THE THERMODYNAMICS OF ENHANCED OIL RECOVERY PROCESSES

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الميكانيكية الحرارية في عمليات الإسترداد الإضافي

روبنسن د. ب، كالوا ه.

تراجع هذه الورقة العلمية الطور السلوكي لخلائط مذيبات الزيت وعلاقتها بعمليات الإسترداد الإضافي. وتقدم الورقة أيضاً نموذجاً لحجب الطور لخليط الهيدروكربونات الشطرية وخلائط الزيت مع المذيبات الهيدروكربونية وغاز ثاني أكسيد الكربون.

المعلومات المدرجة في هذه الورقة جمعت من تجارب دراسات الإسترداد الإضافي لموائع مكمن جنوب شرق حقل الناصر مع دراسات مذيب الغاز الطبيعي المسيل/والغاز الجاف وثاني أكسيد الكربون. اختبارات الإنتفاخ، قياسات إنزان الطور، وإختبارات الأنابيب الدقيقة أجريت باستخدام كلا من المذيبين.

وخلاصتاً وجد أن كلا من الحد الأدنى لمحتوى الإمتزاجية للغاز الطبيعي المسيل في المذيب والحد الأدنى لضغط الإمتزاجية عند إستعال غاز ثاني أكسيد الكربون تقع في نفس الظروف التي عندها نتائج التوقعات النظرية في الحقيقة تدل على حدوث إمتزاج.

وبالرغم من هذا، كل المؤشرات تقترح حدوث إزاحات بكفاءة عالية. نتائج الملاحظات المرئية (البصرية) والحسابات الممثلة ببيانات للمركب الثلاثي تدل على أن إزاحة الهيدروكربونات حدث كنتيجة لنوع من الميكانيكية الموحدة للبخر المكثف.

تفصيل طبيعة ميكانيكية الإزاحة في وجود غاز ثاني أكسيد الكربون تبدو أنها معتمدة على الكمية النسبية للمركبات الخفيفة مقارنة بالمركبات الثقيلة للزيت الأصلي.

ABSTRACT

The phase behavior of solvent-oil mixtures as it relates to enhanced oil recovery operations is reviewed. Typical phase envelopes for a model binary hydrocarbon mixture and for a model binary hydrocarbon mixture and for mixtures of an oil with a hydrocarbon solvent and with ${\rm CO}_2$ are presented.

Experimental data were obtained for an enhanced oil recovery study of the South East Nasser reservoir fluid with a NGL/Dry Gas solvent and with CO₂. Swelling tests, phase equilibrium measurements and slim tube runs were conducted with both solvents.

It is concluded that the minimum miscibility content of NGL in the solvent and the minimum miscibility pressure when using ${\rm CO_2}$ both occur at conditions where theoretical predictions would suggest that misci-

bility has in fact not been achieved. Nevertheless, all key indicators would suggest very efficient displacements supported also with high displacement efficiencies.

A combination of visual observations and calculations represented on a pseudo ternary component diagram suggest that the hydrocarbon displacements correspond to a combined condensing-vaporising type mechanism.

The detailed nature of the displacement mechanism in the presence of carbon dioxide is shown to depend on the relative amount of the lighter compared to the heavier components in the parent oil.

INTRODUCTION

The successful evaluation of the potential for enhanced oil recovery from a conventional reservoir relies on the development of appropriate tools for

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predicting future reservoir performance. The development of these tools requires specific information relating to the reservoir rock characteristics, the reservoir fluid and injection fluid properties and the interaction between these variables. The interaction between the injection solvent and the reservoir fluid is usually quantified through experimental laboratory measurements.

The development of a suitable program of study and the interpretation of the results requires that certain assumptions be made with respect to the nature of the solvent-oil interactions and of the subsequent oil displacement. Two of the more widely assumed mechanisms are the condensing drive and the vaporizing drive. These have been discussed in detail by several authors [1, 2, 3, 4, 5, 6, 7, 8, 9].

