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PC-SAFT Equation of State Applied to Petroleum Reservoir Fluids

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Abstract

The PC-SAFT equation has been proposed as a potential next generation equation of state in the oil industry. It has already obtained widespread use for simulations on polymer systems, which shows that it has a capability of handling phase equilibria for systems with heavy hydrocarbons. A C_7+ characterization procedure for use with the PC-SAFT equation has been developed and used to test how PC-SAFT performs on various types of petroleum reservoir fluids ranging from natural gas mixtures to heavy oils with asphaltenes. Promising results are seen for asphaltene onset pressures and for oil mixtures in general. With the currently published pure component parameters PC-SAFT is inferior to cubic equations of state for simulations on gas and gas condensate mixtures.

Introduction

For more than 50 years cubic equations of state have been a standard for thermodynamic calculations in the oil industry. The cubic equations of state date back to the van der Waals equation¹ from 1873. Several modifications were proposed in the twentieth century. The first cubic equation to obtain widespread use in the oil industry was the Redlich-Kwong equation² from 1949. Today the most commonly applied cubic equations are the Soave (SRK) modification³ of the Redlich-Kwong equation proposed in 1972 and the Peng-Robinson (PR) equation⁴ from 1976. Cubic equations are applicable for both phase equilibrium and density calculations, but generally provide too low liquid densities in their original form. This deficiency was for many practical purposes overcome when Peneloux et al.⁵ in 1982 proposed a volume corrected cubic equation of state providing more accurate liquid densities without influencing phase equilibrium simulation results.

When evaluating the need and potential candidates for a next generation equation of state for use in the oil industry it is obvious to start looking for deficiencies of a volume corrected cubic equation of state. At any particular P and T it is possible

to match the absolute volume by applying a convenient volume correction. To get the correct thermal expansion the volume correction can possibly be made a function of temperature⁶. The volume correction does however not influence the pressure derivative of the volume, which derivative for a liquid is often expressed as compressibility, c_o ,

$$c_o = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (1)$$

Most cubic equations can be represented through the generalized form

$$P = \frac{RT}{V - \delta_1} - \frac{a(T)}{(V - \delta_2)(V + \delta_3)} \quad (2)$$

where P is pressure, R Gas Constant, V molar volume, T absolute temperature, and δ_1 , δ_2 and δ_3 equation of state parameters. For P approaching infinity the molar volume will approach δ_1 (b-parameter for SRK and PR) and the compressibility factor will reduce to

$$Z = \frac{P\delta_1}{RT} \quad (3)$$

which for a constant T expresses a linear increase in compressibility factor with increasing P and a pressure derivative of $\frac{\delta_1}{RT}$. Oil compressibilities at high pressure can be difficult

to match with a cubic equation of state, which shows that Equation (3) may be inappropriate for representing how the compressibility factor varies with pressure at high P.

A correct representation of the volumetric behavior at high pressure is a precondition for accurate predictions of asphaltene onset pressures at reservoir conditions. Asphaltene precipitation takes place because it is thermodynamically favorable for the reservoir fluid to split out an asphaltene phase. If the oil field is produced by natural depletion, the reservoir pressure will decrease with time and asphaltene precipitation may be seen after some time of production. When the Gibbs Free Energy (G) of the split system is lower than of single-phase oil, it is thermodynamically favorable to split out an asphaltene phase. The change in Gibbs Free Energy with changes in P and T can be expressed as

$$dG = V dP - S dT \quad (4)$$

where V is molar volume and S is entropy. The last term in Equation (4) will be zero for T constant and the equation says