Characterization of Reservoir Fluids: A Predictive Model for Interfacial and Bulk Phase Equilibrium Properties

Luís M. C. Pereira[1,2*], *Lourdes F. Vega*[1], *Antonin Chapoy*[2], *Bahman Tohidi*[2]
[1]*Gas Research Center and Chemical Engineering Department. The Petroleum Institute, part of the Khalifa University of Science and Technology (KUST), P.O. Box 2533, Abu Dhabi, UAE.*
[2]*Intitute of Petroleum Engineering, Heriot-Watt University, EH14 4AS, Edinburgh, UK.*

Summary

In this contribution, a robust theoretical approach was applied to predict the interfacial and phase equilibrium properties of real reservoir fluids. The modeling approach was based on an improved version of the Peng-Robinson equation of state (EoS) and on the Density Gradient Theory (DGT) for fluid interfaces. All the EoS and DGT parameters were obtained from literature correlations or calculated through a group-contribution method, leading to the computation of all the fluid properties in a fully predictive manner. The good agreement with volumetric, phase composition and interfacial tension data of multiple contact tests confirmed the superior predictive capabilities of the present modeling approach for describing key PVT properties of reservoir fluids.

Introduction

Accurate description of interfacial and bulk phase equilibrium properties of reservoir fluids is crucial for the deployment of more efficient and economical petroleum engineering processes. In terms of the bulk phases, composition and volumetric properties are of major importance as they dictate the quality and quantity of the produced fluids [1]. Interfacial forces, on the other hand, play a key role in the multiphase flow of fluids in pipelines, surface equipment and reservoirs. A quantitative index of the interfacial forces is given by the interfacial tension. This property, although entirely related to the fluid phases in contact, influences several rock properties such as capillary pressure, wettability and relative permeability [2]. In this sense, interfacial tension is a key parameter that determines the displacement and accumulation of hydrocarbon fluids in the pore spaces of reservoir rocks and, therefore the ultimate recovery [1,2]. Together, interfacial and bulk phase properties are also of paramount importance for the development of more reliable compositional reservoir simulations [1].

Laboratory experiments such as conventional PVT tests are usually carried out to provide information on the phase behavior and other relevant properties of reservoir fluids; however, measurements are often limited only to a few data points and/or in a narrow range of pressure and temperature conditions. For this reason, several empirical correlations have been proposed to estimate the properties of reservoir fluids. A more rigorous approach consists on using an equation of state (EoS) to calculate the effect of pressure, temperature and composition on both phase equilibrium and volumetric properties. Cubic EoSs such as the Soave-Redlich-Kwong (SRK) and the Peng-Robinson (PR) are among the most popular ones because despite their simplicity, they can describe the behavior of many hydrocarbon and natural gas constituents. However, when applied to real reservoir fluids it is necessary to fit several parameters to PVT data, making the process time consuming and based largely on trial and error.

In terms of the interfacial tension, several attempts have been made to predict this property in reservoir fluids. Among all, the Parachor method [3,4] is the most popular and it is currently the standard model in most commercial simulators for the Oil and Gas industry. Another more theoretical sound approach, based on statistical thermodynamics, is the Density Gradient Theory (DGT) [5]. This approach has shown to be a good tool for predicting the interfacial tension of synthetic reservoir fluids over a wide range of conditions [6–8].

The goal of this contribution is to showcase the capabilities of a consistent method for calculating both interfacial and bulk phase equilibrium properties of reservoir fluids. The examined modeling approach combines the robustness and performance of the DGT, with an improved cubic equation of state, the Volume Translated Predictive Peng-Robinson 1978 equation of state (VT-PPR78 EoS).

