

MODELING OF ASPHALTENE PHASE BEHAVIOR WITH THE SAFT  
EQUATION OF STATE

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ABSTRACT

The SAFT equation of state was used to model asphaltene phase behavior in a model live oil and a recombined oil under reservoir conditions. The equation of state parameters for the asphaltenes were fit to precipitation data from oil titrations with n-alkanes at ambient conditions. The SAFT model was then used to predict the asphaltene stability boundaries in the live oils. A lumping scheme that divides the recombined oil into six pseudo-components based on composition, saturates-aromatics-resins-asphaltenes fractionation, and gas-oil-ratio data was introduced. Using this lumping scheme, SAFT predicted stock-tank oil and recombined oil densities that are in excellent agreement with experiment data. For both the model and the recombined oil systems, SAFT predicted asphaltene instability and bubble points agree well with experimental measurements.

## INTRODUCTION

In modern operations, asphaltenes are defined as the heaviest components of carbonaceous sources that are insoluble in paraffins such as n-pentane or n-heptane and soluble in an excess amount of aromatics such as benzene or toluene. It is a collection of polydisperse molecules consisting mostly of polynuclear aromatics with varying proportions of aliphatic and alicyclic moieties and small amounts of heteroatoms (i.e. oxygen, nitrogen, sulfur, and vanadium). As a solubility class, asphaltenes has a solubility parameter ( $\delta$ ) between 19 and 24 MPa<sup>0.5</sup> and a density between 1.13 and 1.20 g/mL at room conditions. (Hirschberg, *et al.*, 1984; Speight and Plancher, 1991; Wiehe, 1996; Wang, 2000)

An understanding of asphaltene phase behavior is important in petroleum production and refining because of its potential to phase separate and aggregate with changes in crude oil temperature, pressure, and composition. These asphaltene aggregates may in turn plug tubulars. As the industry moves towards deeper reservoirs and relies more on integrated production systems, the probability of encountering asphaltene precipitation problems and the costs associated with their remediation will only increase. Hence the development of an equation of state that can accurately model as well as predict asphaltene phase behavior in the reservoirs is greatly desirable.

Thermodynamic models of asphaltene phase behavior in crude oil generally fall under one of two molecular thermodynamic frameworks, mirroring the two prevalent schools of thoughts regarding how asphaltenes are stabilized in crude oil. The first approach assumes that asphaltenes are solvated in crude oil and that these asphaltenes will precipitate if the oil solubility drops below a certain threshold. The Flory-Huggins-regular-solution based models and the equation of state based models are some examples of this approach. (Akbarzadeh, *et al.*, 2002; Cimino, *et al.*, 1995; Nghiem, *et al.*, 1993; Hirschberg, *et al.*, 1984; Wang, 2000) Thermodynamic models in the second category take a colloidal approach to describe asphaltene behavior and the presence of resins becomes critical in providing asphaltene stabilization. The solid-asphaltene colloidal model proposed by Leontaritis and Mansoori (1987), the reversible micellization model proposed by Victorov and Firoozabadi (1996), and the McMillan-Mayer-SAFT based theory proposed by Wu (1998) are some examples in this category.

In this work, the Statistical Associating Fluid Theory (SAFT) equation of state (EoS) was used to model asphaltene phase behavior in a model live oil (mixture of n-C<sub>7</sub> insoluble asphaltenes, toluene, and methane) and a recombined oil (stock tank oil with its separator gas) under reservoir conditions. We compared the theory results with asphaltene precipitation data from titration at ambient conditions (precipitation of asphaltenes from the oils using aliphatic solvents) and from reservoir depressurization (precipitation of asphaltenes from live oils with

pressure depletion) as described in Ting, *et al.* (2002). The goal was to first use the ambient condition titration data to characterize the asphaltenes for use in the SAFT EoS; the asphaltene SAFT parameters could then be used to predict asphaltene phase behavior in live oils under reservoir depressurization.

