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Vapor-Liquid Equilibrium Modeling and Parameter Estimation for Ethanol-Water System with TRIS as Mass Separating Agent

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Abstract: The distillation of ethanol-water mixture is one of the most important operations, which is usually being improved by the addition of mass separating agents (MSA). An example of MSA is tris(hydroxy)aminomethane (TRIS), which has been shown to improve the separation of the ethanol-water mixture. The study of the potential of TRIS as MSA requires the understanding of the vapor-liquid equilibrium (VLE) of the mixture through the use of thermodynamic models. One of the most common thermodynamic models is the UNIFAC Dortmund model, which can predict the VLE of a given mixture by calculating the activity coefficients using the binary interaction parameters. Although several binary interaction parameters are already available for the model for the prediction of VLE of several mixtures, there are parameters that are still not available for some important mixtures. An example of which is the unknown c parameters for the interaction of hydroxyl and amino groups which can be applied for the prediction of the VLE of ethanol (1) + water (2) + TRIS (3) system. Hence, this study involves the estimation of these unknown parameters using the UNIFAC Dortmund model. The parameter estimation process involves the calculation of the activity coefficients using the model, where the initial guesses for the parameters were randomized and iterated until the objective function is minimized. The binary interaction parameters were finally obtained as $c_{12} = 0.06382$ and $c_{21} = 0.06366$ for the CH_2NH_2 (1) and OH (2) interactions. The parameters when applied to the ternary systems containing the hydroxyl-amino interactions calculated the VLE that is consistent with the experimental VLE, with MSE values of 0.08 and 0.0009 and adjusted r^2 values of 0.9963 and 0.9759 for the bubble point and vapor composition data, respectively. The extent of the applicability of the new parameters can be investigated further for other systems containing hydroxyl-amino interactions.

Key Words: Vapor-liquid equilibrium; Modified Raoult's law; UNIFAC Dortmund model; binary interaction parameters; mass separating agent



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1. INTRODUCTION

The dehydration of ethanol through distillation is one of the most common unit operations, producing high purity ethanol that can be used as a disinfectant, as a fuel additive for gasoline and for the production of alcoholic beverages. Due to the presence of azeotropic point in ethanol-water mixture which prevents its further separation, various literatures are investigating different potential mass separating agents (MSA) that can increase the relative volatility of ethanol over water (Ojeda Toro et al., 2017; Pla-Franco et al., 2013; Zhang et al., 2016; Dong et al., 2018; Li et al., 2021; Liu et al., 2021; Peng et al., 2017; Shang et al., 2019; Zhang et al., 2016). The MSA should have high affinity with water in order to separate the ethanol easily by vaporization, where the factors such as cost, availability, environmental impacts and toxicity of the substance are also considered. An example of a potential MSA for ethanol-water mixture is tris(hydroxy)aminomethane, or TRIS, which has previously been shown to be effective in the separation of the mixture because it is capable of shifting the ethanol-water azeotropic point from 97.5% to 99.95% (Bungay et al., 2011). Its effectiveness can be attributed to its hydroxyl and amino groups, allowing it to form strong bonds with water through hydrogen bonding and thereby effectively separating the ethanol from the mixture.

In order to understand the potential of a given component as MSA and to design distillation columns for the separation in a large scale, the vapor-liquid equilibrium (VLE) of the required mixture should be determined. Experimental determination of VLE is shown to be costly and tedious, hence thermodynamic modelling is performed as an alternative. One of the commonly used thermodynamic models is the UNIFAC Dortmund model due of its capability of predicting the VLE with the least possible error for a very wide range of mixtures (Weidlich and Gmehling, 1987). It is because the model uses the group contribution concept which looks at the structural groups of the components. The sum of the contributions of all the structural groups is assumed to give rise to the thermodynamic properties of the mixture (Fredenslund, 2012).

Each interaction of groups is defined by set of constants called the binary interaction parameters. Since it is assumed that the structural groups are the same regardless of the mixture to which they are present, the binary interaction parameters are also

universal, thereby allowing the prediction of VLE of a wide range of mixtures. Currently, there are thousands of available parameters for the UNIFAC Dortmund model which can be found in the Dortmund Data Bank (The UNIFAC Consortium, 2023).

