

Prediction of Vapour-Liquid Equilibria for the Kinetic Study of High Pressure Processes Based on Synthesis Gas.

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The synthesis gas (syngas), a mixture of hydrogen and carbon monoxide, is normally used in the production of a broad range of chemicals and fuels. In many processes gas-liquid reactors (for examples, hydroformylation of olefins, carbonylation of methanol to acetic acid, homologation of alcohols) or gas-liquid-solid reactors (Fisher-Tropsch synthesis, hydrogenation reactions) are employed.

Kinetic studies in gas-liquid and gas-liquid-solid systems are often complicated by the non-ideal behaviour of reagents and/or products that are partitioned between the liquid and the vapour phase. This occurs especially in the case of some of the previously mentioned reactions in which both the solubility of a reagent or a product and the volatility are relatively high. In this case the concentration of the components in the liquid phase can strongly be affected by the amount of the same component in the vapor phase. Besides, as often kinetic data are collected in batch conditions for the liquid phase, activity coefficients of the partitioned components can consistently change during the time as a consequence of changing the composition of the reaction mixture. Therefore, it is necessary, in these cases, to know the vapor-liquid equilibria (VLE) in order to collect and to interpret correctly the kinetic data. The description of phase equilibria, at high pressures, is usually performed by means of an EOS (Equation of State) allowing the calculation of fugacity coefficients, for each component, in both phases determining the partition coefficients. The EOS approach involves the experimental determination of the interaction parameters for all the possible binary system of the mixture. The reaction mixtures in the previously cited reactions are multicomponent mixtures and a complete experimental determination of vapour-liquid equilibria is very hard, mainly taking into account the high pressure and temperatures used. Some group contribution methods (GC-EOS and UNIWAALS) have been developed in the past but the group contribution data are not, at now, sufficiently extended. We suggest the possibility to combine the use of UNIFAC with the RKS-EOS by using the first one to generate equilibrium data in the range of T and P , where UNIFAC gives reliable results (below 10 atm). By interpreting these data sets with RKS-EOS the related interaction parameters for the binaries can easily be determined by regression analysis. These binary interaction parameters can then be extrapolated to higher T and P , allowing, in this way, a predictive description of multicomponent VLE in high pressure. The proposed method has been tested with different binary and ternary systems and has shown performances similar to other predictive methods such GC-EOS and UNIWAALS, but is more simple to be used and can be more widely applied considering the large groups list of UNIFAC.

In this paper we will describe in detail the cited method and we will show, as an example, its application in the kinetic study of methanol homologation .