Theory

The Peng-Robinson 1978 EoS [9] can be expressed in terms of pressure as:

$$P=\frac{RT}{v-b}-\frac{a(T)}{v(v+b)+b(v-b)} \tag{1}$$

$$a(T)=\frac{0.45724R^2T_c^{\,2}}{P_c}\left[1+m(1-\sqrt{T_r})\right]^2 \tag{2}$$

$$m=0.37464+1.5422\omega-0.26992\omega^2 \text{ for } \omega<0.49 \tag{3}$$

$$m=0.3796+1.485\omega-0.1644\omega^2 \text{ for } \omega\geq 0.49 \tag{4}$$

$$b=0.07780\frac{RT_c}{P_c} \tag{5}$$

where a and b are the EoS energy and co-volume parameters, respectively, obtained from critical data, T_c and P_c, and the acentric factor, ω. When dealing with the volume-translated version of this EoS, a volume translation constant (v_c) is used to improve the description of the density curve. In this work, this correction is estimated using the correlation of Miqueu *et al.* [10]. The equation is extended to mixtures by applying the van der Waals one-fluid mixing rules, defined as follows:

$$a=\sum_i\sum_j x_i x_j (1-k_{ij})\sqrt{a_i a_j} \tag{6}$$

$$b=\sum_i x_i b_i \tag{7}$$

$$v_c=\sum x_i v_{c\,i} \tag{8}$$

where k_{ij} is the binary interaction coefficient for the energy parameter between molecules i and j. In this work, the group-contribution method of Jaubert and co-workers [11] is used to predict this coefficient between all the constituents of the reservoir fluid. The full k_{ij} matrix is thus obtained without the need to fit PVT data. This EoS will be referred hereafter as VT-PPR78.

The DGT is based on of the distribution of molecules across the interfacial region and on the Helmholtz free energy of the system which are combined to compute interfacial properties, such as the interfacial tension. Within the DGT formalism, the interfacial tension (γ) of a planar fluid-fluid interface can be computed as follows [5]:

$$\gamma=\int_{-\infty}^{+\infty}\left[\sum_i\sum_j c_{ij}\frac{d\rho_i}{dz}\frac{d\rho_j}{dz}\right]dz \tag{9}$$

where $d\rho_i/dz$ and $d\rho_j/dz$ are the density distribution of molecules i and j across the interface, and c_{ij} is the influence parameter between molecules i and j. This parameter was related to the pure component influence parameters as follows:

$$c_{ij}=\sqrt{c_i c_j} \tag{10}$$

The influence parameters of each component of the reservoir fluid are estimated using the correlation of Miqueu *et al.* [10]. An advantage of this approach over classical ones is that in addition to gaining knowledge on macroscopic interfacial properties, such as the interfacial tension, the DGT also provides important information about the microstructure of interfaces such as interface thickness, density profiles and interface activity [12]. For brevity, this work is limited to the discussion of the results for the interfacial tension. The method used for casting the solution of the equations governing the density distribution can be found in the excellent monograph of Davis [5].

Results and Discussion

Model predictions were compared to volumetric, phase composition and interfacial tension laboratory data from two multiple-contact (MC) tests conducted in a Real Black Oil (RFS-1) and performed at 34.58 MPa and 373 K [13]. MC tests are designed to simulate gas injection processes in oil reservoirs and involve multiple contacts of injection/equilibrium gas with original/equilibrium reservoir oil, in attempt to recreate the conditions of different gas-oil contact zones in a reservoir. Therefore, this comparison represents a very stringent test for evaluating the performance of the current modeling approach. The single phase composition and physical properties of RFS-1 are listed in **Table 1**.

Table 1. *Single phase composition and physical properties of RFS-1* [13].

