Properly Defining the Classical Vaporizing and Condensing Mechanisms When a Gas Is Injected into a Crude Oil

Jean-Noël Jaubert* and Lionel Arras

Laboratoire de Thermodynamique des Séparations, Institut National Polytechnique de Lorraine, Ecole Nationale Supérieure des Industries Chimiques, 1 Rue Grandville, 54000 Nancy, France

Evelyne Neau

Laboratoire de Chimie-Physique, Faculté des Sciences de Luminy, 163 Avenue de Luminy, 13288 Marseille Cedex 9, France

Laurent Avaullee

SE3T, 5 Boulevard Général Koenig, Résidence Michelet-Delattre, Bât. A9, 13009 Marseille, France

In this paper, real crude oils are dealt with which are modeled with an average of 30 components. On the selected examples, *neither* the initial tie line, i.e., the tie line that extends through the original oil composition, *nor* the gas tie line, i.e., the tie line that extends through the injected gas composition, controls the miscibility process. In any case, the miscibility process is controlled by one of the (nc − 3) crossover tie lines, if nc is the number of components in the crude oil. However, it is shown that the miscibility process may be a pure vaporizing gas drive mechanism (VGDM). To be more precise, it is shown that a mixed condensing/vaporizing mechanism may, with increasing pressure, turn into a pure VGDM. This means that the classical definition of a VGDM, i.e., the lowest pressure at which the initial tie line is critical, must be changed. This is the main point of this paper. In the case of a VGDM controlled by a crossover tie line, the MMP (the lowest pressure at which the key crossover tie line becomes critical) may still be computed by a one cell simulation algorithm. Another aim of this paper is to explain what really happens during a one cell simulation and to give proof that such an algorithm may not make critical the initial or the gas tie line.

Introduction

For many years, the mechanisms of development of miscibility have traditionally been simplified and described using ternary phase diagrams. This simplification relied on the apparent similar behavior of real fluids and ternary systems. In this approach, only two key tie lines may control the miscibility process: (1) the initial tie line, i.e., the tie line that extends through the initial oil composition; (2) the injected gas tie line, i.e., the tie line that extends through the injected gas composition. Under these conditions, the miscibility mechanism is respectively a pure vaporizing (VGDM) or a pure condensing (CGDM) gas drive mechanism. As a consequence, if the crude oil is modeled with only 3 pseudocomponents, the minimum miscibility pressure (MMP) may be accurately determined using a classical one cell simulation algorithm. Jensen and Michelsen[1] showed that a negative flash algorithm[2] might also be used for a VGDM.

In 1986, Zick[3] discovered a new combined process called the condensing/vaporizing mechanism (C/VM). This mechanism, which was observed on real petroleum fluids, cannot be explained using the classic ternary approach.

In 1997, Wang and Orr[4] worked on the transport equations of the displacement. A major result of their work was that the flow behavior in slim tube experiments is controlled by a sequence of (nc − 1) key tie lines if nc is the number of components in the oil. These key tie lines are the initial oil and the gas tie line, as well as (nc − 3) crossover tie lines as initially defined by Monroe et al.[5] Multicontact miscible displacement occurs when the pressure is increased sufficiently so that any one of these key tie lines becomes a critical tie line. That pressure is the MMP. To compute the MMP, Wang and Orr[4,6] on one hand and Jessen et al.[7] on the other have developed very fast algorithms based on location of key tie lines. Jaubert et al.[8] have also developed a simplified multicell approach.

The discovery of the existence of these (nc − 3) crossover tie lines by Professor Orr's research group, as well as the discovery of the mixed condensing/vaporizing mechanism (C/VM) by Zick, have profoundly changed the way of explaining the miscibility processes. This means that, a few years ago, many incorrect results were published. This paper seeks to correct some of them.

In this paper, devoted to real petroleum fluids modeled with a realistic $C_{11}+$ characterization, it is shown that care must be taken in determining what mechanism is controlling the development of miscibility. Indeed, in some papers, it is assumed that the process is (1) a mixed C/VM when a crossover tie line controls the miscibility and (2) a VGDM or a CGDM when the initial or the gas tie line, respectively, controls the process. Such an assumption is unfortunately not

* To whom the correspondence should be addressed. Fax: (+33)3 83.35.08.11. Phone: (+33)3 83.17.50.81. E-mail: jaubert@ensic.u-nancy.fr.

always true. For the crude oils selected in this study, a crossover tie line different from the initial or from the gas tie line always controls the miscibility process. However, in some cases the process may be a pure VGDM. More precisely, it is shown that a mixed C/VM may, with increasing pressure, turn into a pure VGDM. This means that the classical definition of a VGDM, i.e., the lowest pressure at which the initial tie line is critical, must be changed. A key point of this paper is thus to give a proper definition of the VGDM and CGDM for multicomponent systems.

This paper also comes back to the description of the one cell simulation algorithm which has been used for many years in petroleum companies in order to compute the MMP. In particular, it is shown that (1) such an algorithm may still be used to compute the MMP when a mixed C/VM turns into a VGDM and (2) such an algorithm does not often make critical the initial or the gas tie line but often makes critical the key crossover tie line which controls the miscibility process. In the case of a C/VM, such an algorithm overestimates the MMP but gives a value closer to the true MMP than the use of a negative flash making critical the initial or the gas tie line. Such results agree with those of Jensen and Michelsen,[1] who explained, ignoring the existence of the crossover tie lines, that a negative flash algorithm could lead to wrong MMP values. In other words, this paper also shows the use and limitations of a 1 cell simulator to compute the MMP.

Visualization of the Key Crossover Tie Line Controlling the Miscibility Process

For this study, three pairs of oil/gas fluids in the database of the French Petroleum Co. TOTAL SA were selected. The three MMPs were experimentally determined by a slim tube test. These crude oils will be noted O_1 to O_3 and the associated injection gases I_1 to I_3. Actually, O_1 and O_2 are strictly identical, but since two different gases (I_1 and I_2) were injected, it was found to be easier to understand if the oil had two different names. The molar compositions of all these fluids are summarized in Table 1.

The $C_{11}+$ characterization procedure developed by Jaubert[9] was applied for all the calculations. Previous papers[10-13] discussed the model's accuracy in predicting, first, the evolution of the relative volume during a constant mass expansion or a differential vaporization and, second, the behavior of the crude oil during a swelling test or a multicontact test. This characterization procedure models the $C_{11}+$ fraction with two pseudocomponents ("$C_{11}-C_{19}$" and "$C_{20}+$"). As the compounds we work with have widely varying volatility, no lumping method was applied. With such a composition model, crude oils are described with 28 or 29 compounds.

