A-UNIFAC Modelling of Binary and Multicomponent Phase Equilibria of Fatty Esters+Water+Methanol+Glycerol

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The production of methyl and ethyl esters of fatty acids is of great industrial interest, considering the direct application of these esters as biodiesel. For biodiesel purification and by-products recovery processes design and optimization, the prediction of the phase behaviour of mixtures containing fatty esters, alcohols, glycerol and water is of utmost importance. In this work we show the capability of a A-UNIFAC to correlate and predict phase behaviour of these mixtures. This G^E model is an extension of UNIFAC that explicitly includes association effects between groups based on the statistical Wertheim theory [1].

For the water-esters binary systems, the residual and association parameters have been previously estimated using low pressure VLE data [1]. The use of these parameters to predict liquid-liquid equilibrium results in good agreement with experimental information on binaries of water with acetic, octanoic or dodecanoic acids methyl esters.

The association effect in methanol and glycerol are represented with the same hydrogen-bonding hydroxyl groups (OH) with two associating sites, one group in methanol and three in glycerol. For the residual contribution, both molecules are considered as molecular groups (CH_3OH and $C_3H_8O_3$). The residual interaction parameters between CH_3OH and $C_3H_8O_3$ were obtained by fitting isothermal liquid-liquid equilibrium data on the ternary system dodecanoic acid methyl ester-methanol–glycerol [2]. The glycerol/paraffin ($C_3H_8O_3/CH_2$) and glycerol/ester ($C_3H_8O_3$/CCOO) interaction parameters were estimated by fitting experimental data on liquid-liquid equilibrium and infinite dilution activity coefficients of the binary systems dodecanoic acid methyl ester-glycerol and hexanoic acid methyl ester-glycerol between 320-438 K [2].

A-UNIFAC with the final set of parameters is able to predict with good agreement experimental data on binary and ternary liquid-liquid equilibria of glycerol + methanol + fatty esters as well as infinite dilution activity coefficient for this system.

References

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