Is It Still Necessary to Measure the Minimum Miscibility Pressure?

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Gas injection processes are among the most effective methods for enhanced oil recovery. A key parameter in the design of a gas injection project is the minimum miscibility pressure (MMP), the pressure at which the local displacement efficiency approaches 100%. From an experimental point of view, the MMP is routinely determined by slim tube displacements. However, because such experiments are very expensive (time-consuming), the question we want to answer in this article is as follows: Is this still necessary to measure the MMP? In other words, may other quicker, easier and cheaper gas injection experiments such as swelling test or multicontact test (MCT) substitute for slim tube test? This paper concludes that when the injected gas is not pure CO_2 (and probably not pure N_2 or pure H_2S), it is enough to fit only two parameters of the equation of state on data including classical PVT data + swelling data + MCT data and then to predict the MMP. The accuracy obtained is similar to the experimental uncertainty. It is thus possible to conclude that the slim tube test may be replaced by swelling tests and MCT, which are much cheaper.

Introduction

Gas injection processes are among the most effective methods for enhanced oil recovery. A key parameter in the design of a gas injection project is the minimum miscibility pressure (MMP), the pressure at which the local displacement efficiency approaches 100%. If the flow is one-dimensional, and if there is no dispersive mixing, then the displacement efficiency is exactly 100% at the MMP. From an experimental point of view, the MMP is routinely determined by slim tube displacements. In those experiments a long (say 10 m or longer), small diameter (say 0.5 cm) tube packed with sand or glass beads is filled with oil that is then displaced by injection gas at a fixed temperature and pressure. The fraction of the initial oil in place recovered after injection of some fixed amount of gas (usually 1.1 or 1.2 pore volume) is measured. The fraction of oil recovered is then plotted as a function of pressure. Typically, recovery increases rapidly with increasing pressure and then levels off. The MMP is usually taken to be the intersection of lines drawn through recovery points in the steeply climbing and level regions as long as the recovery in the level region is above some arbitrary cutoff (often 90%). To determine accurately the MMP, it is in general necessary to perform six displacements at six different pressures. The time required to perform a displacement is about 8 h (a working day). This means 1 week of experimental work is necessary to measure one MMP. The cost of such a work depends on the salary of the engineer who makes the experiment but may be evaluated to 10000 US dollars. It is thus clear that for petroleum companies the slim tube test is a very expensive experiment.

The question we want to answer in this article is as follows: Is it still necessary to measure the MMP? To answer yes to this question, two tracks were explored in this paper. The first possibility consists of developing a purely predictive characterization of the heavy cuts allowing an accurate estimation of the MMP. This is why in the first part of this article a purely predictive $C_{11}+$ characterization, which we recently developed, is tested. This characterization is perfectly able to predict with a good accuracy all the classical PVT experiments. However, because the MMP is a critical pressure and because the cubic equation of state (EOS) often fails to predict critical points of complex mixtures, it is not always possible to predict accurately the MMP. The deviation between the predicted and the experimental MMP varies between 2% and 20%.

When the first possibility fails, another solution is to fit some parameters of the EOS by using experiments which are much less expensive than the slim tube test (e.g., relative volumes during a constant mass expansion, reservoir fluid bubble pressure, relative volumes during a differential vaporization, stock tank oil density, swelling test data, multicontact test data) and then to predict the MMP with the obtained parameters. The key questions we need to answer are (1) which experiments influence the most the value of the MMP and (2) is it possible to predict the MMP after fitting some parameters on these key experiments. This paper will show that a good fit on the swelling test and above all on the multicontact test (MCT) allows a good prediction of the MMP.

By the end, because the swelling test and MCT were not always conducted experimentally, software able to include the MMP in the fitting procedure was developed. Our PVT package is, to our knowledge, the first one in the world that is able to perform such calculations.

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The $C_{11}+$ Characterization Procedure

The compositional model used in this paper is a slightly modified version of a previously published work.[1] Indeed, in comparison to our previous work,[1] it was decided to lump together the nine cuts C_k ($k = 11-19$) in a unique pseudocomponent called "$C_{11}-C_{19}$" in order to reduce the number of components. Indeed, we noticed that such a lumping did not change the predictive power of our compositional model. To do so, the following formulas (well known in petroleum companies), in which x_i is the internal mole fraction of cut C_i in the pseudocomponent $C_{11}-C_{19}$, are used:

$$\begin{cases} T_{c,C_{11}-C_{19}} = \dfrac{\sum_{i=1}^{9} x_i T_{c,i} v_{c,i}}{\sum_{i=1}^{9} x_i v_{c,i}} \\ \omega_{C_{11}-C_{19}} = \sum_{i=1}^{9} x_i \omega_i \\ Z_{RA,C_{11}-C_{19}} = \sum_{i=1}^{9} x_i Z_{RA,i} \\ P_{c,C_{11}-C_{19}} = \\ \quad \sum_{i=1}^{9} x_i P_{c,i} \left[1 - (5.808 + 4.930\omega_{C_{11}-C_{19}}) \left(1 - \dfrac{T_{c,C_{11}-C_{19}}}{\sum_{i=1}^{9} x_i T_{c,i}} \right) \right] \end{cases}$$

Moreover, knowing the amount of each cut C_k ($k = 11-19$) in the reservoir fluid and the groups appearing in each cut C_k, it is possible to compute the groups appearing in the pseudocomponent $C_{11}-C_{19}$. These groups are necessary to estimate the binary interaction parameters.[1]