Recently, considerable discussion has also been given to combined condensing-vaporizing [1, 10, 11] drive mechanisms.

Traditionally, enriched hydrocarbon solvent injection fluids have been thought to result in a condensing drive mechanism and carbon dioxide has been considered to result in a vaporizing drive mechanism. The essential distinguishing feature of these different modes of contact is the behavior of the intermediate (C2-C5) fraction at the point of contact between the solvent and the oil. In a vaporizing drive, there is a net gain in intermediate fraction components in the vapor phase relative to the solvent and in the condensing drive, there is a net gain of intermediate components in the liquid phase relative to the oil. In either case, the equilibrium vapor phase is assumed to move preferentially through the formation. Precise definition of the contacting mechanism has remained elusive because of the lack of experimental evidence on the in-situ nature of the transition zone between the solvent and the oil within the reservoir. We believe the results we are reporting in this paper shed some light on the problem.

The basis for our discussion rests primarily on an extensive enhanced oil recovery study recently carried out on the South East Nasser reservoir oil using both enriched hydrocarbons and carbon dioxide as solvents.

DISPLACEMENT WITH HYDROCARBON SOLVENTS

Fluids

The compositions of the enriched hydrocarbon solvent and the reservoir oil are given in Table 1. However, before examining the swelling and slim tube tests conducted with these fluids, it may be instructive to examine the phase behavior of solvent-oil mixtures.

Table 1. Injection Solvent and Oil Composition

	Concentration, Mole%		
Component	Solvent	Reservoir Oil	
CO ₂	2.17	1.41	
H2S	0.45	1.16	
N2	1.10	0.47	
C1	53.58	18.99	
C2	11.92	9.04	
C3	13.07	5.08	
IC4	5.54	1.76	
NC4	11.26	2.34	
IC5	0.45	2.35	
NC5	0.46	1.34	
C6		4.83	
C7-9		14.46	
C10-14		15.97	
C15-20		9.56	
C21-29		6.36	
C30+		4.88	

Thermodynamic Behavior

For illustrative purposes we could consider a very simple binary system consisting of ethane as the solvent and n-heptane as the oil.

Thermodinamically, the behavior of this system can be represented in three dimensional space in pressure-temperature-composition coordinates. However, it can also be represented in two dimensional space on pressure-temperature coordinates if all composition variables are projected onto the plane. This has been done for selected mixtures of ethane and n-heptane in Fig. 1. Figure 1 shows how the pure solvent (ethane) and the pure oil (n-heptane) are represented by their vapor pressure curves, whereas any mixtures of the solvent and oil are represented by a phase envelope consisting of a bubble point locus, a critical point and a dew point locus.

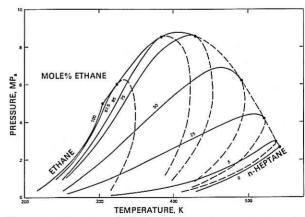


FIG. 1. The phase behavior of the ethane-n-heptane binary system.

A swelling curve for ethane in n-heptane can be envisaged by looking at the points of intersection of an isothermal plane, for example at 350K, with the bubble point locus or the retrograde dew point locus for mixtures successively more rich in ethane. Such a swelling curve is shown in Fig. 2. It will also be noted that there will be one mixture, i.e. one solvent-oil composition that will have its critical temperature at the temperature in question.

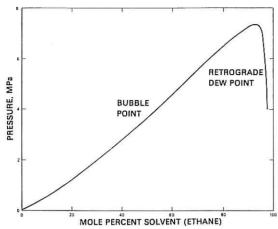


FIG. 2. A simulated swelling curve for a solvent (ethane) in an oil (n-heptane) at 350K.

