



Measurement and corresponding states modeling of asphaltene precipitation in Jilin reservoir oils

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Abstract

The asphaltene precipitation of two reservoir oil samples collected from Jinlin oil field has been studied under pressure and with/without CO₂-injection conditions. No asphaltene precipitation was detected during the pressure depletion processes without CO₂ injection. For the CO₂-injected oil systems, the effects of operating pressure, injected CO₂ concentration, and multiple-contact on the onset and amount of asphaltene precipitation were studied under the reservoir temperature. No asphaltene precipitation was observed when the operating pressure is remote from the minimum miscibility pressure (MMP). However, appreciable asphaltene precipitation was detected when the operating pressure approached or exceeded the MMP. The amount of asphaltene precipitation increased with the concentration of injected CO₂.

A generalized corresponding states principle (CSP) for prediction of asphaltene precipitation data is produced and reported here. The proposed CSP theory complements the scaling equation for asphaltene precipitation under the influence of *n*-alkane precipitants. Based on literature data and the data measured in this work, the parameters and exponents of a corresponding states equation capable of describing the asphaltene precipitation behavior in the studied high-pressure CO₂-injected crude oil systems are reported.

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Keywords: Asphaltene precipitation; Reservoir oil; Pressure depletion; CO₂ injection; Corresponding states principle

1. Introduction

Miscible/partial miscible flooding using CO₂ injection has been shown to be a promising enhanced

oil recovery technique for many reservoirs (Huang and Dyer, 1993; Jiang and Mansoori, 1985; Kawana et al., 1988). Recently, CO₂ has been applied to a number of Chinese petroleum reservoirs, including Jilin, Shandong, Daqing and Jiangsu oil fields.

It is well known that the injection of CO₂ could result in asphaltene precipitation yielding a sticky, asphalt-like substance that clogs the reservoir and

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the production equipment (Vasquez and Mansoori, 2000). This is known to be due to changes in the solubility of heavy components in the reservoir oils in presence of CO₂. This project was designed to systematically study the asphaltene precipitation behavior in Jilin reservoir oil samples due to introduction of CO₂.

In previous reports by various investigating teams (Hu et al., 2000; Hu and Guo, in press; Yang et al., 1999; Park and Mansoori, 1988a,b; Vasquez and Mansoori, 2000; Branco et al., 2001), the effects of temperature and molecular weight of *n*-alkane precipitants and/or CO₂ on the onset and amount of asphaltene precipitation were investigated in the case of various crude oils.

Various experimental techniques for measurement of the onset and amount of asphaltene precipitation and flocculation are presented in the literature (Hirschberg et al., 1984; Kim et al., 1990; Escobedo and Mansoori, 1995, 1997; Espinat, 1993). Also models for prediction of onset and amount of asphaltene precipitation, flocculation and precipitation in static and dynamic cases are available (Kawanaka et al., 1991; Park and Mansoori 1988a,b; Mansoori, 1997).

In this report, we have introduced a generalized corresponding states principle (CSP) for prediction of asphaltene precipitation due to variations of pressure, injection miscible fluid and temperature. In the special experimental case reported here, we have examined the predictive capability of the proposed corresponding states equation approach at various dilution ratios and the type of *n*-alkane precipitants, on the onset and amount of asphaltene precipitation.

In the present report, firstly, we have examined whether asphaltene precipitation could happen during the pressure depletion process without CO₂ injection, and subsequently the effects of operating pressure, injected CO₂ concentration, and multiple-contact operation on the onset and amount of asphaltene precipitation were investigated under the reservoir temperature. Finally, the measured data as well as literature data were used to test the applicability of the proposed corresponding states equation approach to describe the asphaltene precipitation behavior in the high-pressure CO₂-injected reservoir oil systems.

2. Experimental

2.1. Materials

The compositions and basic properties of two recombined Jilin reservoir oils (J1 and J2) studied in this work are given in Table 1 and by using Cavett's method (Cavett, 1962) properties of pseudocomponents from C₆ to C₁₁₊ are calculated and are reported in Table 2. The purity of CO₂ used is 99.95 mol%.

2.2. Minimum miscibility pressure (MMP) measurement

The MMP of CO₂ in reservoir oils J1 and J2 were measured by using a slim tube apparatus with 0.30 cm inside diameter and 18.28 m in length and packed with 170–325 mesh glass beads.

As the MMP measurement is a standard experiment, the description of the experimental procedure is omit-

Table 1
Compositions (mol%) and properties of the recombined crude oils

Components	Compositions (mole fraction)	
	Oil J1	Oil J2
N ₂	1.20	0.96
CO ₂	0.20	0.16
C ₁	30.90	24.06
C ₂	3.50	0.76
C ₃	2.87	3.26
<i>i</i> -C ₄	0.33	0.64
<i>n</i> -C ₄	1.41	2.70
<i>i</i> -C ₅	0.40	0.52
<i>n</i> -C ₅	1.02	1.06
C ₆	1.69	0.70
C ₇	2.46	0.58
C ₈	2.98	1.86
C ₉	2.53	2.30
C ₁₀	2.15	0.82
C ₁₁₊	46.36	59.62
<i>Other properties</i>		
Reservoir <i>T</i> (K)	339	339
Bubble point <i>P</i> (MPa)	10.28	7.42
Reservoir oil viscosity at 339 K and 15 MPa (MPa s)	5.8	6.1
C ₁₁₊ Sp. gr. at 293 K	0.9100	0.9215
C ₁₁₊ mol. wt. (g/mol)	428	442
Resin content (wt.%)	4.60	4.89
<i>n</i> -C ₅ asphaltene content (wt.%)	1.68	1.82

Table 2

Properties of pseudocomponents of crude oil

Pseudocomponents	Boiling point (°F)	Density (g/cc)	MW (g/mol)	T_c (°F)	P_c (°F)	Acentric factor (-)
C ₆	147.0	0.685	84.0	452.2	468.7	0.281
C ₇	197.5	0.722	96.0	512.6	449.4	0.328
C ₈	242.0	0.745	107.0	563.7	427.0	0.368
C ₉	288.0	0.764	121.0	614.8	401.0	0.408
C ₁₀	330.5	0.778	134.0	660.1	374.5	0.445
C ₁₁₊	863.0	0.921	443.2	1159.4	145.2	0.903

ted. The measured MMP for CO₂–Oil J1 and CO₂–Oil J2 systems are 27.64 and 20.2 MPa, respectively.