Predictive Results on 13 Different Crude Oils

TOTALFINAELF performed 15 slim tube tests on 13 reservoir crude oils coming from different countries of the world (we are not allowed to give the name of the countries). For two crude oils, two different gases were injected. The compositional model described in the previous section was used to predict not only these 15 MMPs but also many other measured PVT data. It is here very important to outline that the proposed compositional model is purely predictive in the sense that the only data necessary to perform a flash calculation are, in addition to the reservoir fluid composition, the experimental molar weight and density of each cut from C_{11} to $C_{20}+$. No PVT data are used to estimate the parameters of the EOS. Such a model is able to predict:

1. The reservoir fluid bubble pressure with an average deviation of 3.7% (19 bubble point pressures were measured). For most of the crude oils, the bubble point is only measured at the reservoir temperature, but for two of them, such a pressure was measured at three other temperatures.

2. The stock tank oil density with an average deviation of 1.5% (12 values were determined).

3. The evolution of the relative volume during an isothermal constant mass expansion with an average deviation of 0.8% (197 data points were measured). Let us here recall that the relative volume is defined as $V_{rel} = V_{total}/V_{sat}$, where V_{total} is the total volume occupied by the fluid at pressure P and V_{sat} is the liquid volume at the bubble pressure.

4. The evolution of the relative volume during an isothermal differential vaporization with an average deviation of 1.5% (71 data points were measured). In this case, the relative volume is defined by $V_{rel} = V_{liq}/V_{sat}$, where V_{liq} is the liquid-phase volume at pressure P and V_{sat} is the liquid volume at the bubble pressure.

5. The evolution of the saturation pressure versus quantity of injected gas during a swelling test with an average deviation of 5.4% (42 data points were measured).

6. The evolution of the swollen volume versus quantity of injected gas during a swelling test with an average deviation of 0.7% (42 data points were measured). The swollen volume is defined by $V_{swell} = V_{sat}(k)/V_{sat0}$, where $V_{sat}(k)$ is the volume of the saturated oil at $P = P_{sat}(k)$, i.e., after the injection of k predetermined amounts of gas. V_{sat0} is the saturated crude oil volume (before dissolution of any quantity of gas).

7. The evolution of the density of the saturated swollen crude oil (ρ_{sat}) versus quantity of injected gas with an average deviation of 1.5%. Forty two data points were measured. More detailed information concerning the swelling test may be found elsewhere.[2]

8. The evolution of the partial volume during a MCT (multicontact test) with an average deviation of 24% (13 data points were experimentally determined). In a MCT experiment, a predetermined amount of crude oil and of injection gas are mixed in order to obtain a two-phase system (see ref 2 for more details). The partial volume (PVol) is the ratio of the liquid phase volume by the total cell volume. Although the partial volumes are poorly predicted, our compositional model is able to predict with high accuracy the composition of the phases (liquid and gas) in equilibrium (these results are not shown).

9. The MMP with an average deviation of 7.6% (15 slim tube tests were performed). The algorithm used to calculate the MMP and which takes into account the mixed condensing/vaporizing (C/V) mechanism discovered by Zick[3] is the one developed by Jaubert et al.[4] Though our compositional model describes a crude oil with 29 components, we can imagine that the last version of the algorithm developed by Orr and coworkers[5] could also be used. A discussion on the different algorithms allowing computation the MMP may be found in the articles by Jaubert et al.[4,6] Briefly, our algorithm[4] is based on a cell to cell simulation with very simple flow dynamics (a P/T flash algorithm is only required to compute the MMP). The recovery factors are calculated at three different pressures correctly selected using 500 cells. To eliminate the numerical dispersion, the results are extrapolated to an infinite number of cells. Typically, the recovery factors increase exponentially with pressure. In our algorithm, the MMP is defined as the pressure at which the recovery factor is equal to 97%.

Table 1 gives a summary of all these results. The numerical values of most of the experimental data used in this work and necessary for a researcher in order to repeat the calculations or compare the results with other

Table 1. Results Obtained with the Purely Predictive Compositional Model Used in This Study