The thermodynamics of the solvent-SE Nasser oil system can also be viewed in the same way in two-dimensional space. Here the solvent and the oil are multicomponent mixtures each having its own phase envelope and critical point rather than a vapor pressure curve with its critical point. These phase envelopes are shown in Fig. 3 together with phase envelopes for representative mixtures of the solvent and oil. Again, the points of intersection of an isothermal plane at 350K with the bubble point or retrograde dew point loci would represent a typical swelling curve for this system on pressure-solvent concentration coordinates. Such a curve for this system is shown later.

It may also be seen from Fig. 3 that there will be one mixture of solvent and oil which will have its

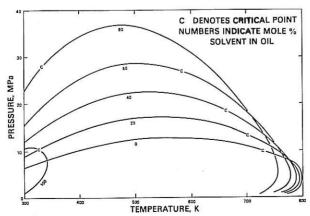


FIG. 3. The influence of hydrocarbon solvent content on the phase behavior of SE Nasser reservoir fluid.

critical point at 350K. By interpolation, this would be a mixture containing about 78 mole% solvent and 22 mole% oil.

Swelling Test

A conventional swelling test was conducted using the solvent and SE Nasser oil defined in Table 1 at a temperature of 350K. The solvent concentrations examined were 15.0, 30.0, 45.6, 62.0 and 8.0 mole%. One of the primary objectives in conducting the swelling test is to obtain data which can be used to characterize the fluids. Thus any phase behavior package such as our EQUI-PHASE [12] phase behavior package can be tuned so that it can be used to predict the behavior of the solvent-oil system. The reason for including the one very high solvent concentration was to make sure some data would be available in the retrograde region. This was considered important because somewhere during the displacement process the solvent concentration was expected to be in the range where retrograde fluids would exist. This condition would normally be encountered in the trailing end of the transition zone.

In addition to the saturation pressure being determined at each solvent concentration, the 62 mole% mixture was analyzed at the saturation pressure of 20.86 MPa and then equilibrated at 8.72 MPa. The resulting equilibrium vapor and liquid phases were then analyzed. This was also done in order to provide some vapor-liquid equilibrium data for the fluid characterization process. The results of the saturation pressure measurements and the phase equilbrium measurements are given in Table 2 and 3. The experimental and calculated saturation pressure values at 350K are compared graphically in Fig. 4.

Table 2. Saturation Pressures for Solvent-Nasser Oil Mixtures at 350K

	Saturation Pressure, MPa		
Solvent Conc.	Experimental	Calculated 8.32	
0	8.13		
15	10.58	10.91	
30	13.78	13.82	
45.6	17.53	17.30	
62	20.86	21.66	
86	34.82*	33.79	

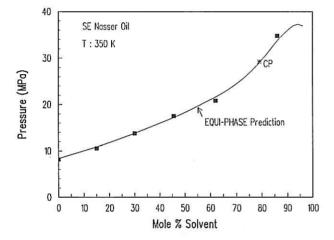
^{*}Estimated.

The composition data taken on the 62 mole% mixture at 20.86 and 8.72 MPa were used to perform an overall molar balance at the flashed condition. A graphical representation of the overall and component balances is given in Fig. 5. Representations such as this are extremely sensitive to any inconsistencies in the data. The degree of consis-

			Concentration	ı, Mole%	
		Experimental		Calcul	lated
Component	Feed	Vapor	Liquid	Vapor	Liquid
N2	0.892	1.658	0.228	1.749	0.242
CO ₂	1.867	2.692	1.284	2.644	1.278
H2S	0.654	0.584	0.617	0.649	0.658
C1	40.488	68.705	20.370	67.930	19.670
C2	10.932	12.223	9.923	12.510	9.731
C3	9.982	7.482	11.502	7.653	11.750
IC4	3.977	2.150	5.197	2.209	5.318
NC4	7.340	3.368	10.051	3.396	10.330
IC5	1.185	0.370	1.808	0.374	1.801
NC5	0.762	0.210	1.200	0.209	1.182
C6	1.798	0.257	3.028	0.283	2.948
C7-C9	5.539	0.257	9.544	0.339	9.484
C10-C14	6.376	0.044	10.979	0.049	11.180
C15-C19	3.414	8 	5.899	0.003	6.002
C20-C29	2,929	n	5.135		5.151

3.234

Table 3. Comparison of Calculated and Experimental Data for the Vapor and Liquid Phase Compositions after flashing the 62% Mixture at 8.72 MPa and 350K



C30 +

1.866

FIG. 4. The influence of solvent concentration on saturation pressure for SE Nasser oil-solvent mixtures.