2.3. Apparatus for measuring the onset and amount of asphaltene precipitation

The schematic diagram of the experimental system is shown in Fig. 1. The major component of the system is a mercury-free, volume variable, visual JEFRI equilibrium cell, retrofitted with optical fiber light transmission probes. The working temperature range of the cell is 243–473 K and the maximum

working pressure is 69 MPa. A modern laser solid detection system (SDS) was adopted to measure the onset of asphaltene precipitation. The incident laser is mounted in front of the equilibrium cell, ensuring the laser beam can be transmitted through the sample chamber before reaching the light detection probe. A magnetic stirrer was used to agitate the sample to accelerate the equilibrium process. The storage cells for injection gas and oil samples are 1000 ml piston cells. The temperature in the air bath (maximum 473 K) can be controlled within ± 0.3 K. The schematic diagram of sampling system is shown in Fig. 2. The

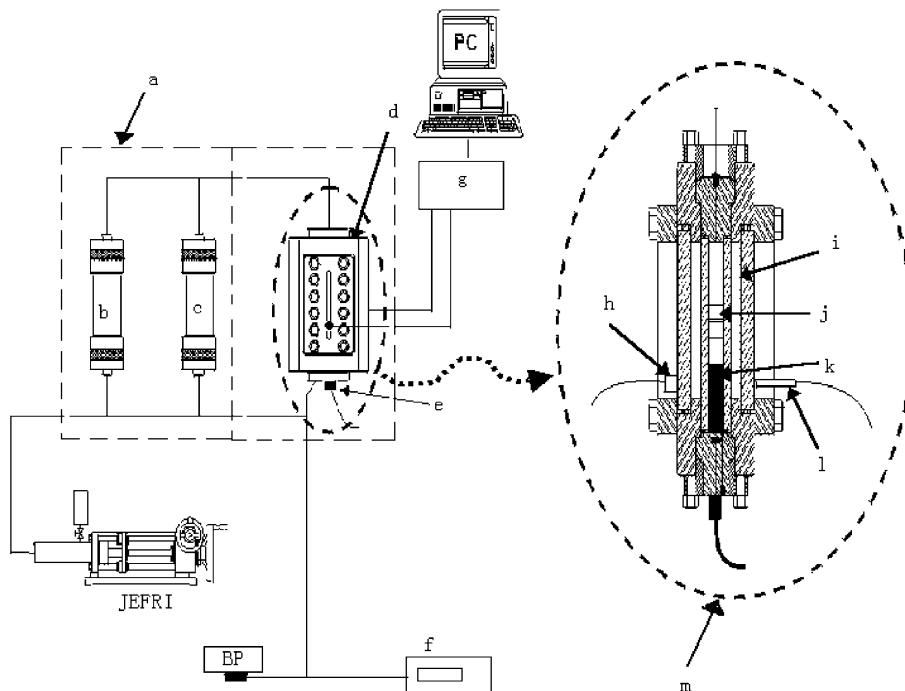


Fig. 1. Schematics of the high-pressure, high-temperature asphaltene precipitation system. (a) Air bath, (b) floating piston oil sample cylinder, (c) floating piston injection gas storage cylinder, (d) windowed equilibrium cell, (e) magnetic stirrer, (f) pressure transducer, (g) SDS system, (h) laser beam receiver, (i) circulation liquid, (j) piston, (k) reservoir fluids, (l) laser emission, (m) side view.

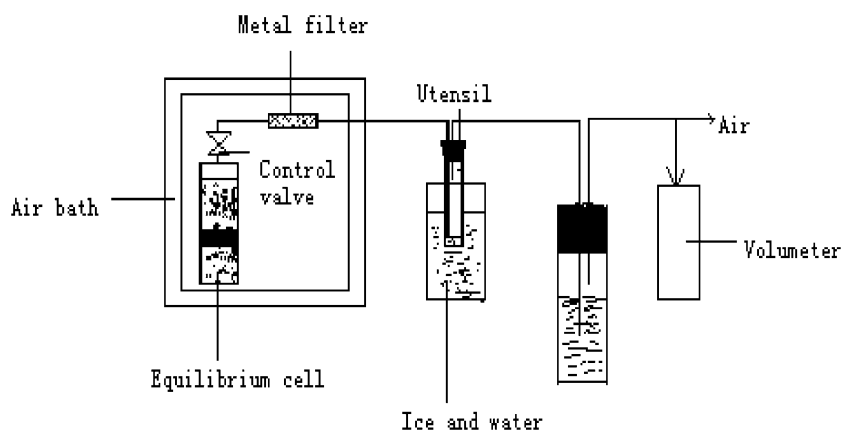


Fig. 2. Sampling system of the high-pressure experimental unit.

high-temperature, high-pressure asphaltene filter is filled with 0.5 μm stainless steel fibers.

2.4. Experiments without CO_2 injection

Firstly, the conventional pressure depletion process has been performed on Oil J1 and Oil J2 under reservoir temperature for examining whether asphaltene precipitation could be happening in the absence of CO_2 injection.

The experimental method is briefly described as follows.