In many of their papers, Orr and co-workers[4,6,14,15] have already shown the crossover tie lines in phase diagrams. In this paper another approach is used. Indeed, an easy way to visualize the crossover tie lines is to simulate the slim tube by a series of mixing cells (cell to cell simulation). This approach was initially developed by Cook et al.[16] and then taken further by Metcalfe et al.[17] and Pedersen et al.[18] Such a simulation may be summarized as follows: In a first step, the program simulates a number of cells of equal volume in a series. The temperature and the pressure are the same in each cell, and the volume is kept constant. All

Table 1. Crude Oils and Injected Gases Composition (Mole Fractions) and Reservoir (Slim Tube Test) Temperature/K

compd	oils $O_1 = O_2$	oil O_3	gas I_1	gas I_2	gas I_3
H_2S	0.003 83		0.010 70		
N_2	0.004 50	0.004 50	0.010 10		0.004 90
CO_2	0.020 70	0.016 40	0.042 40		0.018 20
methane	0.265 76	0.458 50	0.564 70	0.880 00	0.813 90
ethane	0.078 94	0.071 50	0.151 50	0.070 00	0.091 50
propane	0.067 30	0.067 40	0.107 60	0.030 00	0.046 70
isobutane	0.014 85	0.008 40	0.019 20	0.005 00	0.012 40
butane	0.038 99	0.031 10	0.042 30	0.005 00	0.012 40
isopentane	0.019 37	0.010 30	0.014 40	0.005 00	0.002 00
n-pentane	0.025 05	0.016 50	0.015 30	0.005 00	0.002 60
2-m-pentane	0.017 83	0.012 80			
n-hexane	0.015 68	0.012 40	0.011 40		0.000 90
3-m-hexane	0.005 31	0.004 70			
benzene	0.005 38	0.002 40			
cyclohexane	0.022 29	0.022 30			
n-heptane	0.010 13	0.008 30	0.007 50		0.000 60
4-m-heptane	0.012 15	0.007 20			
toluene	0.010 04	0.007 40			
methylcyclohexane	0.010 65	0.020 20			
n-octane	0.008 49	0.008 00	0.002 90		0.001 30
4-m-octane	0.008 66	0.006 20			
ethylbenzene	0.010 43	0.009 20			
ethylcyclohexane	0.006 20	0.006 40			
n-nonane	0.005 22	0.005 20			
4-m-nonane	0.012 67	0.010 20			
propylbenzene	0.004 33	0.003 60			
n-decane	0.003 33	0.003 10			
$C_{11}-C_{19}$	0.162 30	0.104 00			
$C_{20}+$	0.129 62	0.061 80			
reservoir temp/K	394.25	387.45			

the cells initially contain the same fluid (the reservoir oil). A specified amount of gas is added to cell 1 (for instance 25% of the cell volume). It is assumed that perfect mixing takes place and that thermodynamic phase equilibrium is reached. This means that the conditions in the cell can be described by a P/T-flash calculation, here based on a modified Peng–Robinson equation of state.[19] After mixing of the injected gas and the cell fluid, the total volume of the cell will be larger than the assumed cell volume. The excess volume is transferred from cell 1 to cell 2. If two phases are present, the gas phase is moved first. If after moving all the gas phase the cell volume is still larger than the initial cell volume, a part of the liquid phase is also moved. In a second step, the excess volume formed in cell 2 is transferred to cell 3 and so on until production is obtained from the last cell. When one batch calculation has been completed, a new injection into cell 1 can take place and the cell to cell transfer calculation is resumed.

To visualize the different crossover tie lines, it is necessary to record in each cell (or in selected cells) a thermodynamic parameter versus time (proportional to the number of batch calculations). Moreover, the visualization of the numerous key tie lines requires good resolution, which can only be provided by a high number of cells. A typical value is 1000. As the simulation goes on, time is measured in terms of the total quantity of gas injected into the first cell since the beginning of the simulation. This quantity is expressed in "pore volume" in reference to the slim tube test. For instance, 4000 batch calculations are equivalent to one pore volume of gas when the tube is modeled with 1000 cells and when the amount of gas added to cell 1 at each batch equals 25% of the cell volume. As it is important to keep track of the simulation history, diphasic cells are characterized with an aggregate parameter that is recorded as a function of time. In this study, the parameter dc,
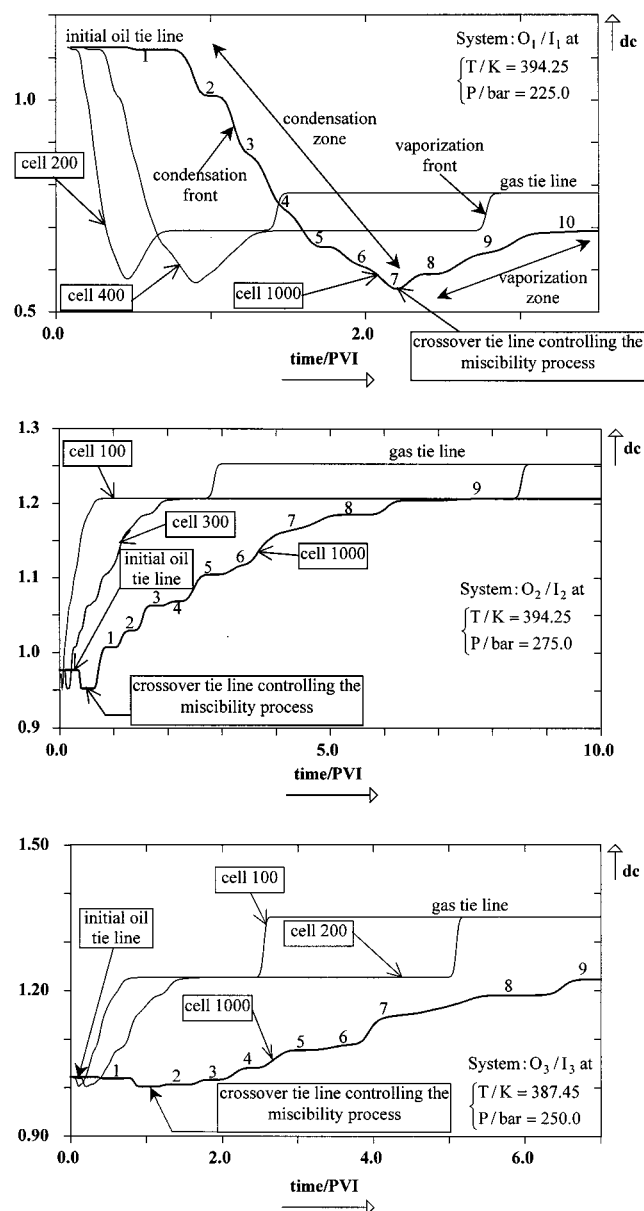
Figure 1. Visualization of the crossover tie lines by plotting the critical distance versus time in selected cells for the 3 investigated systems. Pressure and temperature are constant in each subplot.

defined by Zick (unpublished results) and called the critical distance, was used:

$$dc = \frac{\rho_{liquid\ phase} - \rho_{gas\ phase}}{^1/_2(\rho_{liquid\ phase} + \rho_{gas\ phase})} \qquad dc \geq 0 \qquad (1)$$

$\rho_{liquid\ phase}$ and $\rho_{gas\ phase}$ are respectively the liquid and gas phase density. If a cell becomes critical, both phases will have exactly the same density; thus, $dc = 0$. The closer the critical distance in a cell is to zero, the closer the fluid in this cell is to a critical point.