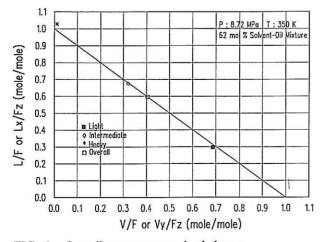


FIG. 5. Overall component molar balance.

tency shown in Fig. 5 indicates an excellent mass balance closure.

3.282

The observations made on the 86 mole% solvent mixture bear further discussion. This mixture appeared in the cell as a bright yellow upper phase and a second lower phase that appeared to be a thick black liquid. An increase in pressure on this system showed that the liquid volume decreased, thereby confirming that the system was in the retrograde region. However, further increases in pressure caused the black lower phase to become more sticky and thick but it never did disappear. Subsequent reductions in pressure caused the renewed formation of yellow liquid which washed the sticky material off the cell walls and re-created the black liquid referred to above.

It was concluded from these observations that the high solvent concentration in the oil had caused asphalthene precipitation at the conditions of the experiment. The upper retrograde dew point was estimated to be 34.82 MPa by graphically interpreting the data on liquid volume vs pressure after subtracting the volume of the asphaltic materials from the total condensed phase volume.

Slim Tube Displacements

During the course of the overall study on the Nasser reservoir fluid a series of slim tube displacements were carried out in order to determine the minimum natural gas liquid content of the solvent mixture required in order to achieve a miscible displacement. Some of the observations and calculations made using a solvent having the composition given in Table 1 (20 mole% NGL; 80 mole% dry gas) are reported here.

The slim tube apparatus consisted of a 6.4 mm O.D. by 12.15 m long stainless steel tube packed with 75 to 106 µm Ottawa Sand to an overall porosity of 35.1%. The total system volume inclusive of all lines and fittings up to the back pressure regulator was 68.88 cm³. The absolute permeability was 3.4 Darcys. A high pressure capillary sight glass located downstream of the slim tube but ahead of the back pressure regulator provided an opportunity to make visual observations of the character of the effluent fluid stream. The flashed oil was collected in a calibrated glass receiver and the gas was measured in a precision gasometer. The entire displacement system exclusive of the collection devices was housed in a thermostated forced circulation air oven where the temperature was controlled at 350K. The run was carried out at a pressure of 15.94 MPa. The duration of the run was 14hr. by which time 1.42 pore volumes of solvent had been injected. After the run had been concluded, the residual oil in place was washed out using a toluene flood and then recovered by rotary evaporation.

In some ways, the sight glass observations made during this run suggested that it was a miscible displacement. However some subtle differences existed and these need to be discussed. Up to about 1.07 PV displacement, only parent oil production was indicated. At this time the first color change was observed. However, produced gas composition data indicated that a methane bank was present. The first indication of this bank occured at 0.79 PV, methane concentration peaked at about 0.96 PV and declined to a minimum which was below the solution gas and solvent composition by 1.10 PV.

Visual observations did not indicate a second phase during this period, suggesting that two phases must have been created somewhere in the transition zone earlier than the 1.07 PV displacement. The gas was undoubtedly rich in methane but of low total volume such that it redissolved in the oil as it moved ahead prior to reaching the sight glass. From this, one could conclude that the displacement is not first contact miscible but may be multiple contact miscible.