	constant mass expansion		differential vaporization		crude oil bubble point	stock tank oil density	isothermal swelling test				isothermal and isobaric multicontact test			minimum miscibility pressure		
fluid name	T/K	ΔV_{rel} (%)	T/K	ΔV_{rel} (%)	ΔP_{sat} (%)	$\Delta\rho$ (%)	gas	$\Delta P_{sat.}$ (%)	ΔV_{swell} (%)	$\Delta\rho_{sat.}$ (%)	gas	type	ΔPvol (%)	gas	mech-anism	ΔMMP (%)
F1	374.85	1.43 (9)[a]			−5.45	1.79								G1	C/V	−2.4
F2	372.05	1.54 (11)			7.55									G2	C/V	2.8
F3	387.35	0.35 (9)	387.35	2.07 (11)[a]	−1.12	0.44	G3 (6)[a]	2.16	1.26	2.42				G3	C/V	−2.5
F4	388.15	0.91 (11)			3.61	3.40	G4 (7)	3.03	0.26	0.34				G4	*b*	2.3
F5	394.25	1.03 (18)	394.25	0.51 (12)	4.39	0.36	G5a (6)	5.05	0.37	1.01				G5a	C/V	−2.8
							G5b (7)	4.75	0.69	1.96	G5c	*c*	37.7	G5d	C/V	9.4
F6	383.15	1.15 (12)			−4.58	1.60								G6a	C/V	−3.5
							G6b (6)	9.05	0.25	1.16				G6b	C/V	−9.8
F7	393.15	1.38 (12)			6.02	4.01								G7	C/V	−5.4
F8	393.15	0.49 (1)			−1.07	1.25								G8	C/V	−21.3
F9	394.25	0.20 (10)	394.25	2.37 (12)	0.57	2.21								G9	*b*	−5.4
	303.25	0.67 (12)			6.12											
	352.45	0.39 (10)			2.19											
	417.85	0.37 (13)			−0.49											
F10	394.25	2.01 (9)			−7.14	0.52								G10	C/V	14.1
F11	373.75	0.72 (9)	373.75	1.57 (11)	−2.88	1.29								G11	C/V	−16.0
F12	376.45	0.49 (9)	376.45	2.13 (11)	3.14	0.35	G12 (4)	4.49	0.25	2.86	G12	*d*	−3.6	G12	C/V	8.6
	299.85	0.44 (9)			5.22											
	360.95	0.31 (9)			1.70							*d*	43.9			
	394.25	0.41 (9)			1.66											
F13	377.55	0.80 (15)	377.55	0.72 (14)	−5.09	0.52	G13 (6)	9.54	1.97	1.20	G13	*c*	5.0	G13	C/V	7.4
												e	32.5			
av		**0.83 (197)[a]**		**1.52 (71)**	**3.68 (19)**	**1.48 (12)**		**5.41 (42)**	**0.73 (42)**	**1.48 (42)**			**24.3 (13)**			**7.6 (15)**

[a] The number in parentheses is the number of data points. [b] Vaporizing. [c] Reverse (four contacts). [d] Reverse (one contact). [e] Forward (three contacts).

methods are published elsewhere.[7] Figure 1 illustrates graphically the results obtained. The compositions of the 13 reservoir crude oils and of the 17 injected gases are given in Table 2. The gas number, on the first line in Table 2 refers to the crude oil number in which it was injected. As an example, gases G_{6a} and G_{6b} were injected in reservoir fluid F_6. Gases G_1 and G_2 and G_7 and G_8 are identical. It was however decided to give two different numbers to these gases in order to identify simply the crude oil in which they were injected. Gases 5b, 5c, and 5d are quasi-identical. The first one (G_{5b}) was used for a swelling test, the second one (G_{5c}) for a multicontact test (MCT), and the last one (G_{5d}) for a slim tube test. These three gases, which were injected in reservoir fluid F_5, should be identical. However, because they were prepared at different times, there exists a slight difference between them. This is absolutely not a problem.

The last line in Table 1 shows evidence that the model described in this paper is able to predict the phase behavior of real crude oils with high accuracy. In our previous paper,[1] it is shown that the results obtained with the proposed compositional model compare competitively with those given by other characterizations currently used in petroleum simulators. However, the MMP is predicted with an average deviation of 7.6%, which is twice higher than the experimental uncertainty. To reduce this deviation, a fitting strategy is proposed.

Fitting Strategy To Reduce the Deviations between Experimental and Calculated MMP

Table 1 shows evidence that 6 MMP values are predicted with a deviation lower than 4%, which is the experimental uncertainty (F1 + G1, F2 + G2, F3 + G3, F4 + G4, F5 + G5a, F6 + G6a). For these six cases, it is thus not necessary to proceed to any fitting procedure since the predictive model leads to very nice results. It is here interesting to outline that for the systems F3 + G3 and F5 + G5a, the deviations on the MMP are very small but the deviations on the swelling data are also very small. We may thus suspect a correlation between the MMP and the swelling data (see below).

Concerning the nine other systems, they have to be divided in two families.

The first family concerns the fluids for which the MMP was the unique injection gas experiment performed (no swelling data and no MCT data are available). The five systems concerned are F7 + G7, F8 + G8, F9 + G9, F10 + G10, and F11 + G11. For these five systems, all the available PVT data (relative volumes, reservoir bubble pressure, stock tank oil density) are accurately predicted. It is thus obvious that by fitting the EOS parameters on these experimental data would not lead to a better prediction of the MMP. Indeed the fitted parameters would be very close to the initial ones (given by the predictive procedure). The unique thing to do is thus to fit the parameters of the EOS on all the experimental data, i.e., to include the MMP in the fitting procedure. This is not an easy task because the MMP is calculated using a simplified slim tube in which numerical dispersion is eliminated by extrapolating the results to an infinite number of cells.[4] To our knowledge, our software is the first one in the world able to fit the parameters of the EOS (T_c, P_c, ω, bips) on the MMP and to simultaneously take into account the mixed condensing/vaporizing mechanism. In this study, only two parameters were fitted: the critical temperature and the critical pressure of the pseudocomponent C_{11}−C_{19}. Such a component was selected because its physical parameters are not well-known and because its amount in the reservoir fluid is quite high. Table 3 shows evidence that the results