The underlying hypothesis of our approach is that molecular size and non-polar van der Waals interactions dominate asphaltene phase behavior in crude oil. This view is supported by: (1) the large effects on intermolecular interactions due to the polynuclear aromatic cores; (2) by the solubility parameter mapping arguments (Wiehe, 1996); (3) by the contrasting solvating and precipitating abilities of non-polar materials of similar sizes and structures (i.e. toluene vs. n-heptane and CS<sub>2</sub> vs. CO<sub>2</sub>); and (4) by the success of using the precipitating refractive index ( $P_{RI}$ ) to describe the stability of asphaltenes in ambient and reservoir condition oil-precipitant mixtures. (Buckley, 1999; Wang, 2000, Ting, *et al.*, 2002) Within this molecular thermodynamic framework, SAFT is a good candidate for asphaltene phase behavior modeling because it is a complete equation of state easily extendable to reservoir conditions and because it has been used successfully to predict the phase behavior of non-polar fluids where molecular size and shape interactions dominate. The EoS will be described in more detail in the next section.

## THEORY

SAFT is a statistical mechanical equation of state developed from Wertheim's first-order perturbation theory. (Wertheim, 1984, 1986; Chapman, *et al.*, 1990) It is similar to group contribution theories in that the fluid of interest is initially considered to be a mixture of independent segments. The theory predicts the change in free energy both upon bonding these segments to form chains and on the further association of the chain-like molecules. The hard-sphere SAFT we use has its reference fluid contribution from the Mansoori-Carnahan-Starling-Leland hard spheres equation of state (Mansoori, *et al.*, 1971), chain formation contribution from Wertheim theory (Chapman, *et al.*, 1988), and mean field contribution from Gross and Sadowski. (Gross and Sadowski, 2001)

SAFT has been used successfully to predict the phase behavior of fluids where molecular size and shape interactions dominate. For instance, it accurately describes the phase behavior of high molecular weight polystyrenes in hexane, the vapor-liquid equilibria of long-chain short-chain alkane mixtures, and the behavior of phenanthrene in mixtures of decane and methane. SAFT requires three parameters for each pure component: the number of segments per molecule ( $m$ ), the molecular segment diameter ( $\sigma$ ), and the segment energy ( $u^0/k$ ). For associating species two more parameters corresponding to association energy and association volume need to be specified. An important feature of SAFT is that

correlations of pure component parameters with molecular weight can be made for n-alkanes and polynuclear aromatics. Furthermore, species with both aromatic and aliphatic characteristics have EoS parameters in between the aromatic and n-alkane correlations in a systematic manner depending on their degree of aromaticity. In the case of asphaltenes, this feature was used to define the upper and lower bounds of the asphaltene SAFT parameters. In the case of other oil sub-fractions, this was used to identify the EoS parameters for representative pseudo-components.

## RESULTS AND DISCUSSIONS

We considered two oils in this study: a model oil that is a mixture of n-C<sub>7</sub> precipitated asphaltenes in toluene (ratio of 1 g asphaltenes per 100 mL toluene at ambient conditions) and a recombined oil (stock-tank oil with its separator gas). Theory calculations were compared to two sets of experiments performed on each of these oils. In the titration experiments at ambient conditions, n-alkane precipitants were added to the model oil or the stock-tank oil. In the reservoir conditions depressurization experiments, the system pressures of the live model oil or the recombined oil were changed to induce asphaltene instability. Methane was added to the model oil to make up the live model oil. All experimental data used in this work are from Ting, *et al.* (2002). The SAFT parameters used in this

work (excluding asphaltenes and recombined oil pseudo-components) are tabulated in Gross and Sadowski (2001).

### Model Oil Investigations

Since the model oil mixtures were made up of well defined species with n-C<sub>7</sub> insoluble asphaltenes, all SAFT parameters except those for the asphaltenes could be found in the literature. The composition and mixture refractive index at the onset of asphaltene aggregation with n-alkane titration was used to fit the asphaltene SAFT parameters. To reduce the number of fitted parameters, all binary interaction parameters between asphaltenes and other species were set to zero. Asphaltenes were assumed to be monodisperse and to have already associated into aggregates. Hence the fundamental units for asphaltenes in this work were not asphaltene monomers but rather pre-associated small aggregate “molecules”. This is consistent with experimental observations indicating the formation of small aggregates from monomers even in good solvents.

The resulting composition (in terms of precipitant volume fraction, or  $\phi_v^{\text{ppt}}$ ) and  $P_{\text{RI}}$  fits for the n-C<sub>7</sub> insoluble asphaltenes are shown in Figure 1. The fitted asphaltene has the following SAFT parameters:  $\sigma = 4.05\text{\AA}$ ,  $m = 80.0$ ,  $u^0/k = 350.8$  K. This asphaltene has a SAFT calculated solubility parameter of  $21.85 \text{ MPa}^{0.5}$  and a molar volume of  $3,334 \text{ cm}^3/\text{mole}$  ( $1.125 \text{ g/cm}^3$  assuming  $MW = 3,750$ ). It

can be seen from Figure 1 that SAFT fitted the experimental data very well. Furthermore, the EoS predicted a precipitant volume fraction maximum around nonane and decane.