Figure 1 gives the evolution of dc versus time in selected cells for the three pairs of fluids. As they summarize the history of a selected cell throughout the simulation, they are generally called "history diagrams". Such plots are isothermal (the reservoir temperature was selected) and isobaric (a pressure far below the experimental MMP was chosen).

It can be easily demonstrated that the first tie line which is met in a history diagram (for small time values)

is the initial tie line. With increasing time, the diphasic fluid in a given cell will finally reach the gas tie line (see the right side of Figure 1). Moreover, Figure 1 evidences that the initial tie line (the first one) and the gas tie line (the last one) are connected by a sequence of condensation fronts (dc is decreasing) followed by a series of vaporization fronts (dc is increasing). A crossover tie line always stands between two consecutive fronts. As the total number of compounds nc is equal to 28 or 29, there should be 26 or 27 crossover tie lines. Because some fronts are propagating at very similar speeds, some of these key tie lines cannot be seen with our resolution: a larger number of cells would be required. As an example, in Figure 1, only 10 or 11 crossover tie lines can be seen. The crossover tie line that controls the miscibility process (the closest to a critical point), coincides with the minimum of dc in the history diagrams. It splits the curve into a condensation and a vaporization zone.

Notes: (1) In a vaporization front, the intermediate oil compounds are scrubbed by the gas. The rich gas then moves forward to the next cells and is replaced by some fresh light gas. Since in a given cell versus time, the oil gets heavier and the gas lighter, the vaporization emphasizes the composition difference between the liquid phase and the fresh gas entering the cell. A vaporization front is thus characterized by an increase in the critical distance. (2) In a condensation front, the intermediate compounds of the gas condense in the oil. The light gas then moves forward to the next cells and is replaced by some fresh rich gas. In a given cell versus time, the oil and the gas phase get richer in intermediate components. As a net result, the condensation reduces the composition difference between the liquid phase and the gas phase. The critical distance also decreases. During a cell to cell simulation, a condensation front is thus characterized by a decrease in the critical distance.

As a conclusion, three real pairs of fluids have been used to show that there is always a crossover tie line, the critical distance of which is smaller than the critical distance of the initial and of the gas tie line. This means that, in the composition space, such a crossover tie line is closer to the critical locus than the initial or the gas tie line. Since the MMP is defined as the lowest pressure at which any one of these key tie lines is critical, it is clear that in all cases a crossover tie line controls the miscibility process. Such a result is applicable to more than 90% of the real petroleum fluids of our very large database. In some rare cases the initial tie line may however control the miscibility process. If such a case appears, dc becomes (at pressures lower than the MMP) an increasing function of time, i.e., dc is formed by a single vaporization zone. At the time of writing, no real pairs of fluids for which the gas tie line controls the miscibility process have been found.

For the three examples selected in this study, at pressures lower than the MMP, the history diagrams are formed by a vaporization and a condensation zone. This does not mean however that the miscibility mechanism is a C/VM. Indeed, in the next section C/VM displacements will be investigated, which, with increasing pressure, turn into a pure vaporizing mechanism. For such displacements, the MMP can easily be calculated with a one cell simulation, even if a crossover tie line controls the miscibility process.

Table 2. Mechanism of Miscibility in a Ternary Approach with Value of the Calculated MMP$_{1cell}$ at the Reservoir Temperature

	system		
	O_1/I_1	O_2/I_2	O_3/I_3
mechanism in a ternary approach	CGDM	VGDM	VGDM
type of contact	backward	forward	forward
MMP$_{1cell}$/bar	312.91	497.21	444.35

Looking More Closely at the One Cell Simulation

This section aims to explain what really happens during a single cell simulation and considers such a simulation in a new perspective. Indeed, many years of practice on ternary diagrams have biased many researchers' understanding of this technique. As an example, it is possible to find written in recent papers the following:

(1) "*during a one cell simulation the pressure is increased until either the initial or the gas tie line is a critical tie line*". Proof will be given in the next section that such a sentence is never exact when one works on real petroleum fluids for which a crossover tie line controls the miscibility process.

(2) "*the one cell simulation works well as long as it is the oil tie line (vaporizing gas drive) or the injection gas tie line (condensing gas drive) that controls miscibility*". It is obvious that this sentence is both rigorous and exact. However, it will be shown that it is too restrictive since one cell simulations may work well even if a crossover tie line controls the miscibility process.

(1) Results of One Cell Simulations. To find out what tie line is made critical during a one cell simulation and in order to correctly know how to call the corresponding MMP, one cell simulations were performed with the three different systems O_1-I_1 to O_3-I_3 in order to determine the MMP$_{1cell}$. More information on this kind of calculation is given by Jensen and Michelsen[1] or by Neau et al.[20] In a ternary approach, the displacement mechanism for both O_2-I_2 and O_3-I_3 would be a vaporizing gas drive, which involves performing forward contacts. O_1-I_1 exhibits features of a CGDM; thus, backward contacts were performed. To find out when forward or backward contacts must be simulated, the criterion developed by Novosad and Costain[21] was used.

The MMP$_{1cell}$ values along with the mechanism of miscibility in a ternary approach are summarized in Table 2.

Figure 2 shows the evolution of the critical distance dc (defined in the first section) versus the contact number at different pressures for the three pairs of fluids investigated in this paper. Because of the logic of one-cell simulation, the curves in Figure 2b,c, defined for a *forward* one cell simulation, display the behavior of a cell that is moving on the edge of the gas front. Symmetrically, the curves shown in Figure 2a and defined for a *backward* one cell simulation display the behavior of a cell which is moving with the oil front if the tube was initially full of gas and if a mobile oil was injected at the entrance. In both cases, the cell under study propagates through out the tube and takes what one could imagine to be pictures (every contact being a new snapshot) of everything it meets on its way. Once put together in a chronological sequence, these pictures provide a view of the slim tube at a fixed time (after injection of a predetermined amount of fluid at the tube entrance). The curves in Figure 2 are not history diagrams as defined in the cell to cell simulation (Figure 1); they are usually called profile diagrams (evaluated at a fixed time). However the analogy between history and profile is strong: a history diagram is equivalent to watching a race from a fixed place (for example on the finish line), whereas a profile is equivalent to looking at the race only once, from a plane. If the pilot of the plane moves his eyes from left to right (he first sees the last runner), his picture of the race is equivalent to a profile obtained during forward contacts. Symmetrically, if he moves his eyes from left to right (he sees the first runner and then the last one), his picture of the race is equivalent to a profile obtained during backward contacts. The views obtained from a profile or from a history are strictly equivalent as long as passing is not allowed. From the above, histories and *forward* profiles may easily be compared if profiles are read from the right to the left. Symmetrically, histories and *backward* profiles may be directly compared, i.e., both read from left to right.