- (1) The equilibrium cell is thoroughly cleaned, evacuated and maintained at a preset temperature (reservoir temperature). For removing any possible solid particles present in the oil, the feed oil is filtered first and then charged into the cell under single-phase condition.
- (2) The light transmittance through the oil is recorded by using a SDS logging system.
- (3) The system pressure is lowered stepwise under isothermal condition down to the bubble point pressure (P_b). At each pressure step the oil in the cell is agitated for 30 min and then the light transmittance data is taken. Meanwhile, a cathetometer is used to check whether vapor phase is formed in the equilibrium cell. In the single-phase region, when the system pressure is lowered, the oil becomes less dense and thus a stronger light signal will be received.

When asphaltene precipitation occurs, the incoming light will be scattered and results in significantly decrease in the intensity of the received light-signal (Espinat, 1993).

- (4) When the system pressure is reduced to lower than P_b , vapor phase will be generated, which will interfere the laser beam transmittance, hence the SDS logging system can no longer be applied to detect the onset of asphaltene precipitation. In this work, the amount of asphaltene precipitation in the two-phase region was determined by filtrating the oil phase.

Fig. 3 shows a typical plot of the measured light transmittance versus system pressure of Oil J1. No inflection point appears during the depletion process down to the bubble point pressure. The measured amount of asphaltene precipitation for J1 and J2 Oils are listed in Table 3. All the above experimental results show that for both oils no asphaltene precipitation was occurred in the single-phase region as well as in the two-phase region (confirmed by filtration results).

2.5. Experiments with CO_2 injection

A series of experiments have been performed to study the effects of various factors on the asphaltene precipitation behavior of CO_2 -injected reservoir oil systems.

For examining the effect of operating pressure on the asphaltene precipitation behavior in the CO_2 -

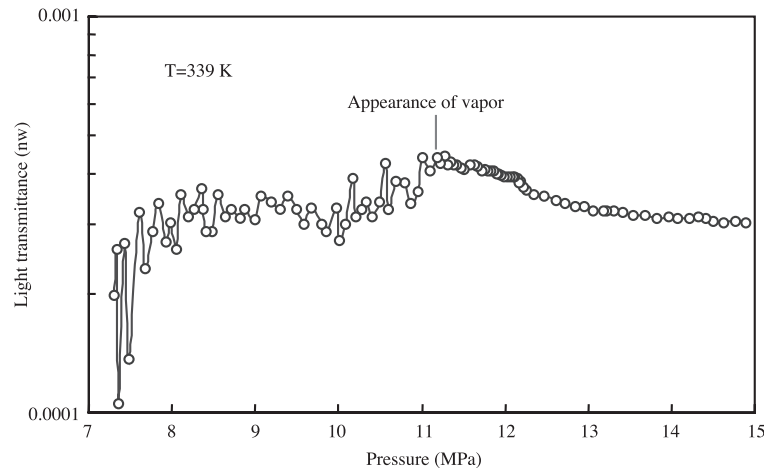


Fig. 3. Plot of light transmittance versus pressure for J1 reservoir oil ($T=339$ K).

injected J1 Oil, three pressures were selected (15, 24 and 28.9 MPa). The experimental procedure is briefly described as follows:

- (1) Maintain the cell at the selected pressure and reservoir temperature (339 K).
- (2) Charge a given amount of oil sample into the cell, and measure the light transmittance data at the specified pressure and temperature.
- (3) Introduce a given amount of CO_2 into the cell at a constant rate of 5 ml/h under isothermal and isobaric conditions. The moles of CO_2 introduced were calculated using Huang equation of state

(Huang et al., 1985) and the corresponding mole composition of the ($\text{CO}_2 + \text{oil}$) mixture was thus determined.

- (4) Agitate the mixture for 1 h and check whether vapor phase is formed (by visual observation). If no vapor phase appears (the oil phase is unsaturated) then take the light transmittance data, otherwise filtrate the oil phase to determine the amount (if any) of asphaltenes precipitated and terminate the experiment.
- (5) Change the operating pressure and repeat steps (1) to (4).

Based on the measured data, the plot of light transmittance versus CO_2/oil mole ratio for the CO_2 -J1 Oil system at $P=15$ MPa is shown in Fig. 4. It clearly shows that no asphaltene precipitation was occurred under this pressure (which was also confirmed by the filtration results).

Fig. 5 shows a similar plot at $P=24$ MPa. After the introduction of CO_2 , an increase in light transmittance was observed. However, when CO_2/oil mole ratio is increased to 1.32 (corresponds to 56.8 mol% CO_2), a sharp decrease in light transmittance occurred, indicating the incipient of asphaltene precipitation. When further increase the CO_2/oil mole ratio to 1.45 (corresponds to 59.2 mol% CO_2), the oil is saturated and vapor phase appears. At this stage, precipitated asphaltenes was detected (21 wt.%, refers to feed oil) after filtration.

Table 3
Pressure depletion data of J1 and J2 reservoir oils ($T=339$ K)

Oil sample	P (MPa)	Phase status	Wt.% of asphaltene deposited
J1	15	Single-phase (oil)	0.0
	13	Single-phase (oil)	0.0
	12	Single-phase (oil)	0.0
	11	Two-phase (oil + vapor)	0.0
	10	Two-phase (oil + vapor)	0.0
J2	6	Two-phase (oil + vapor)	0.0
	25	Single-phase (oil)	0.0
	20	Single-phase (oil)	0.0
	15	Single-phase (oil)	0.0
	10	Two-phase (oil + vapor)	0.0
	6	Two-phase (oil + vapor)	0.0

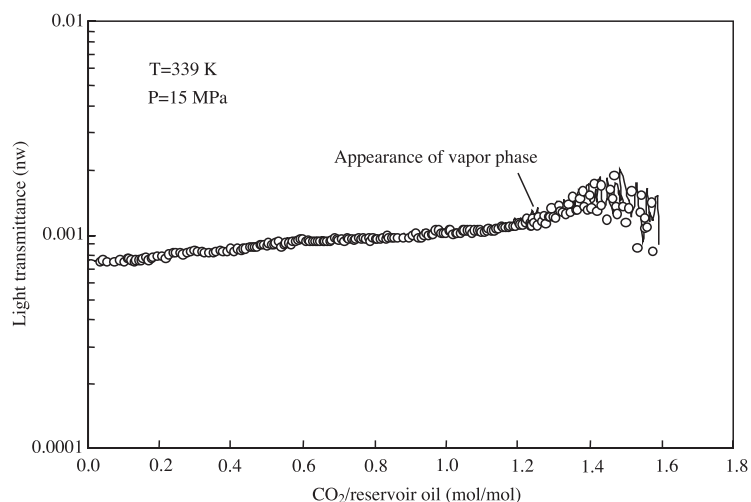


Fig. 4. Plot of light transmittance versus mole ratio (CO_2/oil) for the CO_2 -injected J1 reservoir oil system ($T=339\text{ K}$, $P=15\text{ MPa}$).