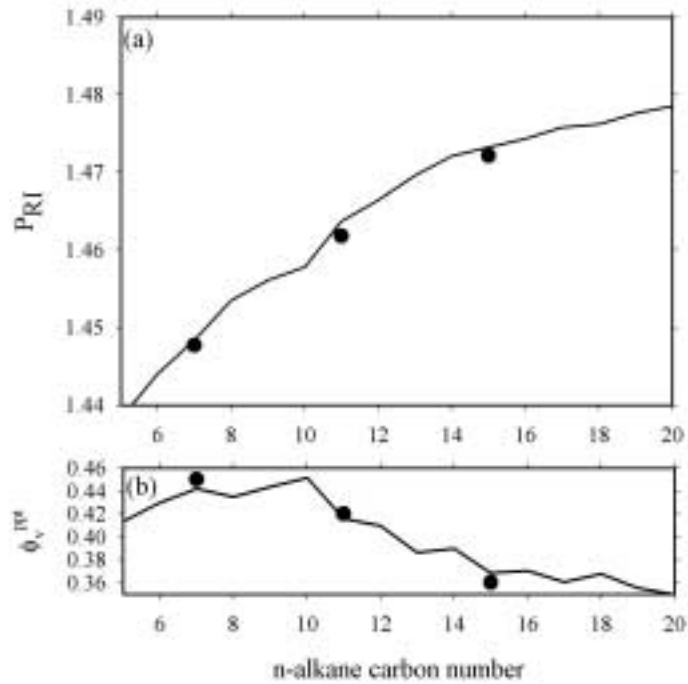


Figure 1. SAFT fits (lines) to model oil asphaltene aggregates  $P_{RI}$  and volume fraction precipitants data (filled circles)

With the asphaltene parameters determined above, SAFT can be used to predict the phase behavior of the model live oil system (mixture of toluene, methane, and asphaltenes). Comparison between SAFT predictions and experimental data shows qualitative agreement (Figure 2). In these calculations, a temperature independent methane-toluene binary interaction parameter of 0.029 (determined from methane-toluene vapor-liquid equilibria at 4°C and above 150°C) was used and all other binary interaction parameters were set to zero. While SAFT predicts



the correct temperature dependence of the asphaltene instability curves, its predictions become worse at higher methane concentrations. In the most part, SAFT calculated asphaltenes are less stable than experimental observations. We believe that the inclusion of asphaltene polydispersity will improve the quality of these predictions.

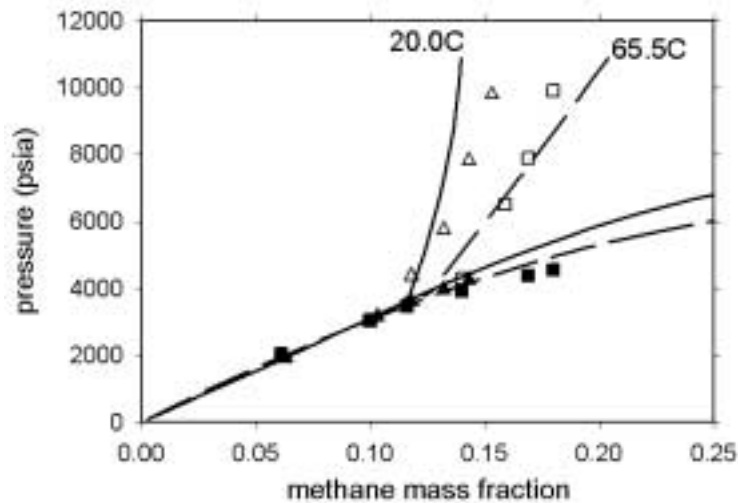


Figure 2. Asphaltene instability onsets (open symbols) and bubble points (filled symbols) for the model oil at 20.0°C (triangles) and 65.5°C (squares). SAFT predictions are drawn as lines.