The first indications of two-phase production were observed at 1.111 PV when a few short bubbles followed by longer bubbles were produced. At 1.113 PV, two-phase flow with a clear liquid was observed. Shortly thereafter a single clear phase was evident. Thus, two-phase flow occured at the trailing edge of the transition zone close to the solvent interface. This phenomenon only lasted about one minute (0.002 PV). This suggests the possibility that an open phase envelope (pseudo ternary coordinates) exists towards the trailing edge of the transition zone and that the fluids in that period are probably dew point fluids. From the overall viewpoint, it appears as

though the displacement started as a condensing drive mechanism but changed to a vaporizing drive mechanism towards the end of the displacement. These combination drives are classically immiscible but can be very efficient, often comparable to first contact or multiple contact miscible displacements.

On the basis of the fluid volumes collected in the separator, the oil volume was 103.0% of the original oil in place. However, when the residual recovery of oil in the tube based on the toluene flood is considered, the recovery reduced to 97.5% of original oil in place. The difference results from the expansion of the liquids caused by the extraction of hydrocarbons from the solvent by the oil. A graphical record of the slim tube recovery is presented in Fig. 6. The curve of cumulative fluid recovery represents the recovery based on oil volume collected in the separator. The calculated cumulative fluid recovery represents the separator volume less the solvent residual as shown at the bottom of the figure.

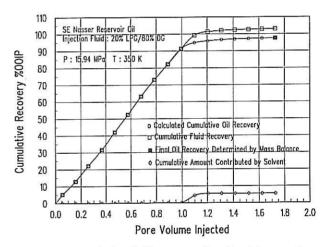


FIG. 6. Cumulative fluid recovery for slim tube run:4

It may be seen that this run, although evidently immiscible, was nevertheless highly efficient. Confirmation of the combined condensing/vaporizing drive mechanism occuring in this displacement will be seen in the pseudo ternary representation shown in Fig. 7. The EQUI-PHASE program with parameters developed from the swelling tests was used with an objective to predict the minimum multiple contact solvent concentration at the operating temperature and pressure of the SE Nasser reservoir.

The predictions suggested an unrealistically high natural gas liquid requirement. On plotting the calculated tie-line data of the contact sequence, it was found that the phase envelopes were open and divergent. Thus it was not possible to calculate the minimum multiple contact solvent concentration. These graphical representations indicate an immiscible drive form a fundamental standpoint. However, it is well known that these drives start as condensing

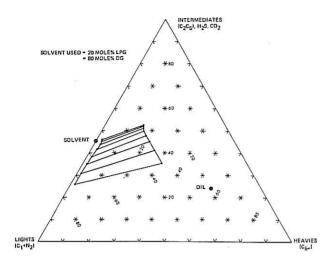


FIG. 7. Pseudo-Ternary plot of reverse contacts for the hydrocarbon solvent-SE Nasser oil system at 15.57 MPa and 350K.

drives and convert to vaporizing drives providing a very efficient displacement, one that is often competitive with either first or multiple contact miscible displacements. Our experience with hydrocarbon solvent-oil displacements covering a wide range of reservoir fluids is that when the operating temperature is above about 335K, hydrocarbon solvent drives normally exhibit this behavior.

DISPLACEMENT WITH CARBON DIOXIDE

The second major portion of the overall enhanced oil recovery study of the SE Nasser reservoir involved the use of carbon dioxide as a displacing fluid. A systematic series of swelling tests were carried out for the purpose of characterizing carbon dioxide-reservoir oil mixtures for the EQUI-PHASE program. This was followed by a series of four slim tube runs in order to determine the minimum pressure required to achieve miscibility.

Thermodynamic Behavior

The thermodynamic behavior of carbon dioxidereservoir fluid mixtures can be viewed in exactly the same way as the ethane-n-heptane and solventoil mixtures discussed earlier. In the case of the carbon dioxide mixtures, the solvent is a pure component and the oil is a multicomponent fluid having a composition similar to that given in Table 1.