Component	Mole%	MW / g.mol^{-1}	SG (T = 288.7 K)
Methane	23.979		
Ethane	3.978		
Propane	5.647		
i-Butane	1.998		
n-Butane	4.118		
i-Pentane	2.090		
n-Pentane	2.890		
C_6	4.104	85	0.666
C_7	6.248	96	0.714
C_8	6.552	105	0.738
C_9	5.197	119	0.761
C_{10}	4.059	133	0.776
C_{11}	3.308	147	0.790
C_{12}	2.638	162	0.801
C_{13}	2.357	173	0.815
C_{14}	2.179	188	0.831
C_{15}	1.947	203	0.837
C_{16}	1.615	220	0.844
C_{17}	1.283	233	0.849
C_{18}	1.265	248	0.856
C_{19}	1.046	262	0.863
C_{20+}	11.503	483	0.947
Temperature / K			373
Saturation Pressure (P^{Sat}) / MPa			9.41
Saturation Density (ρ^{Sat}) / kg.m^{-3}			715

The parameters of each *pseudo*-component of RFS-1 were estimated using the correlations of Riazi and Daubert [14] (for T_c and P_c) and of Edmister [15] (for ω), and their volume translation constants calibrated for a proper description of the saturated density of RFS-1 at 373 K. With these parameters set, the density and phase composition of the two MC tests performed on RFS-1 were predicted with the VT-PPR78 EoS and the results compared to experimental data in **Figures 1** and **2**. As can be seen, the agreement with experimental data stands out as very good, considering that no adjustable parameters were used in the prediction of the phase behavior of the multiple contact tests and the matrix of K_{IJ}s was obtained with a group-contribution approach.

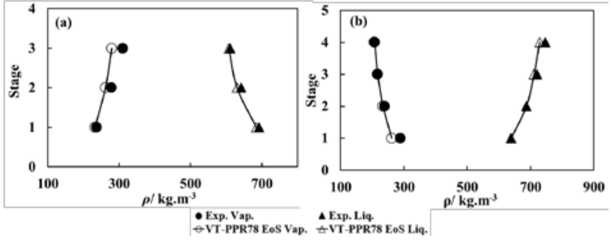

Figure 1. *Predicted and experimental phase densities of multiple contact studies performed on RFS-1 at T = 373 K and P = 34.58 MPa:* ***(a)*** *Forward multiple-contact and* ***(b)*** *Backward multiple-contact. Pure methane was used as the injection gas* [13].

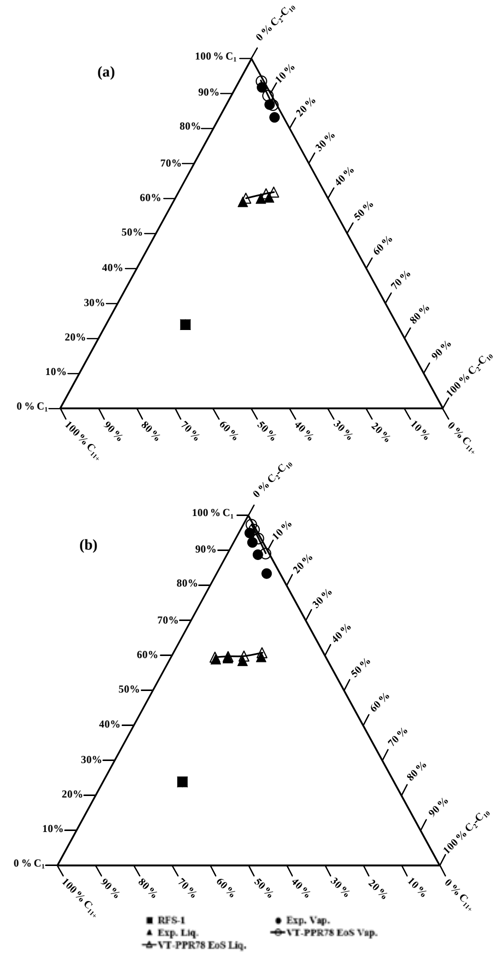

Figure 2. *Predicted and experimental phase compositions of multiple contact studies performed on RFS-1 at T = 373 K and P = 34.58 MPa:* ***(a)*** *Forward multiple-contact and* ***(b)*** *Backward multiple-contact. Pure methane was used as the injection gas* [13].