### Recombined Oil Investigations

To model the phase behavior of the recombined oil, the oil was treated as a 6 component mixture, three sub-fractions to describe the separator gas and three sub-fractions to describe the stock tank oil (Figure 3). The relative amount of each sub-fraction was calculated based on gas-chromatography, saturates-aromatics-resins-asphaltenes fractionation, and gas-oil-ratio data listed in Ting, *et al.* (2002).

The number average molecular weight of the  $N_2+CO_2$  sub-fraction was essentially that of nitrogen's molecular weight because there was very little carbon dioxide in the system. The SAFT parameters for each sub-fraction (except for the asphaltenes) were obtained from correlations with molecular weight for each class of compound. In mixture calculations, the binary interaction parameters between the sub-fractions were obtained from the interaction parameters between representative species of the sub-fractions. For instance, the interaction parameter between propane ( $MW = 44.1$ ) and hexadecane ( $MW = 226.4$ ) was used for the interaction parameter between the saturates and light alkanes sub-fractions. The interaction parameters between separator gas sub-fractions and asphaltenes were set to the same values as between separator gas sub-fractions and the resins+aromatics sub-fraction.

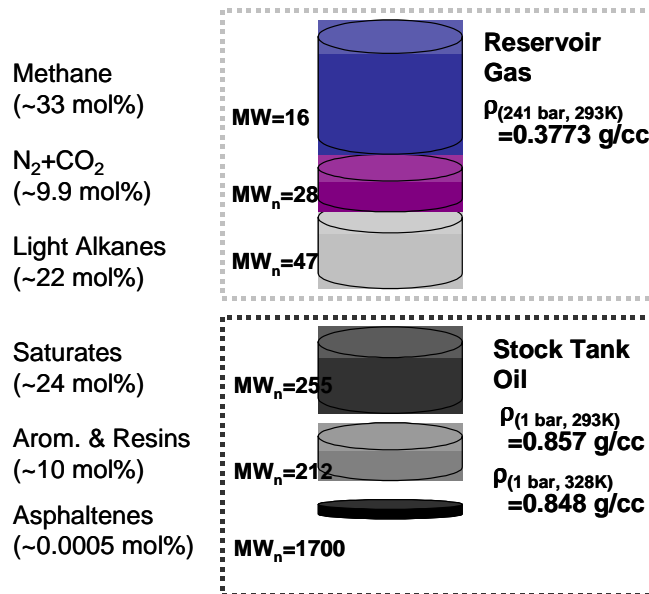


Figure 3. Fractionation of the recombined oil with  $GOR = 152 \text{ m}^3/\text{m}^3$  into a 6 component mixture.

A comparison of the SAFT predicted and experimental densities for the recombined oils shows good agreement (Figure 4). The predicted stock-tank oil densities also do not differ from the measured densities (at 20°C and 55°C) by more than  $\pm 1\%$ . The stock-tank oil was treated as a 3-components mixture in SAFT (see Figure 3).

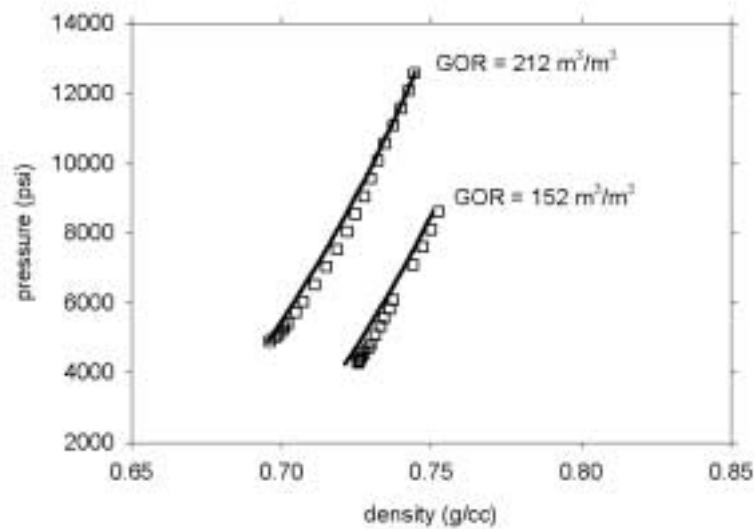


Figure 4. Measured (open squares) and SAFT predicted (lines) recombined oil densities.