The experimental results obtained at $P=28.9\text{ MPa}$ (greater than the MMP of J1 Oil) showed that the onset of asphaltene precipitation occurred at a CO_2 concentration of 61.8 mol%.

The effect of injected CO_2 concentration on the onset and amount of asphaltene precipitation in J2 Reservoir Oil was measured at constant temperature (339 K) and pressure (20 MPa). The measured onset data using the above experimental procedure is 46.8 mol%. In a previous paper (Yang et al., 1999), the amount of asphaltene precipitation under gas injection

have been measured successfully through the change of asphaltene content in the oil phase. Therefore, in this study, the experimental procedure of Yang et al. (1999) was adopted which can be briefly summarized as follows.

- (1) Charge a given amount of oil sample into the equilibrium cell and maintain the system at reservoir temperature (339 K) and selected pressure (20 MPa).
- (2) Introduce a preset amount of CO_2 into the cell.

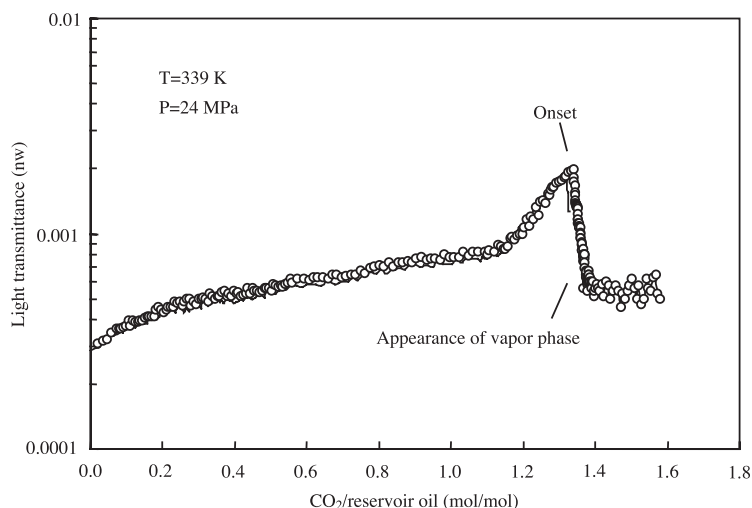


Fig. 5. Plot of light transmittance versus mole ratio (CO_2/oil) for the CO_2 -injected J1 reservoir oil system ($T=339\text{ K}$, $P=24\text{ MPa}$).

- (3) Agitate the (CO₂ + oil) mixture in the cell for 2 h and then allow to settle in vertical position for 72 h to ensure full asphaltene precipitation.
- (4) Sampling the oil phase under constant pressure (by adjusting the floating piston). Open the top valve of the sampling cell slightly to allow the flashed gas to flow into the bubbling flask, and the displaced oil was collected in the oil trap.
- (5) Determine the asphaltene content in the flashed oil by titration with *n*-C₅ according to IP-143 procedure.
- (6) Determine the amount of asphaltene precipitated through the difference between the asphaltene contents in the feed oil and flashed oil. The experimental data obtained for CO₂-J2 Oil system are listed in Table 4.

The effect of multiple-contact extraction on the asphaltene precipitation and oil volume reduction in the CO₂-injected J1 Oil system have been examined.

The experimental procedure of multiple-contact extraction is described below (Hirschberg et al., 1984):

- (1) Introduce given amount of CO₂ into the reservoir oil contained in the equilibrium cell at reservoir temperature and a selected pressure to obtain a CO₂-saturated oil mixture. The selected pressures were 20 and 24 MPa, respectively.
- (2) Charge a given amount of CO₂ (20 mol% of the CO₂-saturated oil mixture) into the equilibrium cell. Agitate the mixture for 1 h and then take the light transmittance data.
- (3) Sampling the equilibrium vapor phase at constant pressure and perform the composition analysis using a Hewlett-Packard 5880 gas chromatograph.

Table 4
Amount of asphaltene deposited in the CO₂-injected oil J2 at 20 MPa and 339 K

CO ₂ injected (mol%)	Asphaltene content in feed oil (wt.%) ^a	Asphaltene deposited (wt.%) ^a	Relative precipitation (%) ^b
51.6	1.76	0.06	3.2
63.8	1.59	0.23	12.6
71.6	1.50	0.32	17.6
80.2	1.40	0.42	22.8

^a Refer to feed oil.

^b Relative precipitation (%) = 100 × asphaltene deposited (wt.%) / asphaltene content in the feed oil (wt.%).

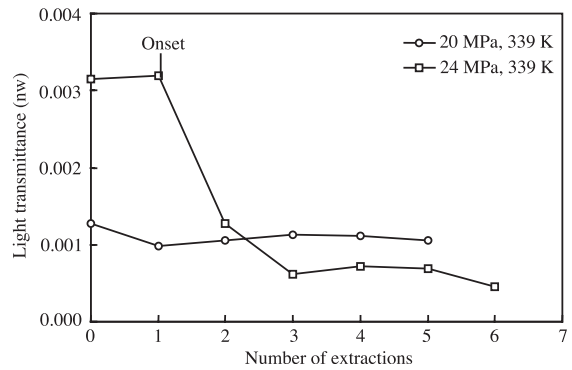


Fig. 6. Plot of light transmittance versus the number of extraction for CO₂-J1 oil system at 339 K and pressures of 20 and 24 MPa.