Although several parameters are already present in the DDB, more parameters are still needed for the prediction of VLE of other important mixtures. An example of which are the unknown hydroxyl-amino c parameters for the system ethanol (1) + water (2) + TRIS (3) which can potentially provide a good prediction for the VLE of the system. Hence, the study focused on the estimation of the unknown c parameters for this system which will allow the prediction of its thermodynamic properties at VLE.

2. METHODOLOGY

2.1 Thermodynamic Models

The VLE of a given mixture at 1 atm can be described using the Modified Raoult's Law given by:

$$y_i P = \gamma_i x_i P_i^{sat} \quad (\text{Eq. 1})$$

where:

- x_i, y_i = mole fraction of component i in the liquid and vapor phase, respectively
- γ_i = activity coefficient of component i
- P_i^{sat} = vapor pressure of component i
- P = total pressure

The activity coefficient can be calculated using various thermodynamic models. The group contribution models are the widely-used set of models which assume that the components are composed of structural groups. In these models, the activity coefficient of a given component i can be calculated using the combinatorial term, accounting for the size and geometry of the components, and the residual term, considering the energies involved in the interaction of the components:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (\text{Eq. 2})$$

where:

- $\ln \gamma_i^C$ = combinatorial term
- $\ln \gamma_i^R$ = residual term

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The most comprehensive among the group contribution models is the UNIFAC Dortmund model, which contains temperature-dependent parameters that can be expressed in terms of the temperature T and the binary interaction parameters of all pairs of structural groups as shown:

$$\tau_{mk} = \exp\left(-\frac{a_{mk} + b_{mk}T + c_{mk}T^2}{T}\right) \quad (\text{Eq. 3})$$

where:

τ_{mk} = temperature-dependent parameter for interacting groups m and k

a_{mk}, b_{mk}, c_{mk} = binary interaction parameters

The parameters allow the calculation of the thermodynamic properties of a given mixture at VLE.

2.2 Parameter Estimation

The parameter estimation method involves the calculation of properties using thermodynamic models and the iteration process for the minimization of objective function (OF). The experimental data for ethanol (1) + water (2) + TRIS (3) ternary system for the parameter estimation were obtained from Bungay et al. (2011) at the condition $P = 101.3$ kPa.

As shown in Fig. 1, the experimental data x_i , the existing a , b and c parameters, and the surface area R_k and volume parameters Q_k of the structural groups in Tables 1 and 2 were used in the optimization program prepared in MATLAB® 2014a. In the program, the equations for the modified Raoult's law as well as the UNIFAC Dortmund model to be used in the iteration process were defined.

Table 1. Surface Area (R_k) and Volume (Q_k) Parameters of the Structural Groups in Ethanol (1) + Water (2) + TRIS (3) System

Main Group	Subgroup	R_k	Q_k
CH ₂	CH ₃	0.6325	1.0608
	CH ₂	0.6325	0.7081
OH	OH, primary	1.2302	0.8927
H ₂ O	H ₂ O	1.7334	2.4561
CH ₂ NH ₂	CNH ₂	1.6607	0.9850

Table 2. Binary Interaction Parameters of Group Pairs in Ethanol (1) + Water (2) + TRIS (3) System

Group 1	Group 2	a_{12}, a_{21}	b_{12}, b_{21}	c_{12}, c_{21}
CH ₂	OH	2,777	-4.674	0.001551
		1,606	-4.746	0.000918
	H ₂ O	1,391.3	-3.6156	0.001144
CH ₂ NH ₂		-17.253	0.8389	0.000902
		6,731.4	4.9683	-0.01025
OH		326.04	-2.6348	0.00336
	H ₂ O	-801.9	3.824	-0.00751
		1,460	-8.673	0.01641
CH ₂ NH ₂		4,286.2	2.468	*to be
		-75.63	-0.1511	estimated
H ₂ O	CH ₂ NH ₂	5.3069	-5.869	0.01032
		-980.6	3.671	-0.00591