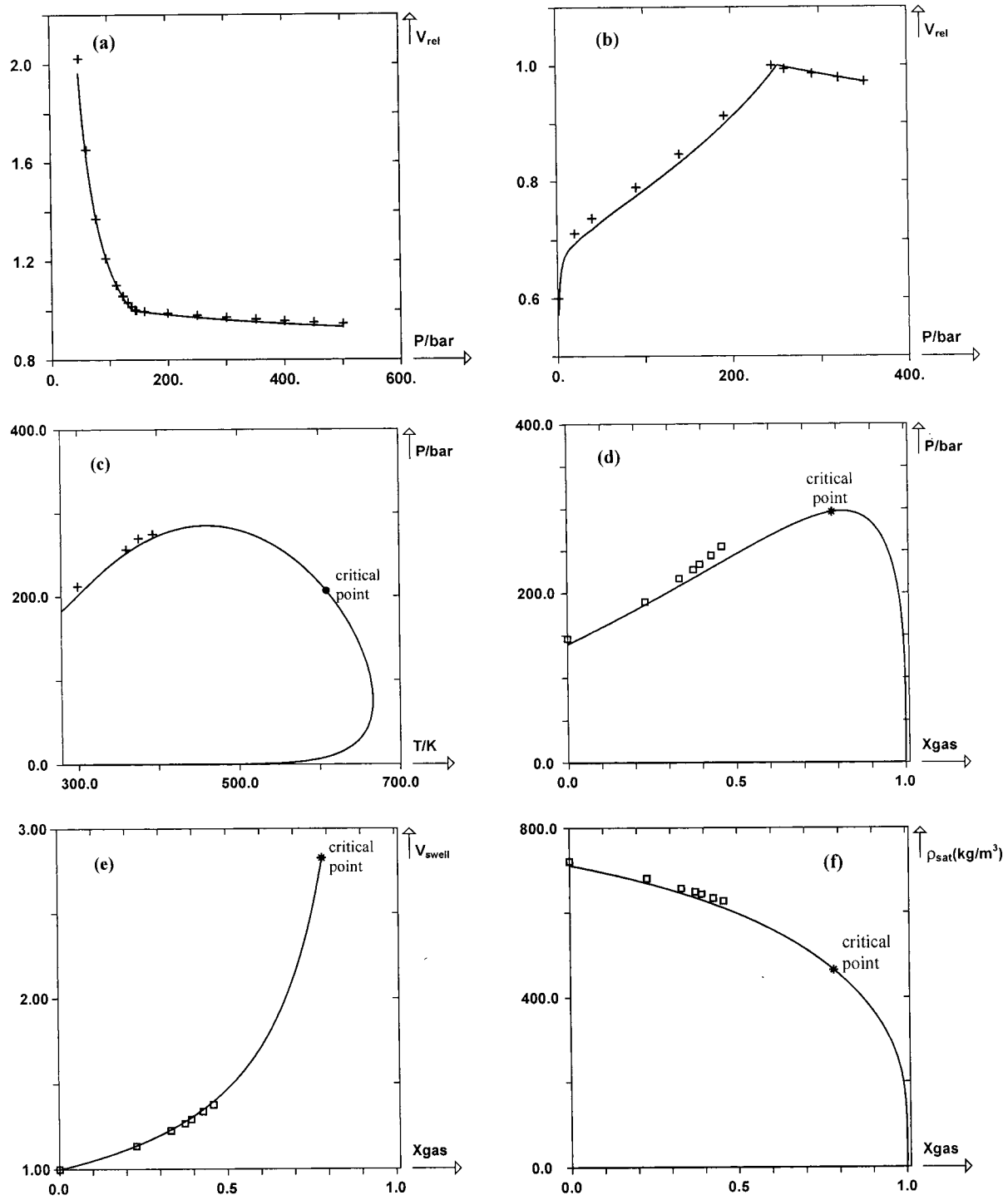

Figure 1. Illustration of the predictive power of the proposed compositional model. Symbols + and □ are the experimental data points. The continuous lines are the predicted values. (a) Constant mass expansion of fluid F5 at T/K = 394.25. The average deviation between calculated and experimental relative volumes is equal to 1.03%. (b) Differential vaporization of fluid F11 at T/K = 373.75. The average deviation between calculated and experimental relative volumes is equal to 1.57%. (c) (P,T) phase envelope of fluid F12 for which four bubble point pressures were measured. The average deviation of these four pressures is equal to 2.92%. (d−f) Swelling test performed on fluid F5 (gas G5b is injected). The average deviations of the saturation pressures, swollen volumes, and densities of the swollen oil are respectively equal to 4.75% (d), 0.69% (e), and 1.96% (f).

obtained are extremely accurate. Indeed this fitting procedure made it possible to estimate the MMP with an average deviation of 2.0%. At the same time, the other PVT properties are also reproduced accurately.

The second family concerns systems for which swelling tests and/or MCT experiments were performed in addition to the slim tube test. The four concerned systems are F5 + G5b, F6 + G6b, F12 + G12, and F13 + G13. It was here decided to fit the critical temperature and the critical pressure of the pseudocomponent C_{11}−C_{19} on all the available experimental data except the MMP and then to predict the MMP with the fitted parameters. Such a procedure is here justified because the partial volumes during MCT are poorly predicted and because the saturation pressures during the swelling tests are not so good. We hope that by reducing the deviations on these data, we will improve the prediction of the MMP. It is here recalled that the question we

Table 2. Molar Composition of the 13 Crude Oils and of the 17 Injected Gases Used in This Paper