So doing, the first tie line encountered in Figure 2b,c is the initial oil tie line (located on the right of the figure). Still reading from right to left, dc first decreases, which reveals condensation fronts. At the end of condensation, the critical distance reaches its minimum. This valley is associated with the crossover tie line that controls the miscibility process. Finally, dc increases as it does for vaporization fronts. In Figure 2a, dc first decreases because condensation prevails. The critical distance then reaches its minimum and finally increases, highlighting a vaporization front.

Note: In Figure 2a, only one vaporization front is perceptible whereas four are visible in Figure 1a. This is because pressures in Figure 2a are higher than in Figure 1a and because the quantity of gas injected between two contacts during the one cell simulation is higher than during the multicell simulation.

Concerning the results of the 1 cell simulation, it can be concluded that, in any of the three plots of Figure 2, the minimum value of the critical distance does not match the values of dc for the initial or the gas tie line. This means that neither of these two tie lines controls the miscibility process. The appearance of a minimum in the variation of dc versus the contact number indicates that the displacement is controlled by a crossover tie line (a similar conclusion was given in the previous section). However, it does not imply that the process is a mixed C/VM.

Some curves in Figure 2 were computed at pressures that are just 0.01 bar below the MMP$_{1cell}$. Looking more closely at these plots, it is obvious that neither the initial (Figure 2b,c) nor the gas (Figure 2a) tie line is critical at the MMP$_{1cell}$. However the key crossover tie line is critical (at a pressure strictly equal to the MMP$_{1cell}$, the minimum value of dc is equal to zero).

As a fundamental conclusion, proof was given that (1) a one cell simulation makes critical the key crossover tie line which controls the displacement and (2) during a one cell simulation the pressure is not increased until either the initial or the gas tie line becomes critical. To make such a tie line critical would require a negative flash algorithm at pressures much higher than the MMP$_{1cell}$ (see Figure 3a–c). As a consequence, a negative flash algorithm may calculate the true MMP only if the initial or the gas tie line controls the miscibility
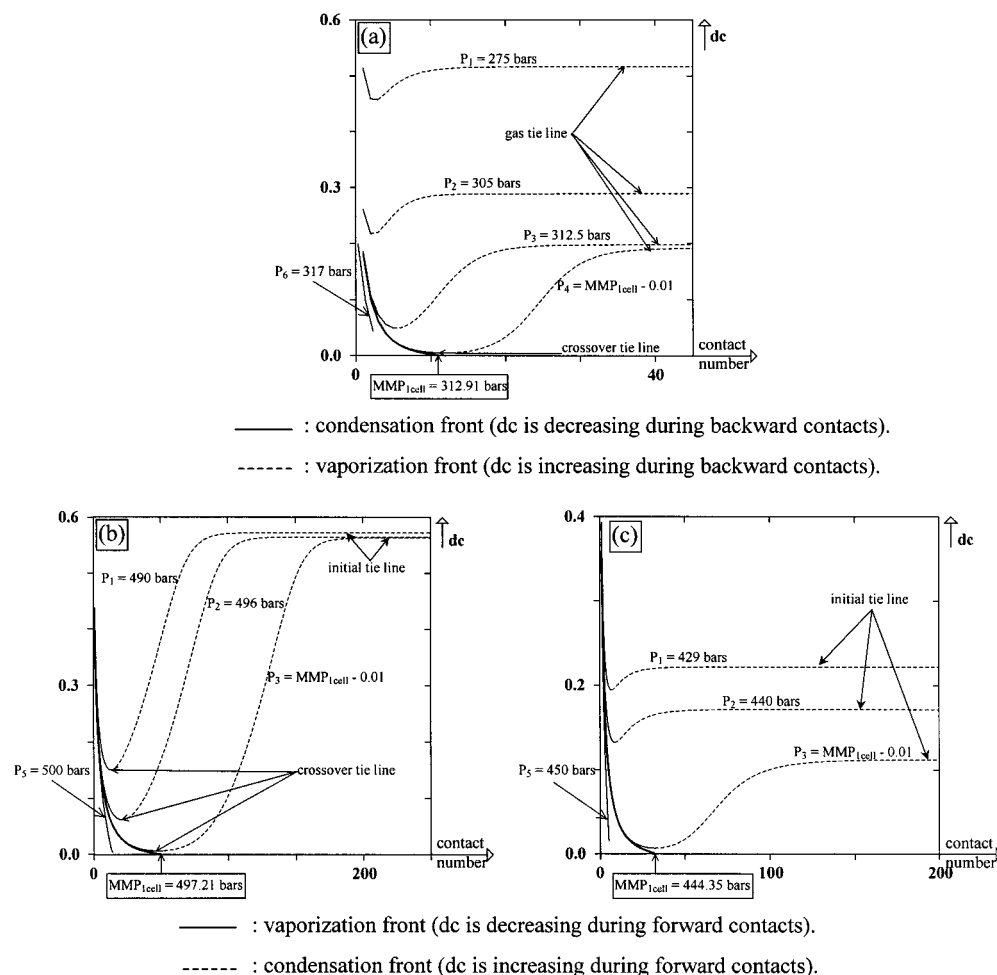
Figure 2. Evolution of the critical distance versus the contact number during isothermal one cell simulations performed at different pressures (isothermal profile diagrams): (a) fluids O_1-I_1 at $T/K = 394.25$ (backward contacts are performed); (b) fluids O_2-I_2 at $T/K = 394.25$ (forward contacts are performed); (c) fluids O_3-I_3 at $T/K = 387.45$ (forward contacts are performed).

process, but these two extreme cases have practically never been observed with real fluids.

Note: As explained previously, in some rare cases (not shown in this paper), the initial tie line may control the miscibility process. In such a case, it is obvious that a one cell simulation makes critical such a tie line (a ternary behavior is observed).

The paramount question that must be addressed is "is the MMP_{1cell} the true MMP?" or in other words "is there a pressure lower than the MMP_{1cell} at which the key crossover tie line is critical?" An answer to this question is given in the next section.