The asphaltene SAFT parameter fitting procedure used in the model oil investigations was used to fit asphaltene SAFT parameters for the stock tank oil. In this case, the stock tank oil was initially mixed with equi-volume of  $\alpha$ -methyl-naphthalene as described in Ting, *et al.* (2002) to redissolve preexisting asphaltene precipitates in the oil. For a given oil/precipitant pair, the addition of asphaltene solvents to the oil shifts the amount of precipitant needed to induce

asphaltene precipitation but does not significantly alter the refractive index at precipitation onset. (Buckley, *et al.*, 1998) As in the model oil investigations, the binary interaction parameters between asphaltenes and the other stock-tank oil components (and  $\alpha$ -methyl-naphthalene) were set to 0. The fitted stock-tank oil asphaltenes has the following parameters:  $\sigma = 4.30A$ ,  $m = 29.5$ ,  $u^0/k = 395$  K. This asphaltene has a SAFT calculated solubility parameter of  $21.85 \text{ MPa}^{0.5}$  and a molar volume of  $1,437 \text{ cm}^3/\text{mol}$  ( $1.18 \text{ g/cm}^3$ , assuming  $MW = 1,700$ ). Results of the fits are given in Figure 5. Comparison with the n-C<sub>7</sub> extracted asphaltenes of the model oil system shows that the stock-tank oil asphaltenes are much smaller and more aromatic.

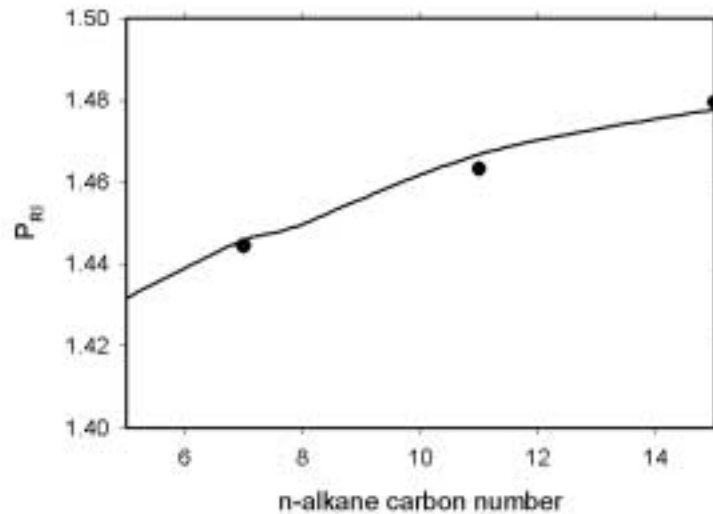


Figure 5. SAFT fits (line) to stock-tank oil mixture asphaltene aggregates  $P_{RI}$  data (filled circles)

The SAFT predicted asphaltene instability onset and bubble point pressures for the recombined oil (at  $71.1^\circ\text{C}$ ) are plotted in Figure 6 together with experimental

data. SAFT predicts accurately both the bubble points and the asphaltene instability onset points for this oil in the composition range investigated. According to the EoS calculations, we would expect asphaltene precipitation problems to occur at pressures above about 2,900 psi.

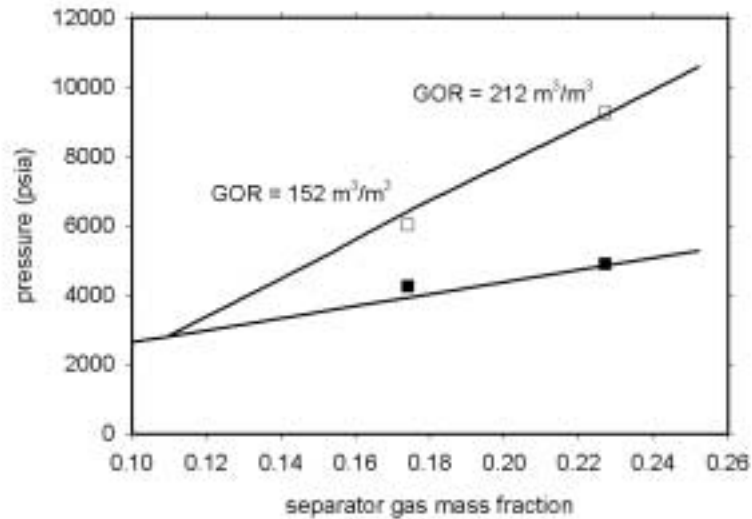


Figure 6. SAFT predictions (lines) for the asphaltene instability onset and mixture bubble points. The open squares are experimental asphaltene instability onsets and the filled squares are the experimental bubble point pressures.

