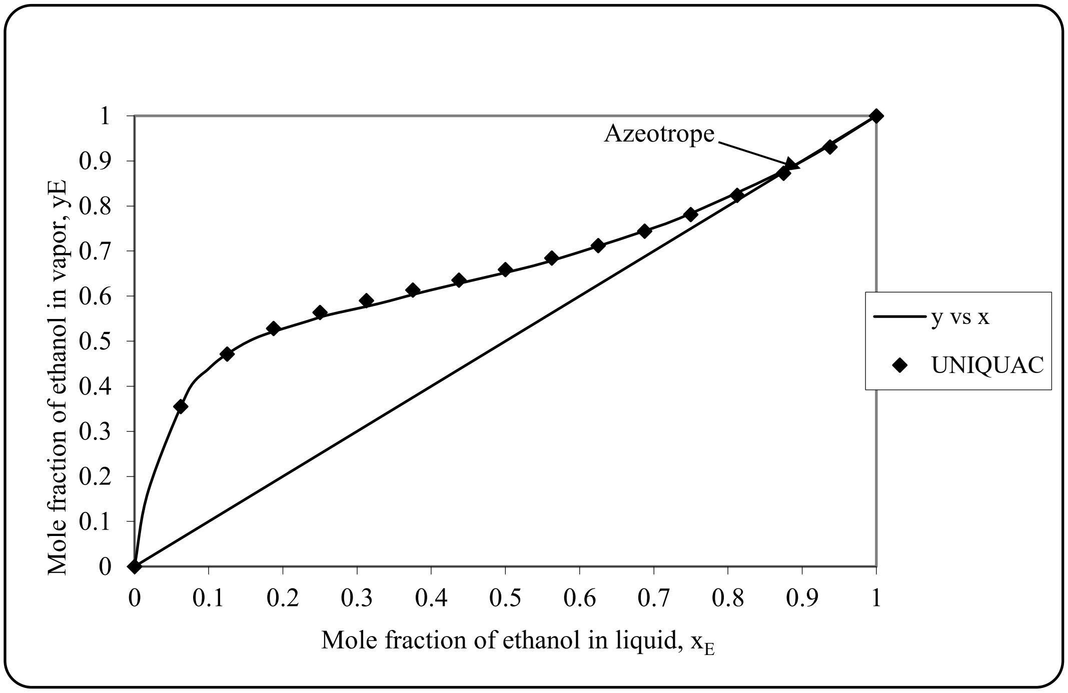

Fig. 3.3. Experimental and UNIQUAC Model

The graph 3.3 shows the comparison between experimental x-y values with the predicted values from the UNIQUAC model and RMD values for vapor mole fraction of ethanol and temperatures at given x values were evaluated as 0.181 and 0.09 respectively.

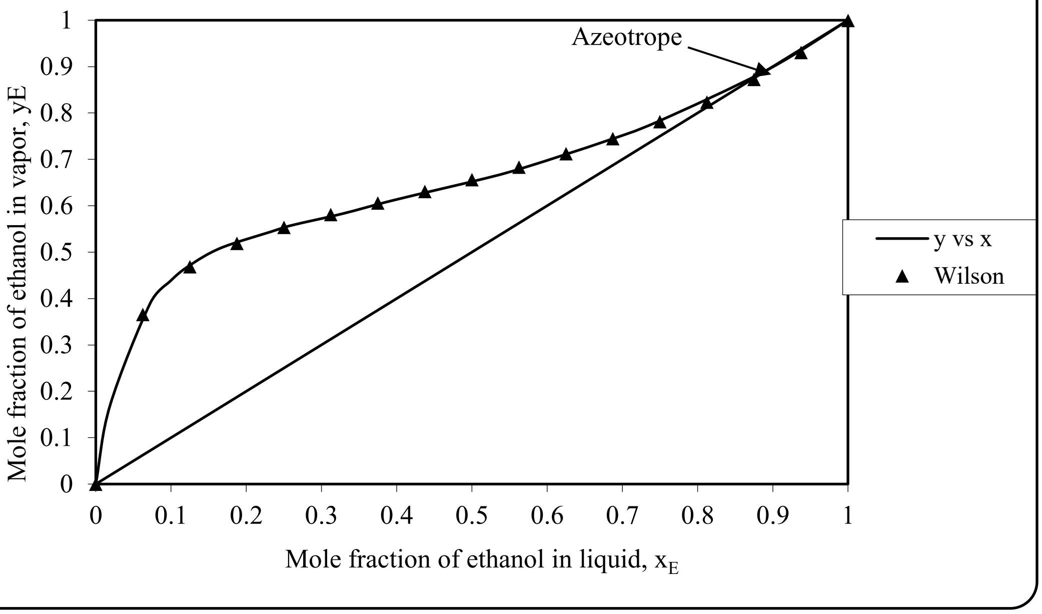

Fig.3.4. Experimental and Wilson Model

The graph 3.3 shows the comparison between experimental x-y values with the predicted values from the Wilson model and RMD values for vapor mole fraction of ethanol and temperatures at given x values were evaluated as 0.0201 and 0.0034 respectively.

Table 3.3: RMSD values for different thermodynamic models using VLE data at 1 atm

Model	RMSD (y)	RMSD (T)
NRTL	0.0106	0.0021
UNIFAC	0.0226	0.256
UNIQUAC	0.0181	0.090
Wilson	0.0201	0.0034

The above table 3.3 shows the RMSD values for predicted models. Among the models evaluated, the **NRTL model** showed the lowest RMSD values as 0.0106 and 0.0021 for both vapor-phase composition and temperature respectively, indicating the best agreement with experimental data.

The NRTL model closely matches with the experimental data over the entire range. UNIQUAC also fit the experimental data in the lower mid composition range. Wilson model slightly deviates at lower concentrations of ethanol. Therefore, the **NRTL thermodynamic model** is recommended for further simulation of the ethanol–water separation process.

4. CONCLUSIONS

According to the simulation results, it was concluded that an azeotrope is formed in the ethanol–water binary mixture at an ethanol mole fraction of 0.8952 and a temperature of 78.15 °C. The ethanol–water system exhibits a significant positive deviation from ideality. Various thermodynamic models were applied to predict the vapor–liquid equilibrium (VLE) of the ethanol–water mixture. The NRTL, UNIFAC, UNIQUAC, and Wilson activity coefficient models were compared with experimental data. Among the models, the NRTL model showed the best agreement, with RMSD(y) = 0.0106 and RMSD(T) = 0.002. Therefore, it was concluded that the NRTL thermodynamic model is the most suitable for further simulation work. The UNIQUAC and Wilson models also produced reasonably accurate results.

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