- (4) Remove the vapor phase at constant pressure and recharge a same amount of CO₂ into the equilibrium cell to achieve multiple-contact extractions.
- (5) Repeat steps (2)–(4) for another extraction.
- (6) Repeat steps (1)–(5) for another operating pressure.

Typical experimental results of the multiple-contact extractions performed at 20 and 24 MPa under reservoir temperature (339 K) are shown in Fig. 6. From Fig. 6, it can be seen that the light transmittance corresponds to each extraction at 20 MPa remains almost constant, indicating that the multiple-contact extraction operated at this pressure (far below MMP) does not induce asphaltene precipitation. However, when the operating pressure is raised to 24 MPa (close to MMP), the light transmittance decreases sharply in the second extraction, indicating that appreciable asphaltene precipitation has been occurred during this contact. Fig. 6 also shows that the change

Table 5
Reduction in volume of CO₂-saturated J1 oil after each extraction at three operating pressures

Extraction no.	Reduction in volume of oil phase (%)		
	20 MPa	24 MPa	28.9 MPa
1	–0.06	–0.85	–4.94
2	–0.74	–2.32	–9.61
3	–1.21	–3.35	–11.02
4	–1.77	–5.32	–14.22
5	–2.41	–6.79	
6		–9.37	

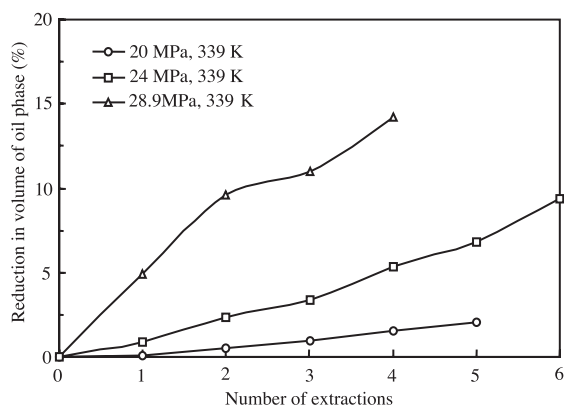


Fig. 7. Plot of volume of reduction (%) in CO₂ saturated oil phase versus the number of extraction for CO₂-injected J1 oil system at 339 K and under pressures of 20, 24 and 28.9 MPa.

of light transmittance after third contact is rather insignificant.

The volume reduction data of CO₂-saturated Oil J1 correspond to each extraction have also been measured, the measured data under 20, 24 and 28.9 MPa are shown in Table 5 and Fig. 7. The volume reduction of CO₂-saturated oil after five extractions at 20 and 24 MPa are 2.42% and 6.79%, respectively. These results indicate that the effect of multiple-contact extraction is not significant under partial miscible conditions. However, the effect is quite significant in the miscible region, as the volume reduction after four extractions at 28.9 MPa (greater than MMP) reaches 14.22%.

3. Analysis of the data

By using an equation of state, we can perform phase equilibrium calculation for the reservoir fluid. We need physical properties for each constituent in order to evaluate the equation parameters. Most of the equations of state make use of the critical properties. For pure components, these properties are readily available but for the pseudo-components or groups they are not. In this case, component properties are generated based on two of the following three properties such as molecular weight, average normal boiling point (NBP), liquid density. By using Cavett's method, properties of pseudocomponents are reported in Table 2. Cavett presented the following set of

equations for critical temperature and pressure, which have wide acceptance for petroleum fractions.

$$T_c = 768.07121 - 1.7133693t_b - 0.0010834003t_b^2 - 0.0089212579(\text{API})t_b + 0.38890584 \times 10^{-6}t_b^3 + 0.5309492(\text{API})t_b^2 + 0.32711 \times 10^{-7}(\text{API})^2t_b^2 \quad (1)$$

$$\log_{10}P_c = 2.8290406 + 0.94120109 \times 10^{-3}t_b - 0.30474749 \times 10^{-5}t_b^2 - 0.2087611 \times 10^{-4}(\text{API})t_b + 0.15184103 \times 10^{-8}t_b^3 + 0.11047899 \times 10^{-7}(\text{API})t_b^2 - 0.48271599 \times 10^{-7}(\text{API})^2t_b + 0.13949619 \times 10^{-9}(\text{API})^2t_b^2 \quad (2)$$

where T_c = critical temperature in degrees Rankine, P_c = critical pressure in Psia, t_b = normal boiling point in degrees Fahrenheit, $\text{API} = \text{API gravity} = 141.5 / (\text{SG}[60^\circ\text{F}] - 131.5)$ where SG stands for liquid specific gravity with respect to water. The acentric factor can be calculated by the Edmister's (1958) equation,

$$\omega = \frac{3}{7} \left(\frac{\log_{10}P_c}{(T_c T_b) - 1} \right) - 1 \quad (3)$$

In the above equation, P_c is in atmospheres, and T_c and T_b are in degrees Kelvin.