In the case of the interfacial tension, as depicted in **Figure 3**, the DGT predictions are far superior to those obtained using the conventional Parachor method. Indeed, the Parachor method severely underpredicted this property for all stages of the MC tests. In the case of the DGT, the highest deviations were observed at the 3rd stage of the forward multiple-contact test, where asphaltene precipitation was noticed during experiments [13]. The presence of asphaltene material will not only change the phase behavior of the system [16], but it will also affect the interfacial tension between the vapor and liquid phases [17]. Asphaltene precipitation is an interesting topic which is beyond the scope of this work. The Parachor values of each fluid component were estimated using the correlation of Fanchi [18] and the method applied using a scaling exponent equal to 4.

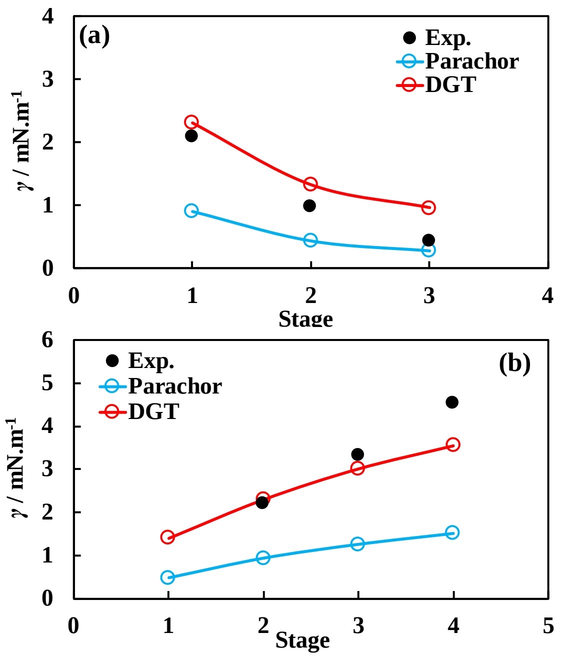

Figure 3. *Predicted and experimental interfacial tensions of multiple contact studies performed on RFS-1 at T = 373 K and P = 34.58 MPa:* ***(a)*** *Forward multiple-contact and* ***(b)*** *Backward multiple-contact. Pure methane was used as the injection gas* [13].

All predictions described above were obtained using full component phase behavior and interfacial tension models, *i.e.*, all 22 components and *pseudo*-components listed in **Table 1** were considered during the calculations. A common practice in reservoir and engineering calculations involves the lumping (or grouping) of components as calculation time generally increases with the number of groups (or components). Therefore, aiming at testing the impact of different lumping schemes, the phase behavior and interfacial tension predictions for the MC tests were repeated using different lumping schemes. As depicted in **Figure 4**, the number of groups can be reduced up to 5, with no significant overall variation (< 4%) in the predictions of the phase densities with the VT-PPR78 EoS and of the interfacial tension with the DGT. On the other hand, the Parachor method appears to be more sensitive to the lumping procedures. It is worth noticing that such lumping procedures significantly reduced the calculation time, in particular with the DGT. As an example, interfacial tension calculations considering full component scheme with the DGT showed an average timespan of 5 min, whereas the same calculations considering 5 groups were obtained in approximately 0.5 s. These results, together with its superior predictive capability, make the developed modeling approach an excellent candidate for reservoir engineering calculations.

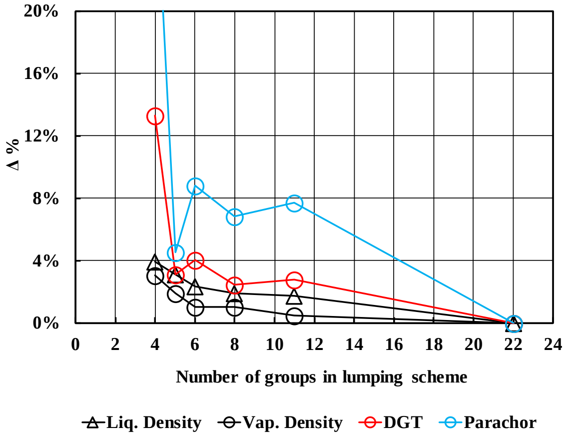

Figure 4. *Overall absolute variations (Δ%) of predictions of the backward multiple-contact test as function of the number of groups considered in each lumping scheme for RFS-1. Overall absolute variations were calculated relative to predictions obtained with the full compositional phase behavior and interfacial tension models (i.e., considering all components and pseudo-components in Table 1).*