(2) A Proper Definition of the Vaporizing and Condensing Processes. In Figure 2, at a pressure strictly equal to the MMP_{1cell}, the cell is critical after a few contacts. At this pressure, the critical distance has then become a monotonic decreasing function of the contact number. This means that the MMP_{1cell} may be defined in a general way as the lowest pressure at which the following holds:

(a) The condensation front(s) have disappeared if forward contacts are made. Because miscibility is reached by vaporization front(s) only, this pressure must be called the vaporizing minimum miscibility pressure ($MMP_{1cell} = MMP_{vaporizing}$). In other words, the vaporizing MMP must *not* be defined as the smallest pressure at which the initial tie line is critical but as the smallest pressure at which miscibility is reached by vaporization fronts only.

(b) The vaporization front(s) have disappeared if backward contacts are performed. Because miscibility is reached by condensation front(s) only, this pressure must be called the condensing MMP. Performing backward contacts: $MMP_{1cell} = MMP_{condensing}$. In other words, the condensing MMP must *not* be defined as the smallest pressure at which the gas tie line is critical but as the smallest pressure at which miscibility is reached by condensation fronts only.

(3) Is the MMP_{1cell} the Correct One? At this stage, to answer this question it was decided to compute the MMP using a standard 1D simulator. Such a simulator was used in order to have reference values for the true MMP and later on to prove that the MMP_{1cell} may be correct. Dispersion effects were reduced by extrapolation of the recovery factors to an infinite number of cells as explained by Whitson.[22] The results are listed in Table 3. For the sake of comparison, the values of MMP_{1cell} are also reprinted.

As far as system O_1/I_1 is concerned, the condensing MMP may *not* be regarded as satisfactory. In Figure 2a, one of the curves ($P = P_1$) was computed at the actual MMP. At this pressure, the dc parameter is still a decreasing–increasing function of the contact number. In addition, a plot of the density of the liquid and gas phase in equilibrium in the single cell during a 1 cell simulation performed at the true MMP is shown in Figure 4a. From this figure, it is clear that the densities of the phases in equilibrium in the single cell converge
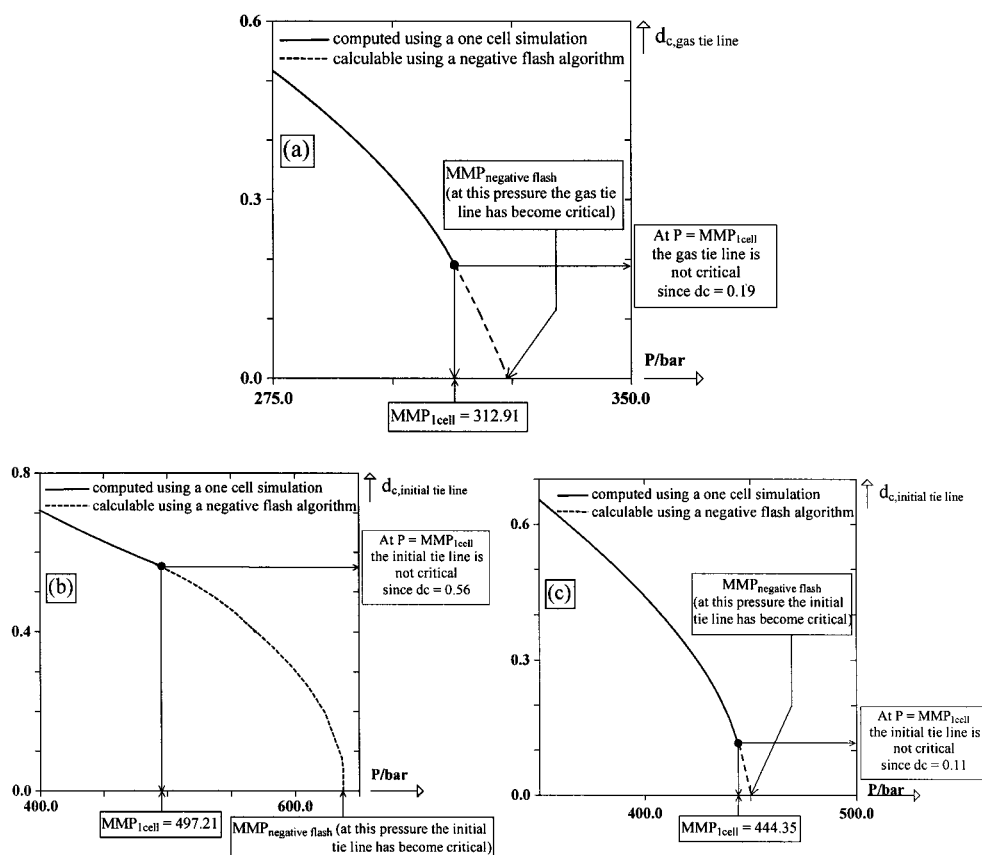
Figure 3. Evolution of the critical distance when liquid and gas phases are located either on the gas (a) or on the initial tie line (b, c) versus pressure: (a) fluids O_1–I_1 at $T/K = 394.25$ (backward contacts are performed); (b) fluids O_2–I_2 at $T/K = 394.25$ (forward contacts are performed); (c) fluids O_3–I_3 at $T/K = 387.45$ (forward contacts are performed).

Table 3. Comparison of the MMP_{1cell} and of the True MMP

system	true MMP/bar (1D simulator)	MMP_{1cell}/bar
O_1/I_1	275.0	$312.91 = MMP_{condensing}$
O_2/I_2	497.2	$497.21 = MMP_{vaporizing}$
O_3/I_3	429.0	$444.35 = MMP_{vaporizing}$

during the first few contacts and then diverge. This simulation, *performed at the true MMP*, indicates that the mechanism is a real mixed C/VM. Since at the true MMP, a critical point is not reached in the single cell, a one cell simulator cannot lead to the actual MMP (the 1D simulator made the key crossover tie line critical at a pressure much lower than the MMP_{1cell}).

The result obtained for system O_1/I_1 is widely applicable. Indeed, working on real petroleum fluids modeled with a realistic number of components, it seems that the condensing mechanism does not exist and is always replaced by a mixed C/VM. Moreover the true MMP ($MMP_{C/VM}$) is always much lower than the condensing MMP.

O_3/I_3 is very similar to O_1/I_1 despite different ternary mechanisms. Figure 2c ($P = P_1 =$ true MMP) and Figure 4c exhibit the features of a real C/VM. Nevertheless, the MMP_{1cell} and the true MMP are much closer for O_3/I_3 than they were for O_1/I_1. When the displacement mechanism is a C/VM, $MMP_{C/VM}$ is always smaller than $MMP_{vaporizing}$. However the difference between these two values may be small since when a C/VM takes place instead of a pure VGDM, condensation often plays a minor role.