Calculated phase envelopes for representative mixtures of carbon dioxide with the oil are shown graphically in Fig. 8. It will be noted that the phase envelope for the 80% mixture goes to very high pressures in a liquid-dense fluid region. Also, at this concentration a three-phase region consist-

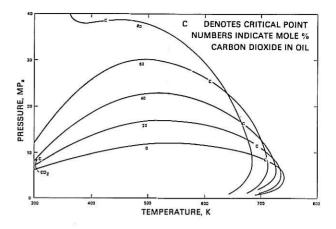


FIG. 8. The influence of carbon dioxide content on the phase behavior of SE Nasser reservoir fluid.

ing of a CO₂-rich liquid, a hydrocarbon-rich liquid and a gas exists in a pressure range from about 4 to 8 MPa at temperatures in the 250 to 325K range. This is not shown on Fig. 8 because of the congestion of lines on the graph.

Swelling Tests

Swelling tests using mixtures of carbon dioxide with SE Nasser reservoir fluid were carried out in a manner similar to those described earlier for the hydrocarbon solvent. Concentration of carbon dioxide of 15.0, 30.0, 45.0 and 60.0 mole% were used with the oil at a temperature of 350K. After the saturation pressure of the final mixture had been obtained at a pressure of 19.44 MPa, a sample of the single phase fluid was analyzed. The mixture was then equilibrated at a pressure of 8.13 MPa and both phases were analyzed. The data from these measurements were used to tune the parameters in the EQUI-PHASE program for use with mixtures of carbon dioxide with SE Nasser fluid. The results of the saturation and phase equilibrium measurements are given in Tables 4 and 5. The experimental and calculated saturation pressures are compared graphically in Fig. 9.

Table 4. Saturation Pressures for Carbon-Dioxide-Nasser
Oil Mixtures at 350K

	Saturation Pressure, MPa		
Solvent Conc.	Experimental	tal Calculated	
0	8.13	8.14	
15	10.16	10.00	
30	12.51	1222	
45	15.20	15.13	
60	19.44	20.15	

Component		Concentration, Mole% Experimental		Calcul	Calculated	
	Feed	Vapor	Liquid	Vapor	Liquid	
N2	0.21	0.33	0.08	0.36	0.05	
CO ₂	59.37	79.31	36.85	79.33	37.30	
H2S	0.49	0.46	0.50	0.49	0.48	
C1	7.76	11.74	3.20	11.77	3.33	
C2	3.70	4.13	3.20	4.13	3.22	
C3	2.15	1.73	2.58	1.70	2.64	
IC4	0.73	0.44	1.03	0.43	1.07	
NC4	0.96	0.49	1.45	0.48	1.50	
IC5	0.96	0.33	1.63	0.33	1.65	
NC5	0.54	0.17	0.95	0.16	0.95	
C6	1.96	0.33	3.78	0.34	3.74	
C7-C9	5.97	0.44	12.21	0.41	12.12	
C10-C14	6.73	0.09	14.30	0.06	14.11	
C15-C19	3.61	0.01	7.71	0.01	7.61	
C20-C29	3.16	_	6.62	_	6.66	
C30+	1.70	(<u></u>	3.91	.77	3.57	

Table 5. Comparison of Calculated and Experimental Data for the Vapor and Liquid Phase Compositions after Flashing the 60% Mixture at 8.13 MPa and 170°F

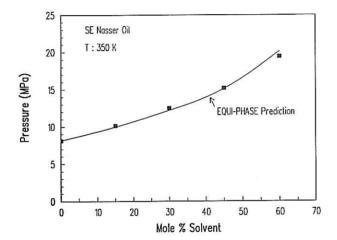


FIG. 9. The influence of CO₂ concentration on saturation pressure for SE Nasser-CO₂ mixtures.

A mass balance closure analysis of the equilibrium data taken on the 60.0 mole% mixture at 8.13 MPa was carried out as in the case of the hydrocarbon solvent. The results were similar to the hydrocarbon case.