Fig. 8 presents the phase behaviors of J2 crude oil A in contact with CO₂ gas at 339 K. By using the

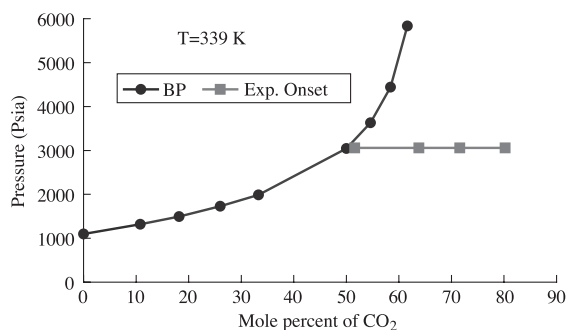


Fig. 8. Phase diagram for mixtures of J2 crude oil and carbon dioxide at 339 K. Region to the upper side of hollow square marks is the observed asphaltene precipitation region (L-V-S).

equation of state approach proposed by Manafi et al. (1999), the bubble pressure of a mixture of carbon dioxide and J2 crude oil are predicted. Experimental bubble pressure of a crude oil is 7.42 MPa (1076.2 Psia) and predicted one is 7.56 MPa (1097.1 Psia) at 339 K. In this figure, predicted bubble pressure for a given mixture are shown as circle marks. Region to upper side of the circle marks is a liquid phase (L) and to the lower side of the circle marks is a liquid–vapor (two phase) region (L-V). Observed onset of asphaltene mole fraction of CO₂ entering the crude oil where the asphaltene precipitation starts to occur is about 0.506 and the observed onset pressure of asphaltene flocculation is about 20 MPa (2900 Psia). Fig. 8 also shows the observed pressure/composition region of asphaltene precipitation for a mixture of carbon dioxide and J2 oil at 339 K. The region to the upper side of hollow square marks is the observed three phase region (L-V-S).

According to previous studies (Park and Mansoori, 1988a,b), the bubble point pressure and onset pressure of asphaltene flocculation of the oil mixtures increase with increasing temperature. These behaviors are consistent with other experimental observations (Branco et al., 2001). However, asphaltene flocculation starts at lower mole fraction of CO₂ gas with increasing temperature. This can also be expected that the energy of a mixture to prevent the interaction of asphaltene clusters to aggregate and precipitate decreases with increasing temperature, i.e., the solubility parameter of a mixture decreases with increasing temperature.

In Fig. 9, the effect of CO₂ mol% for a given mixture of the amount of asphaltene precipitation are reported at 20 MPa. According to this figure, the

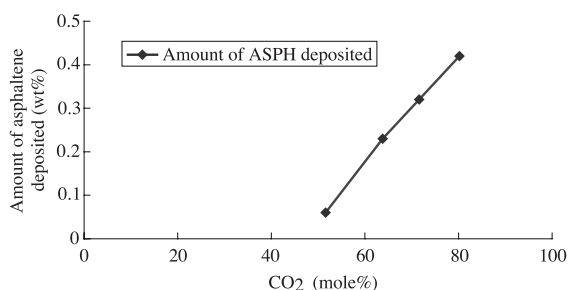


Fig. 9. Effect of CO₂ mol% for a given mixture of the amount of asphaltene precipitation at 20 MPa.

amount of asphaltene deposited increases as the mol% of CO₂ of the mixture increases. As described in our previous publications, it is also expected that the trend of asphaltene precipitation at different pressures decreases as pressure increases.

4. Corresponding states modeling of asphaltene precipitation

The CSP is the most powerful tool available for quantitative prediction of the physical properties of pure fluids and mixtures (Leland and Chappellear, 1968). It is used widely in development of generalized equations and charts for prediction of thermophysical properties of fluids and solids. It is extended to prediction of the behavior complex substances (Mansoori et al., 1980) and prediction of, for example, temperature profile in gas transmission pipelines (Edalat and Mansoori, 1988). The extension of the CSP to mixtures is called the conformal solution theory (CST), which has found applications for prediction of the behavior of mixtures with variety of complexities (Mansoori and Leland, 1972; Massih and Mansoori, 1983; Aghamiri et al., 2001). The fundamental idea behind the CSP and CST is: (i) to identify the variables (called state functions in thermodynamics) and characteristics of the system under consideration which influence the property of the system; (ii) develop dimensionless groups out of the property variables and characteristics; (iv) develop mixing rules for the characteristic parameters in case of a mixture; and (iii) develop generalized CSP and CST equations and charts for calculation of the property of substances and mixtures, which can be then used for variety of systems which will obey the same CSP and CST principles.

In the case of asphaltene precipitation from an oil due to addition of a miscible solvent (like CO₂) to the oil which is usually expressed in units of “weight percent of asphaltene deposited” and shown by W the following variables and characteristics of the oil and solvent are known to influence that (Kawanaka et al., 1991; Park and Mansoori, 1988a,b; Branco et al., 2001):

W_1 The initial weight fraction of asphaltene in the oil before any precipitation.

R	Percentage of the resin present in the oil before addition of the miscible solvent is known to have a strong role on asphaltene precipitation.
T	Temperature variations can cause changes in the oil composition which will affect asphaltene precipitation.
P	Pressure variations also will affect asphaltene precipitation.
T_{ci} 's	Critical temperatures of components of oil and solvent are the characterizing parameters for the properties of the components.
P_{ci} 's	Critical pressures of components of oil and solvent are the characterizing parameters for the properties of the components.
x_i 's	Compositions of components of oil and solvent.
D_r	Dilution ratio or weight ratio of the miscible solvent added and the oil. Asphaltene precipitation is a function of that.
M_a	Molecular weight of asphaltene in the oil before addition of miscible solvent.
M_r	Molecular weight of resin in the oil before addition of miscible solvent.
M_s	Molecular weight of the miscible solvent used is a characterizing parameter for the solvent.
M_o	Molecular weight of the oil under consideration is a result of the components present in the oil and it is a characterizing parameter for the oil.
μ_o	Aromaticity of asphaltene in the oil before addition of miscible solvent.
μ_r	Aromaticity of resin in the oil before addition of miscible solvent.
μ_o	Aromaticity of the oil under consideration has a lot to do with asphaltene deposition. In empirical equations of state this is incorporated into such parameters as the Pitzer acentric factor.
μ_s	Aromaticity of the solvent used. In empirical equations of state this is incorporated into such parameters as the Pitzer acentric factor.