The vaporizing MMP for O_2/I_2 matches the correct MMP even if it was seen before that the miscibility

process is controlled by a crossover tie line. The two values coincide because the mechanism is a pure VGDM: in Figure 2b ($P = P_4$), the dc parameter is, as expected, a decreasing function of the contact number. In Figure 4b, the densities of the phases in equilibrium in the single cell close together until they become identical (a critical point is reached). What is fundamental to outline here for system O_2/I_2 is that at pressures lower than the true MMP = MMP_{1cell} the process is in fact a mixed C/V process (see Figure 2b—$P = P_1$, P_2, P_3—where dc is a decreasing–increasing function in the single cell). However with increasing pressure, this combined mechanism turns into a pure vaporizing mechanism since at the true MMP (the lowest pressure at which the key crossover tie line is critical) all the condensation fronts have disappeared. To our knowledge the evidence of a pure vaporizing mechanism controlled by a crossover tie line has not been reported previously. Only one example is shown here, but such a process is not uncommon. In this section proof was thus given that a 1 cell simulation might work well even if a crossover tie line controls the miscibility.

Remark: For the three systems investigated the following holds:

(a) A crossover tie line controls the miscibility process. This means that at any pressure lower than the MMP_{1cell}, during a one cell simulation, the densities of the phases in equilibrium in the single cell converge during the first few contacts and then diverge.

(b) In the same way at a pressure strictly equal to the MMP_{1cell}, the densities of the phases in equilibrium in the single cell converge until they become identical.
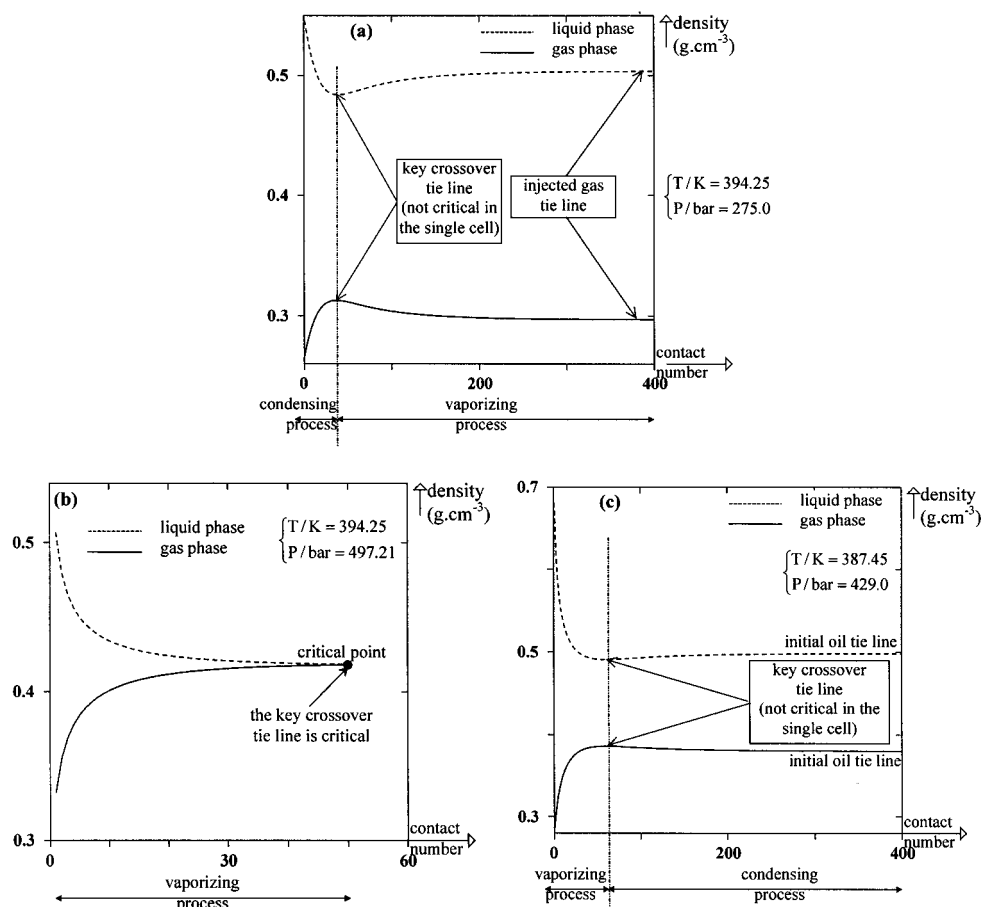
Figure 4. Evolution of the densities of both phases in equilibrium versus the contact number during isothermal one cell simulation performed at the true MMP: (a) Fluids O_1-I_1 at $T/K = 394.25$ (backward contacts are performed); (b) Fluids O_2-I_2 at $T/K = 394.25$ (forward contacts are performed); (c) fluids O_3-I_3 at $T/K = 387.45$ (forward contacts are performed).
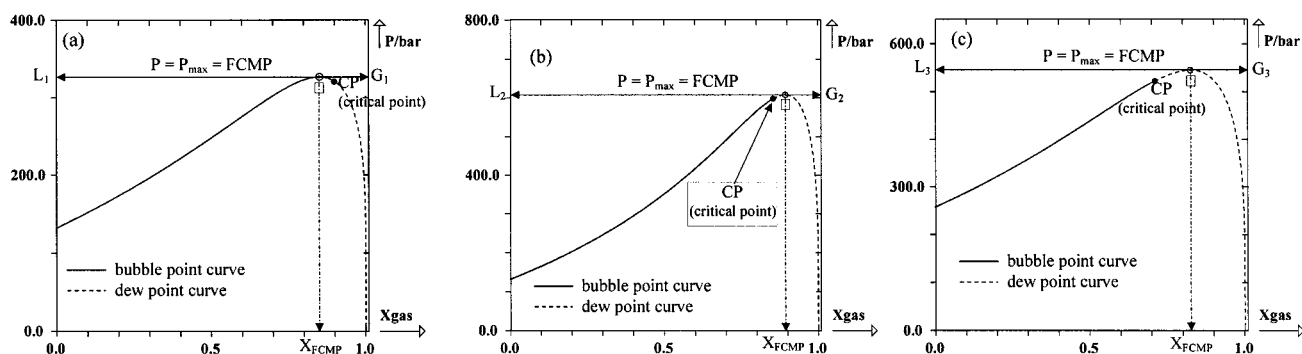

Figure 5. Isothermal P–X curves as obtained during a swelling test for the three systems investigated. The reservoir temperature was selected. (a) The cricondenbar (P_{max}) is located on the bubble curve: backward contacts must be performed to calculate the condensing MMP. (b, c) The cricondenbar (P_{max}) is located on the dew curve: forward contacts must be performed to calculate the vaporizing MMP.

The crossover tie line controlling the process has thus become critical (a figure similar to Figure 4b would be observed for the three systems).