Slim Tube Experiments

In order to determine the minimum miscibility pressure for carbon dioxide with the SE Nasser fluid, a series of slim tube displacements were carried out at 10.44, 13.89, 17.33 and 20.78 MPa.

Observations made during the 17.33 MPa run may be used as an example of the behavior of the fluids during the run. The black color of the original oil appeared in the sight glass for the first 0.99 PV of solvent injected. The color then changed to dark

brown and at 1.02 PV, very small bubbles were observed near the top of the sight glass. The color had changed to yellow after 1.04 PV and a gas/liquid interface extended along the full length of the capillary. Immediately thereafter, the vapor phase disappeared, leaving only a very light yellow liquid being produced. No methane bank was detected from the off-gas analysis during the entire displacement. The overall recovery based on separator volumes was 102.7% of original oil in place while the recovery based on toluene residual determination was 97.2%. On the basis of the short transition zone, the absence of the methane bank and the level of recovery, the run was judged to be miscible.

A graphical representation of the recovery profile is shown in Fig. 10. As in the case of the hydrocarbon solvent displacement shown in Fig. 6, both the recovery based on separator volumes and on volumes corrected by the toluene extracted residuals are shown.

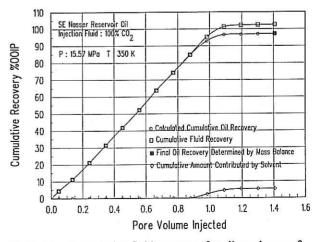


FIG. 10. Cumulative fluid recovery for slim tube run:3.

On the basis of the recoveries obtained at all four pressures, the minimum miscibility pressure for carbon dioxide with SE Nasser oil was found to be 15.57 MPa at 350K. This was obtained by interpolation of the recovery data for the four runs shown in Fig. 11. The runs at 17.33 and 20.78 MPa were judged to be miscible and those at 10.44 and 13.89 were judged to be immiscible.

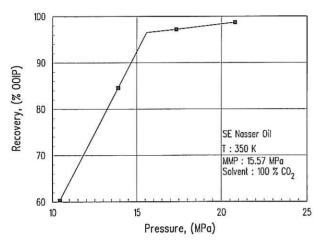


FIG. 11. Recovery vs pressure.

Predictions and Discussions

The parameters required for the EQUI-PHASE Enhanced Oil Recovery package were evaluated from the swelling test and vapor liquid equilibrium data. Since it has been widely assumed [1, 9, 13, 14, 15] that carbon dioxide displacements are vaporizing drives, this methodology was used for initiating the minimum miscibility pressure prediction. The predictions indicated an open divergent envelope at both 20.78 and 15.57 MPa on a pseudo ternary diagram. The results for the 15.57 MPa case are shown in Fig. 12. We are not aware that this kind of divergent behavior has ever been observed before for a carbon dioxide system.

The behavior of the oil in the presence of carbon dioxide bears further discussion. Normally, in carbon dioxide slim tube displacements the separator recovery is less than the toluene extracted recovery of the original oil in place. This happens because during a vaporizing drive, components which were originally part of the oil are taken away with the gas thereby causing a shrinkage of the oil. However, in the work reported here, three of the runs had separator recoveries which were higher than the toluene based recoveries. These were the runs at the three higher pressures.

It is well known that carbon dioxide can extract higher carbon numbered compounds from oils, particularly in the C7 to C20 range [9, 13, 15]. It is also known that when carbon dioxide dissolves in oil it causes significant swelling. This is particularly true

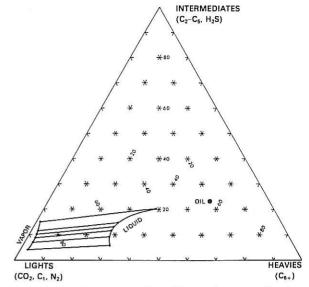


FIG. 12. Pseudo-Ternary plot of forward contacts for the CO₂-SE Nasser oil system at 15.94 MPa and 350K.

for heavier oils and bitumens which have a significant content in the C15-C30+ range. It is possible that a swelling and an extractive type mechanism are acting simultaneously and interactively in such a way that the relative magnitude of each will determine whether the separator based recovery will be greater or less than the toluene based recovery. The information gained from these and related experiments with carbon dioxide suggest that the C6+ distribution in the oil plays an important role in determining which effect will dominate.

