Phase Equilibria Calculations Using Scilab – An Educational Approach

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Abstract

This paper describes the use of Scilab language in an optimization discipline oriented to computational modeling with engineering applications. In this work, we studied the phase equilibrium problem – particularly, vapor-liquid equilibrium – at high pressures using an optimization approach. Vapor-liquid equilibrium calculations are performed using Soave equation (Soave, G. Equilibrium constants form a modified Redlich-Kwong equation of state, Chem. Eng. Sci. 27, 1197-1203, 1972). for both phases, with classical mixing rules and null binary interaction parameters. First, we modeled the vapor-liquid coexistence problem using the classical isofugacity approach (Smith, J. M., Van Ness, H. C., Abbott, M. M., Introduction to Chemical Engineering Thermodynamics, McGraw-Hill, 5th Edition, 1996). Thus, the resulting nonlinear algebraic system was solved using multivariate Newton-Raphson method and basins of attraction were obtained. Basins of attraction indicate regions of convergence/ non-convergence for a set of initial estimates. In Scilab context, basins of attraction were constructed using MATPLOT command. This nonlinear system can also be expressed as a non-negative objective-function (sum of squares or sum of absolute values), to be minimized with constraints over the molar fractions, since the molar fractions are in the range (0,1). Then, this nonlinear programming problem was solved using Newton, steepest descent, Marquadt and Simulated Annealing algorithms. Convergence aspects of these algorithms were discussed for this kind of problem. Surfaces of objective-functions and contour curves were also presented, indicating the neighborhood of the minimum. Results were obtained for binary, ternary and multicomponent mixtures at several pressures, and include dew and bubble point calculations. Thus, the results include vapor or liquid compositions and dew/bubble point temperatures. All programs were developed using Scilab 5.1.1 language and this thermodynamic phenomenon was used to present optimization concepts and nonlinear algebraic systems for graduate students.

Key words: *equations of state, Soave equation, Optimization, Scilab*