Comp	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11	F12	F13	G1	G2	G3	G4	G5a	G5b	G5c	G5d	G6a	G6b	G7	G8	G9	G10	G11	G12	G13
H_2S	-	-	-	-	0.383	-	-	-	2.320	0.355	-	1.490	-	-	-	-	-	-	1.000	1.000	1.070	0.250	-	-	-	2.350	2.720	-	3.810	-
N_2	0.180	0.200	0.450	0.350	0.450	-	-	0.083	0.249	0.400	0.670	0.320	1.252	0.480	0.480	0.490	0.410	-	1.150	0.970	1.010	0.420	0.450	-	-	0.270	0.220	0.470	0.200	-
CO_2	0.820	1.340	1.640	3.140	2.070	0.774	2.130	1.824	3.601	2.548	0.860	2.800	0.897	4.960	4.960	1.820	1.650	-	4.380	3.910	4.240	2.850	2.190	4.350	4.350	4.350	4.430	2.250	7.570	100.00
CH_4	22.920	23.640	45.850	54.260	26.576	36.203	31.280	32.165	47.642	47.244	46.630	45.290	37.543	58.050	58.050	81.390	81.710	88.000	55.760	55.830	56.470	75.550	76.650	81.140	81.140	73.090	66.100	85.340	64.900	-
C_2H_6	7.210	8.560	7.150	8.570	7.894	9.736	7.510	7.627	6.497	6.937	6.830	9.110	5.476	17.090	17.090	9.150	9.160	7.000	15.030	15.350	15.150	14.340	12.020	10.310	10.310	6.000	6.410	7.620	15.030	-
C_3H_8	7.370	6.680	6.740	5.720	6.730	6.745	6.930	7.221	4.500	4.805	6.210	5.500	4.196	11.970	11.970	4.670	4.540	3.000	10.870	11.120	10.760	5.520	5.260	3.320	3.320	3.480	12.040	2.980	5.760	-
i-C_4	1.580	1.250	0.840	0.760	1.485	1.287	0.270	1.894	1.169	1.190	0.920	1.060	1.104	1.230	1.230	0.500	0.480	0.500	2.000	2.040	1.920	0.370	0.740	-	-	0.810	0.500	0.320	0.630	-
n-C_4	5.230	4.050	3.110	2.450	3.899	3.672	5.990	4.613	2.866	3.063	3.330	3.070	2.902	3.730	3.730	1.240	1.210	0.500	4.370	4.400	4.230	0.590	1.490	0.880	0.880	1.760	6.930	0.690	1.290	-
i-C_5	2.250	1.780	1.030	0.750	1.937	1.557	0.970	2.132	1.400	1.441	1.200	1.240	1.360	0.750	0.750	0.200	0.190	0.500	1.590	1.560	1.440	0.050	0.330	-	-	0.730	0.240	0.120	0.250	-
n-C_5	3.600	2.670	1.650	1.200	2.505	2.337	3.770	2.886	1.899	1.964	1.930	1.820	1.875	0.910	0.910	0.260	0.260	0.500	1.620	1.560	1.530	0.050	0.410	-	-	0.920	0.230	0.150	0.280	-
i-C_6	-	-	1.280	-	1.783	1.520	-	2.166	1.318	1.411	1.240	1.210	1.282	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.060	-	-
n-C_6	4.840	4.030	1.240	1.530	1.568	1.770	4.370	1.919	1.418	1.466	1.240	1.170	1.452	0.530	0.530	0.090	0.130	-	1.320	1.200	1.140	0.010	0.260	-	-	1.150	0.120	-	0.150	-
i-C_7	-	-	0.470	-	0.531	1.031	-	2.023	0.450	0.477	1.080	0.350	0.557	-	-	-	-	-				-	-	-	-	-	-	-	-	-
Aro C_7	-	-	0.240	-	0.538	0.260	-	0.245	0.180	0.193	0.250	0.180	0.313	-	-	-	-	-				-	-	-	-	-	-	-	-	-
Cyclic C_7	-	-	2.230	-	2.229	0.873	-	0.353	1.259	1.296	0.950	1.690	1.621	-	-	-	-	-				-	-	-	-	-	-	-	-	-
n-C_7	4.720	4.570	0.830	2.600	1.013	1.344	4.500	1.588	1.028	1.035	1.750	0.620	1.249	0.190	0.190	0.060	0.120	-	0.760	0.840	0.750	-	0.120	-	-	1.100	0.030	-	0.100	-
i-C_8	-	-	0.720	-	1.215	0.309	-	1.582	0.792	0.782	1.160	0.470	0.835	-	-	-	-	-				-	-	-	-	-	-	-	-	-
Aro C_8	-	-	0.740	-	1.004	1.007	-	0.673	0.487	0.524	0.760	0.490	0.201	-	-	-	-	-				-	-	-	-	-	-	-	-	-
Cyclic C_8	-	-	2.020	-	1.065	0.986	-	0.567	0.808	0.834	0.950	1.340	1.533	-	-	-	-	-				-	-	-	-	-	-	-	-	-
n-C_8	4.520	4.280	0.800	3.020	0.849	1.304	4.080	1.165	0.761	0.779	1.150	0.530	0.986	0.080	0.080	0.130	0.130	-	0.150	0.220	0.290	-	0.080	-	-	0.920	0.030	-	0.030	-
i-C_9	-	-	0.620	-	0.866	0.703	-	1.565	0.634	0.630	0.730	0.570	0.895	-	-	-	-	-	-			-	-	-	-	-	-	-	-	-
Aro C_9	-	-	0.920	-	1.043	1.256	-	1.291	0.840	0.812	1.000	0.850	0.590	-	-	-	-	-	-			-	-	-	-	-	-	-	-	-
Cyclic C_9	-	-	0.640	-	0.620	0.547	-	-	0.335	0.487	0.420	0.590	0.772	-	-	-	-	-	-			-	-	-	-	-	-	-	-	-
n-C_9	4.070	3.880	0.520	2.100	0.522	0.828	3.960	0.906	0.542	0.525	0.700	0.480	0.809	0.030	0.030	-	0.010	-	-			-	-	-	-	0.730	-	-	-	-
i-C_{10}	-	-	1.020	-	1.267	1.276	-	1.491	0.906	0.943	0.830	1.300	1.348	-	-	-	-	-	-			-	-	-	-	-	-	-	-	-
Aro C_{10}	-	-	0.360	-	0.433	0.752	-	1.020	0.515	0.590	0.530	0.450	0.333	-	-	-	-	-	-			-	-	-	-	-	-	-	-	-
n-C_{10}	3.500	2.930	0.310	1.740	0.333	0.629	3.420	0.760	0.369	0.440	0.430	0.400	0.500	-	-	-	-	-	-			-	-	-	-	0.470	-	-	-	-
C_{11}	2.910	3.150	1.810	1.360	2.635	2.481	2.790	2.780	1.780	2.022	1.620	1.740	2.447	-	-	-	-	-	-			-	-	-	-	-	-	-	-	-
C_{12}	2.420	3.190	1.470	1.100	2.285	2.067	2.400	2.068	1.464	1.692	1.440	1.420	2.092	-	-	-	-	-	-			-	-	-	-	-	-	-	-	-
C_{13}	1.990	3.050	1.450	1.110	2.364	1.917	2.040	1.751	1.275	1.501	1.450	1.310	1.789	-	-	-	-	-	-			-	-	-	-	-	-	-	-	-
C_{14}	1.740	1.160	1.280	0.950	2.038	1.469	1.790	1.924	1.063	1.327	1.280	1.150	1.789	-	-	-	-	-	-			-	-	-	-	-	-	-	-	-
C_{15}	2.020	1.980	1.150	0.860	1.752	1.215	1.460	1.233	0.994	1.162	1.080	1.000	1.885	-	-	-	-	-	-			-	-	-	-	-	-	-	-	-
C_{16}	1.390	1.720	0.910	0.680	1.589	1.158	1.240	1.192	0.817	0.967	0.860	0.880	1.568	-	-	-	-	-	-			-	-	-	-	-	-	-	-	-
C_{17}	1.210	1.600	0.820	0.600	1.492	0.985	1.040	0.962	0.666	0.765	0.790	0.760	1.417	-	-	-	-	-	-			-	-	-	-	-	-	-	-	-
C_{18}	0.900	1.160	0.800	0.560	1.263	0.952	0.900	0.815	0.637	0.783	0.700	0.690	0.865	-	-	-	-	-	-			-	-	-	-	-	-	-	-	-
C_{19}	1.170	1.100	0.710	0.510	0.812	0.903	0.830	0.814	0.498	0.605	0.480	0.620	1.098	-	-	-	-	-	-			-	-	-	-	-	-	-	-	-
C_{20}+	11.440	12.030	6.180	4.080	12.962	8.147	6.330	6.702	6.021	6.005	6.550	6.040	13.169																	
C_{11}+														-	-	-	-	-	-			-	-	-	-	1.870	-	-	-	-