Conclusion

The accurate description of interface and phase equilibrium properties of reservoir fluids over a broad range of pressures, temperatures and compositions is of paramount importance for petroleum engineering operations. With this in mind, a new approach for computing the phase behavior and interfacial tension has been developed and tested by comparison with real reservoir fluid data. The DGT + VT-PPR78 EoS approach strength relies on its predictive features and accuracy for representing PVT data of reservoir fluids. Moreover, the fact that the model calculations remain nearly unaffected by lumping schemes turn this model a more attractive alternative for petroleum applications and reservoir simulations.

References

[1] A. Danesh, PVT and phase behaviour of petroleum reservoir fluids, Elsevier Publishing, 1998.
[2] A.Y. Dandekar, Petroleum reservoir rock and fluid properties, CRC Press Taylor & Francis Group, 2006.
[3] D. Macleod, Trans. Faraday Soc. 2 (1923) 2–5.
[4] S. Sugden, The Variation of Surface Tension with Temperature and Some Related Functions, Birkbeck College, University of London, London, 1923.
[5] H.T. Davis, Statistical mechanics of phases, interfaces and thin films, Wiley, 1995.
[6] L.M.C. Pereira, A. Chapoy, R. Burgass, M.B. Oliveira, J.A.P. Coutinho, B. Tohidi, J. Chem. Thermodyn. 93 (2016) 404–415.
[7] L.M.C. Pereira, A. Chapoy, R. Burgass, B. Tohidi, J. Chem. Thermodyn. 97 (2016) 55–69.
[8] L.M.C. Pereira, A. Chapoy, R. Burgass, B. Tohidi, Adv. Water Resour. 103 (2017) 64–75.
[9] D.B. Robinson, D.-Y. Peng, The characterization of the heptanes and heavier fractions for the GPA Peng-Robinson programs, Gas Processors Association, Research Report RR-28, 1978.
[10] C. Miqueu, B. Mendiboure, A. Graciaa, J. Lachaise, Fluid Phase Equilib. 207 (2003) 225–246.
[11] X. Xu, J.-N. Jaubert, R. Privat, P. Duchet-Suchaux, F. Braña-Mulero, Ind. Eng. Chem. Res. 54 (2015) 2816–2824.
[12] L.M.C. Pereira. Interfacial tension of reservoir fluids: an integrated experimental and modelling investigation (PhD Thesis). Heriot-Watt University, 2016.
[13] Reservoir Fluid Studies: 1990-1993 Programme, Final Report, Heriot-Watt University, UK.
[14] M.R. Riazi, T.E. Daubert, Ind. Eng. Chem. Res. 26 (1987) 755–759.
[15] W.C. Edmister, Pet. Refin. 37 (1958) 173–179.
[16] A. Firoozabadi, A. Khalid, SPE Reserv. Eng. 1 (1986) 575–582.
[17] H. Doryani, Y. Kazemzadeh, R. Parsaei, M.R. Malayeri, M. Riazi, J. Nat. Gas Sci. Eng. 26 (2015) 538–548.
[18] J.R. Fanchi, SPE Reserv. Eng. 5 (1990) 433–436.

Acknowledgements

Part of the material in this contribution has already been presented as part of the PhD program of LMCP at Heriot-Watt University, UK. LMCP acknowledges the financial support from Galp Energia through his PhD grant.