ABSTRACT

Distillation is one of the most important separation processes, where one of its common application is the separation of alcohol-water mixtures through the addition of mass separating agents (MSAs), especially in the biodiesel industry. To design a distillation column for this process, the vapor-liquid equilibrium (VLE) of a given mixture is important, which can be calculated by modelling using the group contribution models. The application of these models does not require experimental data, thereby freeing the industries from experimentations that consumes too much resources. The most comprehensive group contribution model existing so far is the UNIFAC Dortmund model, which can accurately predict the VLE of a wide range of systems. Although the model can certainly provide good prediction results at VLE, some problems are encountered such as the existing UNIFAC Dortmund parameters that are causing high errors when applied for the prediction of VLE, and the absence of parameters for certain interactions. Therefore, this study was conducted which aimed at the VLE modelling of 19 different systems with and without MSAs using the UNIFAC Dortmund model, where the estimation of the new parameters for the CNH_2-OH interaction and the revision of the existing binary interaction parameters involving NaCl and KCl and were performed. To determine the parameters, optimization programs were created using MATLAB, where the calculated parameters were applied in the prediction of VLE of the systems considered. The resulting VLE were compared to the experimental VLE of the systems found in the literatures. Results showed that the new parameters for the CNH_2-OH interaction provided good prediction results for the ethanol, water and TRIS system. Furthermore, the revised parameters for NaCl and KCl predicted the VLE of systems with salt that are in good agreement with the experimental VLE of these systems, showing that they are more reliable for prediction than the existing parameters from the literature. Poor prediction results are obtained for quaternary mixtures with high percentage of water and salt, and aqueous systems with high percentage of glycerol or ethylene glycol. In these systems, it was found out that the UNIFAC Dortmund model does not consider the proximity effects such as the effect of the OH groups of glycerol with each other and the effect of the alkyl chain towards a given OH group within an alcohol molecule.

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LIST OF ACRONYMS AND SYMBOLS

Acronym	Meaning
VLE	Vapor-Liquid Equilibrium
UNIFAC Dortmund	UNIQUAC Functional-group Activity Coefficients (Dortmund)
MSA	Mass Separating Agent
SQP	Sequential Quadratic Programming
SE	Standard Error (Regression)
RMSE	Root Mean Square Error
AAD	Average Absolute Deviation
%AARD	Percent Average Absolute Relative Deviation
MSE	Mean Squared Error
SSE	Sum of Squared Errors

Variable	Meaning
T	Temperature
P	Pressure
x	Liquid mole fraction
x'	Liquid mole fraction in solute-free basis
y	Vapor mole fraction
γ	Activity coefficient
w	Mass (in g) of salt per 100 g solvent
a_{mk}, b_{mk}, c_{mk}	Binary interaction parameters
r^2	Coefficient of determination

Subscript	Meaning
i/j	Component
s	Salt
m/k	Subgroup