Table 3. Deviations Obtained after Fitting Only Two Parameters ($T_{C,C_{11}-C_{19}}$ and $P_{C,C_{11}-C_{19}}$) on All the Available Experimental Data (the MMP is Included in the Fitting Procedure)

fluid name	constant mass expansion, ΔV_{rel} (%)	differential vaporization, ΔV_{rel} (%)	crude oil bubble point, $\Delta P_{sat.}$ (%)	stock tank oil density, $\Delta\rho$ (%)	minimum miscibility pressure, ΔMMP (%)
F7	1.09		3.64	−3.40	−0.4
F8	0.38		4.84	−2.55	−0.5
F9	0.41	2.86	1.44	−2.21	−0.6
	0.67		6.12		
	0.45		2.57		
	0.46		0.72		
F10	1.55	-	−5.88	8.10	7.5
F11	0.58	1.78	2.73	0.09	−0.8
av	0.73 (0.79)[a]	2.34 (1.99)	3.49 (3.31)	3.27 (1.86)	**2.0 (12.4)**

[a] The number in parentheses is the average deviation obtained with the predictive model.

Table 4. Deviations Obtained after Fitting Only Two Parameters on All the Available Experimental Data Except the MMP and MMP Prediction with the Fitted Parameters

	constant mass expansion	differential vaporization	crude oil bubble point	stock tank oil density	isothermal swelling test				isothermal and isobaric MCT			minimum miscibility pressure[a]		
fluid name	ΔV_{rel} (%)	ΔV_{rel} (%)	$\Delta P_{sat.}$ (%)	$\Delta\rho$ (%)	gas	ΔP_{sat} (%)	ΔV_{swell} (%)	$\Delta\rho_{sat.}$ (%)	gas	type	ΔPvol (%)	gas	mech-anism	ΔMMP (%)
F5	0.88	0.44	0.56	1.14	G5b	1.26	0.27	1.54	G5b	*b*	16.5	G5b	C/V	1.1
F6	0.71		3.50	2.52	G6b	1.91	0.42	3.41				G6b	C/V	5.6
F12	0.33	1.44	−0.90	3.43	G12	1.70	0.21	3.45	G12	*c*	−6.7	G12	C/V	−4.7
	0.09		1.84											
	0.69		−2.24							*c*	15.5			
	0.74		−2.67											
av	**0.62**	**0.92**	**1.95**	**2.36**		**1.59**	**0.31**	**2.65**			**14.7**			**3.8**
	(0.72)[d]	**(1.28)**	**(3.45)**	**(0.77)**		**(6.21)**	**(0.43)**	**(1.89)**			**(33.1)**			**(9.3)**

[a] Prediction. [b] Reverse (four contacts). [c] Reverse (one contact). [d] The number in parentheses is the average obtained with the predictive model.