Initial guesses were supplied in the program for the bubble points and c parameters for the hydroxyl-amino group interactions, which are the unknown values. The initial guesses were used for the calculation of activity coefficients and vapor mole fraction values. The values were iterated using the command *fmincon* to satisfy the equation $\sum y = 1$ and to minimize the following objective function:

$$OF = \sum_{j=1}^n \sum_{i=1}^2 \left(\frac{y_{ij}^{exp} - y_{ij}^{cal}}{y_{ij}^{exp}} \right)^2 \quad (\text{Eq. 4})$$

where:

y_{ij}^{exp} = experimental vapor mole fraction

y_{ij}^{cal} = calculated vapor mole fraction (model)

n = number of data points

When the equations and OF are satisfied, the final values for the parameters are accepted as the new UNIFAC Dortmund c parameters for the hydroxyl-amino group interactions. The entire procedure was repeated for thousands of initial guesses by randomization (Jain, Attarde & Gupta, 2017). Finally, the new parameters were applied in the calculation of VLE of ethanol (1) + water (2) + TRIS (3) ternary system, which were compared to the experimental VLE of Bungay et al. (2011).



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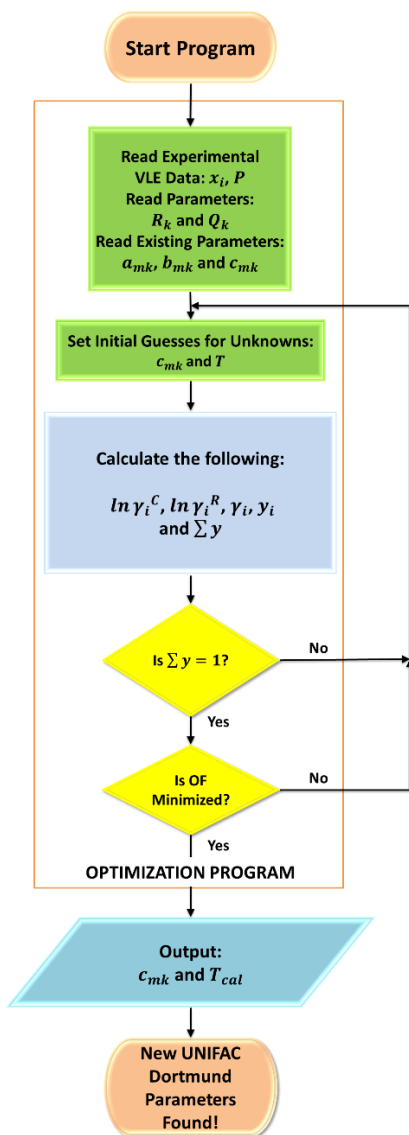


Fig. 1. Parameter Estimation Using the UNIFAC-Dortmund Model

3. RESULTS AND DISCUSSION

The new UNIFAC Dortmund binary interaction parameters c for the amino and hydroxyl groups were calculated as shown in Table 2.

Table 2. Calculated UNIFAC Dortmund c Parameters for the Hydroxyl-amino Interaction

Main Group 1	Main Group 2	Binary Interaction Parameters	
		c_{12}	c_{21}
CH_2NH_2	OH	0.06382	0.06366

Table 3. Experimental and Calculated VLE for Ethanol (1) + Water (2) + TRIS (3) System

Bubble Point (T , K)			
Expt.	Calc.	Expt.	Calc.
365.15	366.04	365.15	365.97
360.15	361.02	359.15	360.07
358.65	359.12	356.15	356.79
356.15	356.09	355.15	355.38
354.65	354.48	354.15	354.01
353.65	353.53	353.15	353.26
352.15	352.27	352.65	352.89
352.15	351.93	352.15	352.07
351.65	351.48	351.65	351.86
365.15	365.87	364.65	365.64
359.15	359.92	359.15	360.25
356.65	356.53	356.15	357.01
354.65	354.53	354.15	354.43
353.65	353.51	353.65	353.31
352.15	352.37	352.65	352.35
351.65	351.71	352.65	351.94
351.65	351.58	351.65	351.84
351.65	351.56	351.65	351.82