However, for systems O_1/I_1 and O_3/I_3 at the true MMP, a critical point is not reached in the single cell, meaning that the process is a C/VM whereas for system O_2/I_2 such a critical point is reached, meaning that the process is a pure VGDM controlled by a crossover tie line.

Since MMP_{1cell} sometimes equals the true MMP, a fast and reliable algorithm that computes its value is proposed in the next section. A way of easily finding out if such a value matches the true MMP is also explained.

(4) Computation of a Fast One Cell Simulator: Determination of the Miscibility Mechanism. The process mechanism, the value of MMP_{1cell}, and the confirmation of whether this value is correct are obtained through the following steps:

Step 1: Calculation of the FCMP (first contact minimum miscibility pressure). The FCMP is defined as the lowest pressure at which the injection gas $G°$ and the crude oil $L°$ are first contact miscible. This pressure may be easily determined by simulating a swelling test and locating the stationary point at the top of the P–X diagram as shown in Figure 5. Indeed, the FCMP coincides with the cricondenbar P_{max} (the maximum two phases pressure).

In such a diagram, the amount of injected gas, noted as X_{gas} is defined by:

X_{gas} = [number of moles of gas]/
[number of moles of gas +
number of moles of reservoir crude oil]

Once the FCMP is known, a P−T flash calculation is to be performed at the reservoir temperature and at a pressure just below the FCMP for a fluid of global composition $Z = X_{FCMP}G° + (1 − X_{FMCP})L°$. In the previous expression, X_{FCMP} is the cricondenbar abscissa in the P−X diagram. Such a point is represented by a square in Figure 5. The output of this two phase flash calculation reveals whether the cricondenbar is located on the bubble curve (the amount of liquid is close to 100%) or on the dew curve (the amount of gas is close to 100%). Indeed, in 1988, Novosad and Costain[21] demonstrated the following:

If the cricondenbar (P_{max}) is located on the bubble curve (see Figure 5a), the process is a CGDM rather than a VGDM. Under these conditions, backward contacts must be performed to determine the MMP_{1cell}, and in such a case $MMP_{1cell} = MMP_{condensing}$. As previously explained, working on real petroleum fluids, such a MMP is never the true MMP and in such a case the process is always a mixed C/VM. The correct MMP, always smaller than the $MMP_{condensing}$, must be determined by a 1D simulator or by the key tie line intersection approach.

If the cricondenbar is a dew point (see Figure 5b,c), the process is a VGDM rather than a CGDM. Forward contacts must be performed to determine the MMP_{1cell} and in such a case $MMP_{1cell} = MMP_{vaporizing}$. Such a MMP may be the correct one (see below).

In all cases MMP_{1cell} < FCMP.

Notes: (1) If the cricondenbar is found on the bubble curve and if forward contacts are simulated, the MMP_{1cell} will always equal the FCMP. Symmetrically, if the cricondenbar in the P−X diagram is located on the dew curve and if backward contacts are simulated, MMP_{1cell} = FCMP should always be computed. This remark applies whatever the fluids and the displacement mechanism. If the cricondenbar and the critical point in the P−X diagram are merged, $MMP_{1cell} = MMP_{vaporizing} = MMP_{condensing}$ = FCMP will be observed. (2) The relative position of the initial and gas tie lines on the history diagram (as in Figure 1) may be misleading if one wants to find out if the process is rather a VGDM or a CGDM. Examples were found for which $d_{c,gas\ tie\ line} < d_{c,initial\ tie\ line}$ and $MMP_{VGDM} < MMP_{CGDM}$ = FCMP.

Step 2: Isothermal forward or backward contacts are to be simulated at pressures lower than the FCMP. For a given pressure, after each contact the value of the critical distance dc in the cell (compulsory diphasic) is to be recorded versus time (i.e. versus the contact number).

Different cases may appear as follows.

Case 1: At the working pressure, after a few contacts, the cell remains monophasic whatever the quantity of fluid that is added (original oil for forward contacts or injection gas for backward contacts). The critical distance will always be a decreasing function of the contact number which shows that either a vaporization front (forward contacts) or a condensation front (backward contacts) is being simulated. In this case, the pressure is higher than the MMP_{1cell} and a new lower pressure must be chosen.

Case 2: The critical distance first decreases, then reaches a minimum, and finally increases until it hits the initial or the gas tie line (depending on the contact type). In such a case, a crossover tie line controls the miscibility process. As soon as the dc function starts increasing, the simulation can be stopped because the working pressure is lower than the MMP_{1cell}. A higher pressure has to be chosen for the next simulation.

Case 3: The dc function is a monotonic decreasing function of the contact number, and after many contacts, the composition of both phases in equilibrium in the cell remains the same (dc is constant). In this case if forward contacts are performed, the mechanism is a vaporizing process and the initial tie line controls the miscibility process (rarely observed), or if backward contacts are performed, the mechanism is a condensing process and the gas tie line controls the miscibility process (never observed with the fluids of our database).

The MMP_{1cell} will be the correct MMP. A direct tie line approach like a negative flash algorithm may also be used to compute the MMP.

Step 3: Once a pressure higher (step 2, case 1) and a pressure lower than the MMP_{1cell} (step 2, case 2 or 3) have been found, a simple dichotomy makes it easy to find the MMP_{1cell}. In all cases, it will be found that MMP_{1cell} < FCMP.

Notes: (1) It was observed that pressure does not affect the relative position of the key crossover tie lines. Increasing pressure, a pure VGDM that is controlled by a crossover tie line, will never turn into a VGDM that would be controlled by the initial tie line. (2) In the case where $MMP_{1cell} = MMP_{vaporizing}$, a 1-D simulator may be used to check if the value is correct. It is recommended that a simulation at $P = 0.97 MMP_{vaporizing}$ be run first. By the end of the computation, if the dispersion-free recovery factor is close to 100%, then the mechanism is a mixed C/VM. On the other hand, if the dispersion-free recovery factor is significantly less than 100%, the process is a pure VGDM and the MMP_{1cell} is the correct value. This means that if a 1D simulator is normally used to compute the MMP, it is advised to first compute the MMP_{1cell} with the proposed algorithm (a few seconds are needed) and to make a single run at $P = 0.97 MMP_{vaporizing}$. By the end of this single run, it will be possible to determine whether the MMP_{1cell} is the correct one. If this is the case, further 1D simulator runs at different pressures will not be necessary.

If an algorithm based on location of key tie lines is normally used to determine the MMP, it will be only necessary to make a one cell simulation at this pressure to determine the correct mechanism (see the discussion relative to Figure 4).

Significant acceleration of the one-cell simulator could be achieved if the MMP_{1cell} did not depend on the mixing proportions. The next paragraph addresses this issue.

