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Project Summary

Vapor/Liquid Equilibria of Constituents from Coal Gasification in Refrigerated Methanol

Te Chang, R. M. Rousseau, and J. K. Ferrell

A thermodynamic framework was established for developing a model of the phase equilibria of mixtures of methanol and the major constituents found in gases produced from coal. Two approaches were used to model the equilibrium behavior: (1) an equation of state was used to describe both gas and liquid phases, and (2) an equation of state was used to describe the gas, while a solution model involving activity coefficients was used to describe the liquid. The approach chosen for each species was based on the component volatility. An experimental apparatus was constructed to obtain data against which the model predictions could be tested. The apparatus was evaluated by comparison of experimental P-T-x data on mixtures of carbon dioxide (CO_2) and methanol with those from the literature. The comparison was favorable. P-T-x-y data on mixtures of CO_2, methanol, and water, and mixtures of CO_2, nitrogen, and methanol at temperatures in a range of −30 to 25°C and pressures up to 54 atm (5472 kP) were obtained. Comparisons of the calculated and measured values of bubble point pressures and/or liquid compositions of the dissolved gases were satisfactory.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The objective of this effort was to develop a thermodynamic framework that could be used to describe the equilibrium behavior of methanol with compounds found in the gas produced from coal. The approach that was taken divided the constituents into three groups: Group I consisted of supercritical components, Group II consisted of compounds that are normally gases at the conditions of interest, and Group III contained compounds that are liquids at the conditions of interest. This division was used to select either an equation of state or an activity coefficient formulation of the equilibrium criteria. Once this selection was made, appropriate parameters in the formulation were evaluated from binary data obtained from the literature and experiments that were part of this study. With the parameters evaluated in this way, it is possible to predict the behavior of systems containing any number of the components from Group I, II, and/or III.

Accomplishments/Results

A vapor/liquid equilibrium (VLE) apparatus was developed along with a sampling technique and analytical method to obtain equilibrium data on systems having high gas solubilities. Good data were obtained from this apparatus for CO_2 solubilities in methanol with and without an inert gas (nitrogen), and in mixtures of methanol and water. However, low solubilities of nitrogen in methanol cannot be measured accurately.

Bubble point pressure variance provided a useful objective function in the parameter search procedure for both equation-of-state and activity coefficient methods. This search procedure, which includes a bubble point pressure calculation, does not require measurement of vapor-phase composition.

Mathias' polar correction factor improved the calculation of vapor pressures with the Soave-Redlich-Kwong (SRK) equation of state for polar compounds of methanol and water, but this factor may not be necessary for ethyl mercaptan and dimethyl sulfide.

Temperature-dependent binary interaction parameters in the extended SRK equation of state have greatly improved the accuracy of correlations of methanol-containing binary VLE systems consisting of constituents from coal gasification. Temperature-independent binary interaction parameters are satisfactory for gas/gas mixtures. These parameters are applicable in a broad range of temperatures.

Phase equilibrium calculations using the extended SRK equation of state were satisfactory for mixtures of methanol/gas systems as long as the gas component had a mole fraction in the liquid less than 0.6. They did not provide satisfactory predictions for those systems at high gas concentrations in the liquid phase. However, absorption-stripping processes that condition synthetic gas mixtures operate at liquid circulation rates that maintain the levels of dissolved gases below those at which the equation of state loses its accuracy.

The extended SRK equation of state tends to predict false liquid/liquid/gas (LLG) three-phase equilibria in methanol/light-hydrocarbon and methanol/acid-gas systems. This is believed to be caused by the quadratic mixing rules for interaction parameters.

The use of the optimized parameter sets enables the equation of state to predict the behavior of a methanol-containing multicomponent system; comparisons between experimental data and bubble point pressure calculations for methanol/H_2/N_2, methanol/CO/N_2, and methanol/CO_2/H_2O mixtures were good.

A simple gas solubility calculation using the extended SRK equation of state was effective in calculating mixed-gas solubilities in a pure solvent and pure-gas solubilities in a mixed solvent.

The activity coefficient models using the four-suffix Margules, Wilson, and UNIQUAC equation are excellent for binary systems that contain condensable components (those from Groups II and III). They are especially useful in describing the vapor/liquid equilibrium behavior of systems containing volatile liquids; e.g., methanol, mercaptans, and sulfides. The determined parameters in these models may be used to describe the multi-component system without further adjustment, but there is no guarantee for describing the behavior of a system containing a supercritical component.

The Wilson and UNIQUAC equations are superior to the four-suffix Margules equation for most of the systems studied. The former two equations have a good built-in temperature-dependent relationship and do not predict false phase separations for methanol/acid-gas and methanol/light-hydrocarbon systems.

Recently developed equations of state—which include density dependent mixing rules based on the two-fluid, local composition theories—should be useful in future applications describing the vapor/liquid equilibrium behavior of systems having components covering a broad range of densities or with polar or hydrogen-bonding components. Coal-produced gas that is conditioned with a physical solvent is an example of such a system.

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