Ethanol Vapor Mole Fraction (y_1)			
Expt.	Calc.	Expt.	Calc.
0.217	0.251	0.246	0.256
0.378	0.402	0.478	0.431
0.463	0.455	0.577	0.524
0.569	0.541	0.633	0.567
0.604	0.594	0.678	0.619
0.643	0.633	0.719	0.657
0.705	0.714	0.749	0.680
0.734	0.751	0.823	0.761
0.862	0.848	0.862	0.799
0.222	0.258	0.291	0.268
0.463	0.434	0.493	0.427
0.569	0.530	0.604	0.519
0.643	0.595	0.678	0.605
0.691	0.638	0.764	0.659
0.749	0.714	0.837	0.739
0.837	0.808	0.886	0.810
0.886	0.860	0.923	0.852
0.910	0.890	0.936	0.872



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The parameters provided the least possible error in the modeling of the VLE of the ternary system ethanol (1) + water (2) + TRIS (3) using the UNIFAC Dortmund model. This can be shown from the comparison of the calculated bubble points and vapor composition values to the experimental values of Bungay et al. (2011) as shown in Table 3, where a good agreement with the experimental values can be observed. Hence, the new parameters can be used for the prediction of the VLE of the ternary system at different conditions.

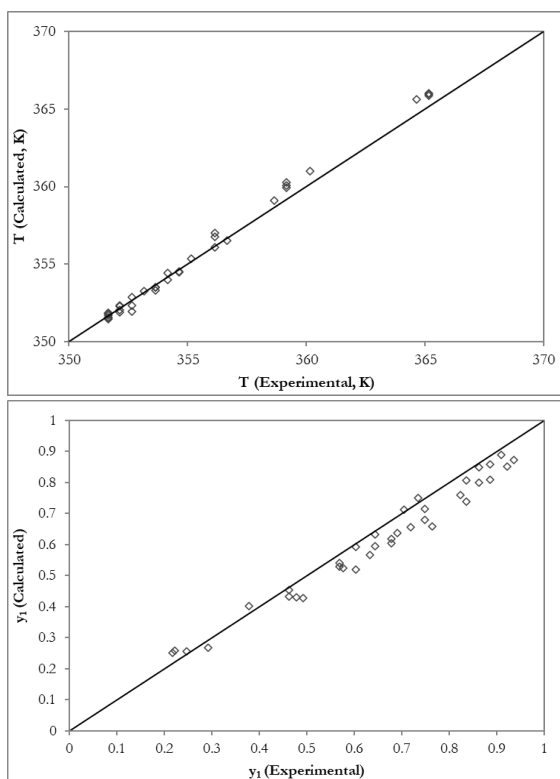


Fig. 2. Comparison of the Experimental and Calculated Data of Ethanol (1) + Water (2) + TRIS (3) System

The quality of the predictions using the new parameters can be shown further by plotting the calculated values against the experimental values for the bubble point and vapor composition of the ternary system in Fig. 2. The proximity of the points along the diagonal indicates the good agreement of both the

calculated and the experimental values. The corresponding metrics for this agreement were calculated in Table 4. The low values for the sum of squared errors (SSE) and mean squared errors (MSE) as well as the r^2 values that are close to 1 show how the calculated values are slightly different from the experimental values. Hence, the new parameters are reliable in the prediction of the VLE of the ternary system. The applicability of the new parameters may be determined further by applying them to other systems containing hydroxyl-amino interactions.

Table 4. Calculated Errors and Coefficients of Variation from the VLE Modeling Using the UNIFAC-Dortmund Model

Metrics	Values for T	Values for y_1
SSE	2.68	0.0290
MSE	0.08	0.0009
r^2	0.9963	0.9759
r^2 , adjusted	0.9962	0.9752

4. CONCLUSIONS

The study was able to estimate for the first time the c parameters for the CH_2NH_2 (1) and OH (2) interactions using the UNIFAC-Dortmund model, which were found to be $c_{12} = 0.06382$ and $c_{21} = 0.06366$. These parameters for hydroxyl-amino group interactions were found to be important for the prediction of the VLE of the system ethanol + water + TRIS at 101.3 kPa. The calculated bubble points and vapor composition data of the ternary system using the new parameters were found to be close to the experimental data from the literature, with MSE values of 0.08 and 0.0009 and adjusted r^2 values of 0.9963 and 0.9759 for the bubble point and vapor composition data, respectively. Future studies can further investigate the applicability of the new parameters to other systems containing the interactions of amino and hydroxyl groups.

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