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Application of the CPA Equation of State to Reservoir Fluids in Presence of Water and Polar Chemicals

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Abstract

The complex phase equilibrium between reservoir fluids and associating compounds like water, methanol and glycols has become more and more important as the increasing global energy demand pushes the oil industry to target reservoirs with extreme or complicated conditions, such as deep or offshore reservoirs. Conventional equations of state (EoS) with classical mixing rules can not satisfactorily predict or even correlate the phase equilibrium of those systems. A promising model for such systems is the Cubic-Plus-Association (CPA) EoS which has been successfully applied to well-defined systems containing associating compounds. In this work, CPA is extended to reservoir fluids in presence of water and polar chemicals by using a newly developed characterization procedure for ill-defined C_{7+} fractions. Satisfactory results are obtained for multicomponent systems using a minimum number of adjustable parameters which are obtained from binary systems. Modeling of mutual solubility between light hydrocarbons and water is also addressed.

1. Introduction

Cubic equations of state (EoS) are the most widely used thermodynamic models for phase equilibrium calculation and physical property estimation in petroleum engineering. The two most famous ones are the Soave-Redlich-Kwong EoS (Soave, 1972) and the Peng-Robinson EoS (Peng and Robinson, 1976), both proposed in 1970s but still prevailing in routine applications.

These cubic equations were developed originally for hydrocarbon mixtures. However, as more and more oil and gas production aims at deep or offshore reservoirs, one has to deal with systems containing other complex compounds. One such example is water, which usually coexists with reservoir fluids but is hard to model by cubic EoS due to its polar and associating nature. Although it can be argued that water is just an inert phase, which is true at low temperatures and pressures, its mutual solubility with reservoir fluids at high pressure/high temperature (HP/HT) conditions can be appreciable. Other associating compounds can also be added to reservoir fluids. A typical scenario for offshore development is the addition of methanol or glycols into unprocessed well stream as gas hydrate inhibitors, which results in a complex system of hydrocarbons, water and methanol/glycols, hard to describe using the conventional cubic EoS.

To describe the above complex systems containing associating compounds, empirical/semi-empirical modifications of cubic EoS or more rigorous EoS models explicitly accounting for association are needed. Among the first category is the introduction of unconventional mixing rules. For hydrocarbon-water systems, composition dependent interaction parameters can be used to describe the mutual solubility between the hydrocarbon phase and the aqueous phase (Zuo et al., 1996). But Michelsen and Kistenmacher (1990) have pointed out the thermodynamic inconsistency in this method. Complex local composition based mixing rules (Huron and Vidal, 1979; Michelsen, 1990; Wong and Sandler, 1992) can also be combined with a cubic EoS to describe systems containing polar compounds and asymmetric systems. However, those mixing rules are semi-empirical and their prediction ability for multicomponent systems is sometimes questioned. Among the second category are various association EoS, such as the statistical associating fluid theory (SAFT) EoS (Huang and Radosz, 1990) and its variants (McCabe et al., 1999; Gross and Sadowski, 2002), which employ the Wertheim association term (Chapman et al., 1990), and the EoS based on the chemical approach (Anderko, 1991; Pires et al., 2001). The Cubic-Plus-Association (CPA) EoS developed by Kontogeorgis et al. (1996, 1999), which combines the conventional SRK term with the same Wertheim association term as in the SAFT-family EoS, also belongs to this category. The CPA EoS gives a better and more physical description of systems containing associating compounds compared with the empirical or semi-empirical modifications of cubic EoS, and it can be easily reduced to the SRK EoS for non-associating compounds. Previous studies have provided extensive tests of CPA for well-defined systems containing associating compounds, most of which have already been summarized in a recent review by Kontogeorgis et al. (2006a