Table 5. Deviations Obtained after Fitting Only Two Parameters on All the Available Experimental Data Including the MMP

	constant mass expansion	differential vaporization	crude oil bubble point	stock tank oil density	isothermal swelling test				isothermal and isobaric MCT			minimum miscibility pressure		
fluid name	ΔV_{rel} (%)	ΔV_{rel} (%)	$\Delta P_{sat.}$ (%)	$\Delta\rho$ (%)	gas	$\Delta P_{sat.}$ (%)	ΔV_{swell} (%)	$\Delta\rho_{sat}$ (%)	gas	type	ΔPvol (%)	gas	mech-anism	ΔMMP (%)
F13	1.82	1.37	−10.1	−8.10	G13	6.17	2.66	5.56	G13	*a*	4.5	G13	C/V	**0.3**
										b	2.7			

[a] Reverse (four contacts). [b] Forward (three contacts).

want to answer is, is it still necessary to measure the MMP? In other words, may other gas injection experiments such as swelling test or MCT substitute for slim tube test. The results obtained for the first three systems (F5 + G5b, F6 + G6b, F12 + G12) are given in Table 4 and are illustrated in Figure 2. From this table it becomes obvious that for these three examples the MMP may be estimated with high accuracy (average deviation of 3.8%) after fitting only two parameters on data including swelling test and MCT. The best result (1.1% deviation) is obtained for the system F5 + G5b in which four contacts were performed during the MCT. Moreover the worst result (5.6% deviation) is obtained for system F6 + G6b in which no MCT experiments are available. An intermediate result (4.7% deviation) is obtained for system F12 + G12 in which two experiments of backward MCT were conducted but for which only one contact was performed. These results seem to indicate that to predict accurately the MMP, it is necessary to perform a swelling test but above all MCT experiments. The accuracy on the MMP seems to be directly proportional to the contact number (four contacts are however enough to obtain the MMP with a deviation of 1%).

Concerning the last system F13 + G13, it was not possible using the same strategy to obtain accurate results. This is because the injected gas is pure CO_2. It is indeed well-known that the PR EOS is not able to properly predict the phase behavior of mixtures containing a large amount of CO_2. As an example, using the compositional model described in this paper, it is impossible to compute a dew point pressure as soon as the amount of CO_2 injected in the reservoir fluid is higher than 85%. Indeed, the saturation pressure becomes higher than 10^6 bar, which is the maximum working pressure of our software. This phenomenon is visible in Figure 3. A similar behavior was observed during the simulation of a swelling test when pure nitrogen (N_2) or pure hydrogen sulfide (H_2S) is injected. In this last particular case, it was thus decided to include the MMP in the fitting procedure. The results are given in Table 5. This table provides evidence that by fitting the critical pressure and the critical temperature of the $C_{11}-C_{19}$ pseudocomponent, it was possible

