ABSTRACT

In this work, experimentally determined Vapour-Liquid Equilibrium (VLE) data of binary and multi-component systems has been reported. The systems chosen for study are components of important industrial streams from bio-diesel industry, acetic acid esterification process and eco-friendly gasoline-additives manufacturing industry. Experimental studies have been carried out at sub-atmospheric and local atmospheric pressures. Experimental data for the systems reported in this work were found to be scarce or unavailable at the conditions studied, in an extensive literature survey. Data reported in this work fills gaps in existing data. VLE data of binary systems, Methanol + Water, Methanol + Glycerol and Water + Glycerol measured experimentally under vacuum and local atmospheric conditions reported in this work and published in the *Journal of Chemical Thermodynamics*, volume *42 (2010)* pgs. *621-624*, has been included in the latest update of ASPEN database.

In this study, a modified Sweitoslawski ebulliometer was used for experimental determination of VLE data. A Sweitoslawski ebulliomter is a dynamic recirculation still with circulation of both the vapour and liquid phases. Pure component vapour pressures of Methanol and Isopropyl alcohol (IPA) were studied. Experimental VLE data over the entire concentration range has been studied for the following binary mixtures: Methanol + Water, Water + Glycerol, Methanol + Glycerol, mixtures of diisopropyl ether (DIPE) with Methanol and IPA, Methanol + IPA, IPA+ Glycerol, IPA + Water, Methanol+ Methyl acetate, at sub-atmospheric and local atmospheric pressures. Ternary mixtures, Methanol + Water + Glycerol and Methanol + DIPE + IPA and quaternary mixtures of Methanol + IPA + Water + Glycerol were studied.

Experimental VLE data of three binary systems, Methanol + Water, Water + Glycerol and Methanol + Glycerol at different pressures was correlated with Wilson model. This data was also fitted to the Legendre First Order polynomial. Wilson model represented the VLE behaviour of these three binary well. Methyl acetate + Methanol data at three sub-atmospheric and local atmospheric pressure was correlated with Wilson, NRTL, UNIQUAC activity coefficient models, Peng-Robinson (PR) and Peng-Robinson-Stryjek-Vera (PRSV) EoS in combination with Wong-Sandler (WS) mixing rules. This data was also compared with predictions from UNIFAC model. Among the six different thermodynamic models applied,

NRTL gave the best fit to VLE data of Methyl acetate + Methanol system at 44.66, 55.73, 66.66 and 96.3 kPa. This binary system exhibits an azeotrope. Azeotropic conditions calculated from NRTL model at 96.3 kPa are in agreement with literature data available at 101.3 kPa. Azeotropic point shifts to the left w.r.to x_1 as pressure increases i.e. azeotrope is formed at lower concentrations of Methyl acetate as pressure increases.

Experimental data of Diisopropyl ether (DIPE) + IPA, Methanol + DIPE, systems at four pressures, 53.33, 66.66, 79.99 and 94.79 kPa, was correlated with Legendre First order polynomial, Wilson, NRTL, UNIQUAC models, PR + WS and Soave-Redlich-Kwong (SRK) + WS EoS, UNIFAC group-contribution models. NRTL model gave the best fit to these two systems from among the different models used. Both the systems containing DIPE exhibit minimum-boiling azeotropes. Azeotropic compositions and temperatures of these two systems calculated from NRTL model have been listed in a table along with azeotropic data from literature. VLE data of Methanol + IPA and IPA + Glycerol measured at sub-atmospheric (53.33, 66.66, 79.99 kPa) and local atmospheric pressures (94.79 and 94.93 kPa respectively) has been correlated with Wilson, NRTL, UNIQUAC, UNIFAC, SRK +WS and PR +WS. Wilson and NRTL models represented Methanol + IPA system well at all pressures with NRTL giving a slightly better fit. Wilson model gave the best fit to IPA + Glycerol binary system. IPA + Water binary data at 94.66 kPa was correlated with Wilson and NRTL models with Wilson model performing better than NRTL. Performance of Wilson model parameters of IPA + Water at 94.66 kPa in representing literature data has been tabulated.

Prediction of VLE behaviour of Methanol + Water + Glycerol ternary system at 96 kPa, with Wilson and NRTL models was done using only binary interaction parameters of the constituent systems. Wilson activity coefficient model represented the three binary sub-systems as well as this ternary well. Methanol + DIPE + IPA ternary system data at 53.33, 66.66, 79.99 and 95.33 kPa was compared with values calculated from NRTL as this model gave the best fit to the three constituent binary systems. NRTL also represented the ternary system Methanol + DIPE + IPA well. For the quaternary system of Methanol + IPA + Water + Glycerol, performance of Wilson was found to be better than that of NRTL at all the pressures studied in this work. Wilson model gave a good fit to the data of five of the six constituent binary systems and was nearly as good as NRTL for the Methanol + IPA binary mixture. This quaternary system was studied at four pressures, 53.33, 66.66, 79.99 and 95.2 kPa.

Experimental VLE data and analysis of binary and multi-component mixtures presented in this work has been reported in five publications, in the journals, Journal of Chemical Thermodynamics [162], Journal of Chemical and Engineering Data [165] and Fluid Phase Equilibria [164, 165, 167]. The list of publications along with reprints has been given in APPENDIX II.