## CONCLUSIONS

A method has been presented to characterize the recombined oil and the asphaltenes for use in the SAFT equation of state. The recombined oil was modeled as a six-component mixture, with three pseudo-components for the stock-tank oil and three pseudo-components for the separator gas. The average molecular weight and the amount of each sub-fraction was determined from gas-

chromatography, saturates-aromatics-resins-asphaltenes fractionation, and gas-oil-ratio information. SAFT parameters for each sub-fraction (except for the asphaltenes) was obtained from correlations with molecular weight for each class of compounds. The SAFT predicted densities for the stock-tank oil and the recombined oils agree very well with experimental measurements.

$P_{RI}$  data was used to characterize the asphaltene's SAFT parameters. For both the model oil and the stock-tank oil, good agreements were obtained between experimental and fitted  $P_{RI}$  even with a binary interaction parameter of zero between asphaltenes and the other species. While the stock-tank oil and the model oil asphaltenes thus obtained have almost the same solubility parameter, according to SAFT, the stock-tank oil asphaltenes are much smaller and more aromatic.

For both the model and the recombined oil systems, SAFT predicted asphaltene instability and bubble points agree well with experimental measurements.

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## REFERENCES

- Akbarzadeh, K., Ayatollahi, Sh., Moshfeghian, M., Alboudwarej, H. Svrcek, W.Y., and Yarranton, H.W. Prediction of Asphaltene Precipitation with a Modified SRK EOS. AIChE Spring National Meeting, New Orleans, LA., 2002.
- Buckley, J.S., Hirasaki, G.J., Liu, Y., von Drasek, S., Wang, J., and Gill, B.S. 1998. Pet. Sci. Tech. 16: 251.
- Buckley, J.S. 1999. Energy Fuels. 13: 328.
- Chapman, W.G., Jackson, G., and Gubbins, K.E. 1988. Mol. Phys. 65: 1057.
- Chapman, W.G., Gubbins, K.E., Jackson, G., and Radosz, M. 1990. Ind. Eng. Chem. Res. 29: 1709.
- Cimino, R., Correra, S., and Sacomani, P.A. Thermodynamic Modeling for Prediction of Asphaltene Deposition in Live Oils. SPE International Symposium on Oilfield Chemistry, San Antonio, TX., 1995.
- Gross, J. and Sadowski, G. 2001. Ind. Eng. Chem. Res. 40: 1244.
- Hirschberg, A., de Jong, L.N.J., Schipper, B.A., and Meijer, J.G. 1984. Soc. Pet. Eng. J. 24: 283.
- Leontaritis, K.J. and Mansoori, G.A. Asphaltene Flocculation During Oil Production and Processing: A Thermodynamic Colloidal Model. SPE International Symposium on Oilfield Chemistry, San Antonio, TX., 1987.
- Mansoori, G.A., Carnahan, N.F., Starling, K.E., and Leland, T.W. 1971. J. Chem. Phys. 54: 1523.
- Nghiem, L.X., Hassam, M.S., Nutakki, R., and George, A.E.D. Efficient Modeling of Asphaltene Precipitation. SPE Annual Technical Conference and Exhibition, Houston, TX., 1993.

Speight, J.G. and Plancher, H. Molecular Models for Petroleum Asphaltenes and Implications for Asphalt Science and Technology. Proceedings of the International Symposium on the Chemistry of Bitumens, 1991.

Ting, P.D., Wang, J.X., Buckley, J.S., Creek, J., Hamammi, A., Hirasaki, G.J., and Chapman, W.G. Fluid Characterization and Measurements of Asphaltene Stability in Model and Recombined Oils at Reservoir Conditions. In preparation.

Victorov, A.I. and Firoozabadi, A. 1996. AIChE J. 42: 1753.

Wang, J.X. 2000. Predicting Asphaltene Flocculation in Crude Oils. Ph.D. Thesis. Socorro, NM.

Wertheim, M.S. 1984. J. Stat. Phys. 35: 19, 35.

Wertheim, M.S. 1986. J. Stat. Phys. 42: 459, 477.

Wiehe, I.A. 1996. Fuel Sci. Tech. Intl. 14: 289.

Wu, J. 1998. Molecular Thermodynamics of Some Highly Asymmetric Liquid Mixtures. Ph.D. Thesis. Berkeley, CA.