In an attempt to explain this phenomenon, all of the displacement data available from our laboratory with pure carbon dioxide or high carbon dioxide solvents were analyzed. Studies on five different reservoir oils were available. The C6+ composition of each of these oils was grouped into five sub-fractions, namely C6-10, C11-15, C16-20, C21-25 and C26-30+. The resulting composition distributions are shown in Fig. 13. It will be seen that oils A, B and C have a high concentration of the lighter fractions (C6-C15) relative to the heavier fractions.

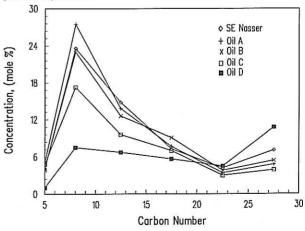


FIG. 13. C7+ component distribution of several oils.

With this information as background, a comparison was made between the separator based and toluene based recoveries at several pressures for each carbon dioxide displacement that had been run. The results of these comparisons are given in Fig. 14 which represents the difference between the two recoveries as a function of pressure. As a general observation, it will be seen that the difference becomes smaller and more negative as the pressure declines. These declining regions represent the immiscible displacements and in one sense this plot is analogous to the recovery-pressure plot shown in Fig. 11.

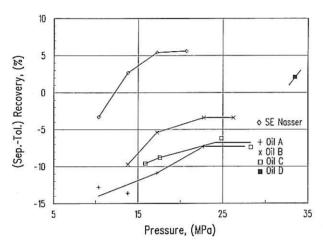


FIG. 14. The effect of oil character on the difference between seperator and toluene recoveries.

If one contemplates the recovery mechanism, it is realized that a lower separator recovery will be obtained when a significant fraction of the oil is extracted by carbon dioxide within the slim tube and goes with it in the off-gas after the back pressure regulator. The lighter extracted compounds in the C6–C15 range would yield very little liquid in the separator. Thus the difference between separator and toluene based recoveries tend to be negative.

On the other hand, positive differences are observed between the separator and toluene based recoveries for the oils (Oil D and SE Nasser) that have a substantially higher heavy fraction (C25-C30+). It appears that these oils swell significantly in the presence of dissolved carbon dioxide and that the evolution of carbon dioxide at the separator is relatively slow. In other words, the measured high separator recoveries observed may include some transient effects due to swelling, where the carbon dioxide does not come out of solution immediately.

At the grossly immiscible low pressure displacement for the SE Nasser oil as shown at 10.44 MPa on Fig. 14, the carbon dioxide evidently still acts as a good extractant and removes a significant fraction of

the light and intermediate compounds from the oil. However, the swelling of the heavier components is reduced because of the lower carbon dioxide solubility at the low pressure.

The above observations indicate the influence oil composition can have on the behavior of the oil during carbon dioxide displacements.

CONCLUSIONS

The use of enriched gas hydrocarbon solvents as displacing fluids often leads to a combined condensing/vaporizing drive mechanism where miscibility may not be attained. Nevertheless, the displacement efficiency and thus the degree of recovery possible with these fluids is often comparable to that obtained with first contact or multiple contact miscible solvents.

The response of a reservoir oil to carbon dioxide depends, to a considerable extent, on the relative amounts of the C6-C15 fraction and the C25-C30+ fraction in the oil. The C6-C15 components tend to be extracted by the carbon dioxide, thereby decreasing the apparent liquid production. The C25-C30+ compounds on the other hand tend to swell in the presence of carbon dioxide and hence increase the apparent volume of liquid produced.

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