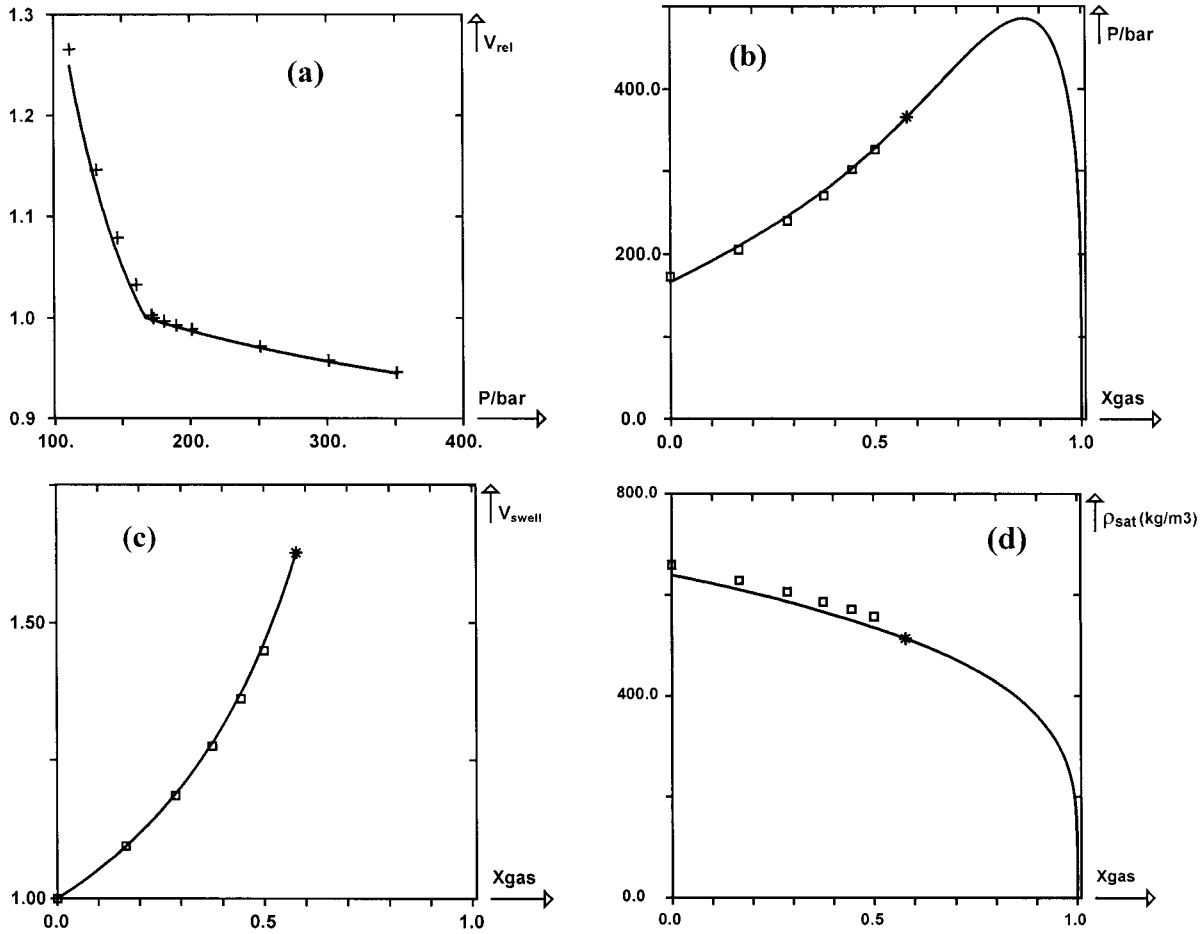

Figure 2. Illustration of the results obtained when two parameters are fitted on all the available experimental data points except the MMP. Symbols + and □ are the experimental data points. The continuous lines are the calculated values with the fitted parameters. (a) Constant mass expansion of fluid F6 at T/K = 383.15. The average deviation between calculated and experimental relative volumes is equal to 0.71%. (b−d) Swelling test performed on fluid F6 (gas G6b is injected). The average deviations of the saturation pressures, swollen volumes, and densities of the swollen oil are respectively equal to 1.91% (b), 0.42% (c), and 3.41% (d).

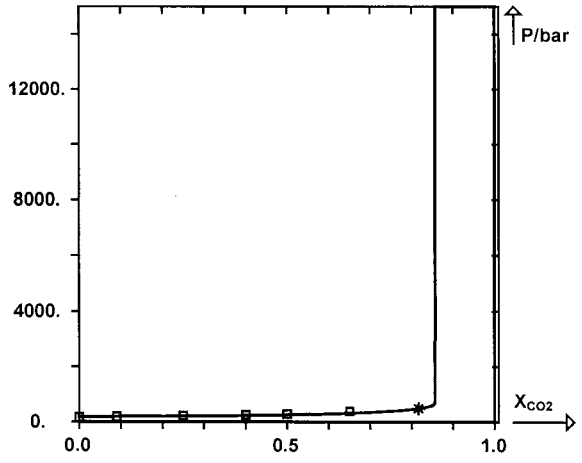

Figure 3. Swelling test performed on fluid F13 (pure CO_2 is injected): evolution of the saturation pressure versus quantity of injected gas. Experimental data points are shown as boxes. The continuous lines are the predicted values (the calculation becomes impossible as soon as x_{CO_2} becomes higher than 0.85).

to exactly match the experimental MMP value. However some other data, such as the bubble point reservoir pressure, are not reproduced very accurately. What is also here very interesting to outline is that the partial volumes during the MCT experiments are also very accurately calculated with the fitted parameters. Once more, there is a correlation between a good prediction of these relative volumes and the MMP. However because of the behavior shown in Figure 3, it was not possible to predict accurately the MMP after fitting two parameters on data which did not include the MMP.

Conclusion

In the first part of this paper, a slightly modified version of a previously developed compositional model coupled to a predictive cubic EOS is tested. Such a model is able to predict the classical *PVT* data (relative volumes, bubble pressures, swelling test data, . . .) with high accuracy. However, the partial volumes during a MCT and the MMP are not always precisely predicted. The classical solution for this kind of problem is to fit some parameters of the EOS on the experimental data in order to reduce the deviations between experimental and calculated values. When no other solutions were available, such a procedure was used with high success in this paper. In particular our software is uniquely able to take into account the MMP described by a mixed condensing/vaporizing mechanism in the fitting procedure. The main problem with such a procedure comes from the MMP needs to be experimentally determined. But because the determination of the MMP with a slim tube is a very expensive experiment, the petroleum companies wish to avoid such an experiment. This paper gives a solution to this problem. Indeed, we have shown that when the injected gas is not pure CO_2 (and probably

not pure N_2 or pure H_2S), it is enough to fit only two parameters of the EOS on data including classical PVT data + swelling data + MCT data and then to predict the MMP. During MCT experiments, this paper shows that it is very important to perform a few contacts (four contacts seems to be enough). We can then conclude that the slim tube test may be replaced by swelling tests and MCTs, which are much cheaper.

In conclusion, when the injected gas is not pure CO_2 (or N_2 or H_2S), it is not necessary to measure the MMP.

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