When a vaporizing process is simulated, the cell is full of saturated gas from the previous contact. At each new contact, a given amount of original oil is added so that a new diphasic fluid may form. If the oil addition is very small compared with the gas quantity, the new fluid will be close to a dew state (the result of the flash calculation will indicate that the cell is essentially formed by a gas phase in equilibrium with a very small amount of liquid phase). Such contacts are called nonoptimized contacts in the following text. Another option is to add as much oil as possible so that the cell gets very close to a bubble state (the flash calculation
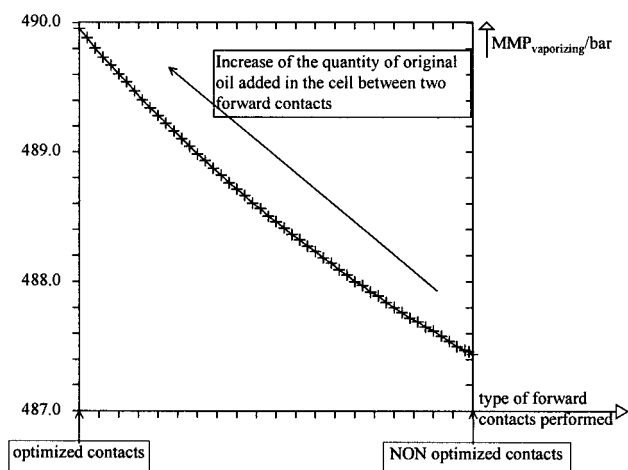
Figure 6. Evolution of the vaporizing MMP versus the type of contacts (optimized or not) performed.

will indicate that the cell is essentially formed by a liquid phase in equilibrium with a very small amount of gas phase). Such contacts are defined as optimized contacts.

Numerous simulations were performed on real petroleum fluids in order to determine if the type of contact could influence the value of MMP_{1cell}. It was found that the type of contact hardly changed the MMP_{1cell}. The optimized contacts overestimate the MMP_{1cell} by less than 0.5% when the displacement is controlled by a crossover tie line and do not have any influence at all when either the initial or the gas tie line controls the miscibility process.

Figure 6 is representative of the results obtained. In this study, a separator gas was injected into a real crude oil. Optimized contacts were made first and the calculated vaporizing MMP was 490 bar (see the left of Figure 6). In a second step, nonoptimized contacts were performed: each time the quantity of original oil that was added was close to zero. The MMP_{1cell} that came out was 487.4 (see the right of Figure 6). Finally, all the intermediate situations were described to get the quasi continuous curve in Figure 6.

Since, when forward contacts are performed, the influence of the quantity of oil added may be neglected, it is advised, to reduce considerably calculation time (the number of contacts, at a given pressure), to perform optimized contacts i.e., to always inject the maximum quantity of original oil (forward contacts) or the maximum quantity of injection gas (backward contacts) in order to obtain a diphasic cell. The difference in calculation time when performing optimized or non optimized contacts may be higher than a ratio of one thousand.

Conclusion: Optimized contacts vastly reduce the time required to compute MMP_{1cell}. It takes only few seconds on a PC with a Pentium II processor whereas it can still be a matter of hours with nonoptimized contacts.

Conclusion

This study devoted to multicomponent fluids has demonstrated different key points which are summarized below:

In all the studied cases, a *crossover* tie line different from the initial or the gas tie line controls the miscibility process. As a consequence, it is never possible to use a direct tie line approach based on a negative flash

algorithm to determine the true MMP. Indeed such an algorithm would make critical the initial or the gas tie line and would overestimate the MMP.

The process was found to be either a pure VGDM or a mixed C/VM. This means that, contrary to what is currently explained in the literature, a pure VGDM may develop even when the initial tie line does not control the miscibility process. In such a case, a one cell simulation algorithm is sufficient to calculate the true MMP.

The definition of the pure VGDM or pure CGDM, currently available in the literature, i.e., the lowest pressure at which the initial oil or gas tie line, respectively, is critical, needs to be changed. Being conscious that, when working on multicomponent systems, a crossover tie line usually controls the miscibility process, a new definition of both of these mechanisms was given.

When a vaporizing mechanism controlled by a crossover tie line takes place: condensation and vaporization fronts are observed during a one cell simulation at pressures lower than the true MMP. At a pressure strictly equal to the true MMP, all the condensation fronts have disappeared, meaning that in all cases a C/VM has turned into a pure vaporizing process.

Contrary to what may be found in the literature, it was shown that during a static (one cell) multicontact process, if the pressure is increased to the first point where the process leads to a miscible condition, neither the injection gas nor the crude oil is on a critical tie line extension. This means that in the one cell simulation it is the key crossover tie line that is made critical and not the initial or the gas tie line. To be very precise, it is recalled that if the initial or the gas tie line effectively controls the miscibility process, a 1 cell simulator obviously makes such a tie line critical. Such a ternary behavior is however very rare (not observed with the fluids used in this study).

A single cell multicontact algorithm may be a helpful tool to determine the miscibility mechanism. In particular, if the MMP is normally computed with an algorithm based on the location of the key tie lines, a single cell simulation performed at the MMP will indicate easily the process mechanism.

If the MMP is normally computed with a 1D simulator, a single run at $P = 0.97MMP_{vaporizing}$ will indicate whether the MMP_{1cell} determined using a single cell simulator is the correct one. In doing so, further runs at different pressures with the 1D simulator will not be necessary.

Using a realistic modeling of the different fractions, the pure CGDM was never observed (it probably does not exist).

The mixed C/V process may replace either a pure CGDM or a pure VGDM. It is the most common mechanism.

If the displacement mechanism is a pure VGDM, it is always observed that FCMP > MMP_{1cell} = $MMP_{vaporizing}$. If the process is a mixed C/V mechanism, it is always observed that FCMP > MMP_{1cell} > $MMP_{C/VM}$ (true MMP). In the latter case a 1D simulator, a multicell approach[8] or an algorithm based on location of key tie line must be used to compute the MMP.

The only way to know whether a displacement mechanism is rather a pure VGDM than a pure CGDM is to locate the cricondenbar in the P−X diagram. For example, if $MMP_{vaporizing}$ < $MMP_{condensing}$, it does not mean that the critical distance corresponding to the

initial tie line is smaller than the one of the gas tie line. Using a ternary approach, i.e., focusing only on the initial and on the gas tie line, if such case appeared (initial tie line "less critical" than the gas tie line), it would be concluded that the mechanism is rather a CGDM than a VGDM, which may be incorrect.

Another important conclusion of this paper is that when working on multicomponent systems, it is necessary to forget the ternary systems and diagrams. The essential reason is that when working on ternary systems, only the initial or the gas tie line may control the miscibility process, whereas working on real fluids neither of these key tie lines are generally helpful.

Acknowledgment

Nomenclature

dc = critical distance
P = pressure
P_{max} = cricondenbar in the P−X diagram
T = temperature
X_{gas} = relative amount of injected gas

Greek Letters

ρ = density

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