From the above list of variables and characteristics of the system the following seven reduced (dimensionless) groups can be identified: $W_r = W/W_1$, $D_r =$ di-

lution ratio, $T_r = T/T_{pc}$, $P_r = P/P_{pc}$, $M_{r1} = M_s/M_o$, $M_{r2} = M_a/M_r$, $R_r = R_o/W_o$, $\mu_r = \mu_a/\mu_r$, $\omega_m =$ acentric factor of the mixture of oil and solvent, which is a function of compositions.

In the above definitions subscript r stands for reduced, T_r and P_r are the reduced temperature and pressure, respectively; T_{pc} and P_{pc} are the pseudo-critical temperature and pressure, respectively, of the mixture of oil and solvent under consideration. It must be pointed out that pseudo-critical temperature and pressure are functions of compositions, critical temperatures and critical pressures of components of oil and solvent. As a result, we can propose the following functional form:

$$W_r = f(D_r, R_r M_{r1}, M_{r2}, \mu_r, T_r, P_r, \omega_m) \quad (4)$$

In the process of asphaltene precipitation, in principle, we are interested to study variation of W_r with respect to D_r . As a result, let us define variables X and function Y by the following expressions:

$$X = D_r M_{r1}^Z M_{r2}^\psi R_r^\xi \mu_r^\zeta \quad (z\psi\xi\zeta) \text{ are constants} \quad (5)$$

$$Y = W_r M_{r1}^Z M_{r2}^\eta R_r^\phi \mu_r^\theta \quad (z'\eta\phi\theta) \text{ are constants} \quad (6)$$

Then, we consider the following polynomial equation to represent the relation between Y and X :

$$Y = a(T_r P_r \omega_m) + b(T_r P_r \omega_m)X + c(T_r P_r \omega_m)X^2 + d(T_r P_r \omega_m)X^3 + \dots \quad \text{for } X \geq X^c \quad (7)$$

Where X^c denotes the value of X at the onset point of asphaltene precipitation. By setting Y in Eq. (7) equal to zero (when $W_r = 0$) this equation can be solved for X^c . Since parameters a, b, c, d, \dots are functions of temperature and pressure, then X^c will be a function of temperature, i.e.

$$X^c = X^c(T_r P_r \omega_m) \quad (8)$$

Then the critical solvent to oil, or dilution, ratio at the onset of asphaltene precipitation (D_r^c) can be calculated by knowing X^c , molecular weight ratios M_{r1} and M_{r2} , original oil resin to asphaltene weight

ratio R_r and aromaticity ratio of asphaltene to resin μ_r , by the following expression:

$$D_r^c = X^c M_{r1}^{-z} M_{r2}^{-\psi} R_r^{-\zeta} \mu_r^{-\xi} \quad (9)$$

It can be readily seen from Eqs. (4)–(9) that the properties of asphaltene alone are not involved in the CSP treatment of asphaltene precipitation and its onset point. However, properties of asphaltene, resin and other components of the oil and miscible solvent are all the contributing factors on asphaltene precipitation.

We can now assume that since we have considered properties of asphaltene, resin, oil and solvent as variables and characteristics of the system in the corresponding state formulation of asphaltene precipitation the eight exponents (z , ψ , ζ , ξ , z' , η , φ , θ), which appear in Eqs. (1) and (2) are universal and they will apply to every possible oil and solvents.

5. Application

In order to apply Eq. (7) as a generalized CSP equation for the corresponding states treatment of asphaltene precipitation, it is necessary to have in hand experimental data for all the characteristics of oil, solvent, asphaltene and resin, as presented above, as well as analytic expressions for parameters $a(T_r P_r \omega_m)$, $b(T_r P_r \omega_m)$, $c(T_r P_r \omega_m)$, $d(T_r P_r \omega_m)$, ... appearing in Eq. (7). In order to develop T and P dependent parameters a , b , c , d , ... appearing in Eq. (7), it is necessary to perform variety of precipitation tests on various oils by variety of solvents and at different temperatures and pressures. For now, such extensive database is not available and as a result a thorough CSP treatment of asphaltene precipitation is not likely. Due to the lack of such a database, we perform limited CSP treatment of the asphaltene precipitation at isothermal and isobaric conditions.

At constant temperature and pressure, Eq. (7) will reduce to the following form:

$$Y = a + bX + cX^2 + dX^3 \quad (10)$$

In previous works, investigators (Hu et al., 2000; Hu and Guo, in press; Yang et al., 1999) used a scaling equation approach in the form of Eq. (10) to describe asphaltene precipitation at constant tempera-

ture and pressure as a result of addition of various normal paraffins to petroleum. They used the following expressions for X and Y :

$$X = D_r / (M_s)^z \quad (z \text{ is constant}) \quad (11)$$

$$Y = D_r / (M_s)^{z'} \quad (z' \text{ is constant}) \quad (12)$$

Eqs. (11) and (12) are special forms of Eqs. (5) and (6), respectively, if all the other terms in the right hand sides of Eqs. (1) and (2) are assumed to be constant, which are actually the case for the data collected and analyzed by these previous investigators and others in each case. Eqs. (10)–(12) were successfully applied to describe the asphaltene precipitation behavior in various cases of addition of normal alkanes to petroleum at constant temperatures and pressures. It should be noted that Eqs. (11) and (12) do not consist of dimensionless groups. It was shown (Hu et al., 2000; Hu and Guo, in press) that exponent z' is a universal constant ($z' = -2$), while exponent z depends on the composition of the oil and its value is generally within the range of $0.10 \leq z \leq 0.5$. Of course, parameter z should become also universal if we could have a more thorough and diverse database for asphaltene precipitation. Generalization of Eqs. (10)–(12) to various oil/solvent systems was not in principle possible even though from the order-of-magnitude point of view it seems acceptable. The objective of this work is to examine the applicability of the above mentioned CSP approach to correlate/predict the asphaltene precipitation data in high-pressure CO₂-injected oil systems.

Srivastava et al. (1995) have measured the amount of asphaltene precipitation data in two CO₂-injected Weyburn reservoir oils (termed here as Oil A1 and Oil A2). In this section, Eqs. (10)–(12) are tested against the asphaltene precipitation data reported by Srivastava et al. (1995). The test procedure is as follows:

- (1) Perform flash calculation (based on an appropriate equation of state) on the CO₂-injected Oil A1 at given temperature, pressure and injected-CO₂ concentration to determine the equilibrium phase compositions.
- (2) From the calculated liquid phase compositions evaluate the mole percent of CO₂ in liquid phase.
- (3) Keep $z' = -2$ and adjust z to obtain optimum fit to the amount of asphaltene precipitation data of

Oil A1 (Srivastava et al., 1995). The resulting CSP equation is as follows:

$$Y = 83.24 - 342.66X + 371.72X^2 - 31.28X^3$$

$$(z = 0.1, z' = -2) \quad (13)$$

- (4) Based on Eq. (13) to predict the asphaltene precipitation data of Oil A2 and then compare with the experimental data.

The test results are presented in Fig. 10, which clearly shows that the corresponding states approach can be satisfactorily applied to correlate/predict the amount of asphaltene precipitation occurred in high-pressure CO₂-injected oil systems.

The critical solvent to oil dilution ratio D_r^c is defined as the dilution ratio at the onset point of asphaltene precipitation. The value of D_r^c can be determined from a series of asphaltene precipitation data at various dilution ratios and extrapolating to zero precipitation ($W=0$). The extrapolation can be achieved either graphically or mathematically using the CSP approach. As we showed before according to Eq. (9), the critical dilution ratio at the onset of asphaltene precipitation is related to the ratio of molecular weight of the solvent and oil, molecular weight ratios, resin to asphaltene ratio and polarity ratio. In the special case of constant, molecular weight

ratios, resin to asphaltene ratio and polarity ratio Eq. (9) can be written in the following form:

$$D_r^c = X^c M_s^{-z} \quad (z \text{ is constant}) \quad (14)$$

Since all the precipitation data for a given oil using different n-paraffin solvents can be represented by a single curve (Rassamdana et al., 1996; Hu et al., 2000; Hu and Guo, in press), the value of X_c must be the same for all solvents. Hence, Eq. (14) can be rewritten as $D_r^c = k M_s^{-z}$, where k is a constant for the selected oil.

In this work, Eq. (14) was used to predict the onset of asphaltene precipitation from the measured amount of asphaltene precipitation data. The amount of asphaltene precipitation measured for CO₂-injected J2 Oil system can be well represented by the following third order polynomial:

$$Y = 2.909 - 50.51X + 82.88X^2 - 4.15X^3 \quad (15)$$

Based on Eqs. (14) and (15), the predicted critical dilution ratio is $D_r^c = 48.2$ mol% CO₂, which agrees well with the measured data, $D_r^c = 46.8$ mol% CO₂. Similarly, based on Eqs. (13) and (14), the predicted onset point of asphaltene precipitation in the CO₂-injected Weyburn reservoir oil (Oil A1) is $D_r^c = 41$ mol% CO₂, which is also in good agreement with the experimental data, $D_r^c = 43$ mol% CO₂ (Srivastava et al., 1995).

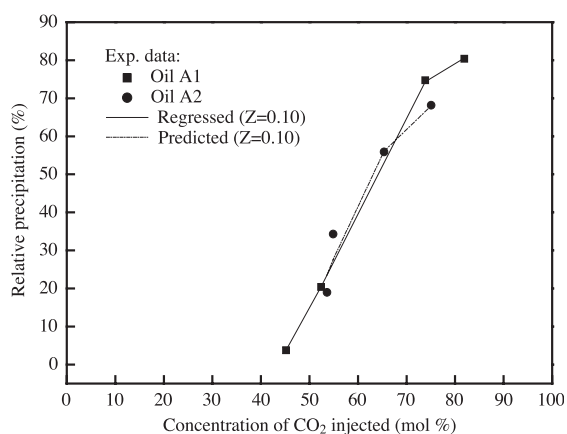


Fig. 10. Comparison of calculated and experimental asphaltene precipitation in CO₂-injected Weyburn reservoir oils (Srivastava et al., 1995).

6. Conclusions

- (1) The asphaltene precipitation behavior in the pressure depletion process (without CO₂ injection) has been examined for two Jilin reservoir oils. No asphaltene precipitation was detected.
- (2) The MMP determined for J1 and J2 reservoir Oils are 27.6 and 20.2 MPa, respectively.
- (3) A generalized corresponding states theory for prediction of asphaltene precipitation from petroleum fluids as a result of addition of miscible solvents at various temperatures and pressures is presented. The proposed CSP theory complements the scaling equation for asphaltene precipitation.
- (4) The onset and amount of asphaltene precipitation in the CO₂-injected Jilin crude oil systems have

been systematically studied under the reservoir temperature and various operating conditions. No asphaltene precipitation was detected in Oil J1 at a pressure of 15 MPa (far from MMP). However, appreciable asphaltene precipitation was observed under operating pressures of 24 (close to MMP) and 28 MPa (greater than MMP). The amount of asphaltene precipitation in Oil J2 increases with injected CO₂ concentration.

- (5) The effect of multiple-contact extraction on the asphaltene precipitation and volume reduction of CO₂-saturated J1 Oil have been studied and found that when the operating pressure is lower than MMP, the effect on volume reduction is not significant.
- (6) The proposed generalized corresponding states theory, which complements the scaling equation approach, is capable of extending to correlate/predict the asphaltene precipitation data in the high-pressure CO₂-injected reservoir oil systems.

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References

- Aghamiri, S.F., Modarress, H., Mansoori, G.A., 2001. A new theoretical approach to the hydrogen-bonded fluids based on the conformal solution concept. *J. Phys. Chem. B* 105, 2820–2825.
- Branco, V.A.M., Mansoori, G.A., De Almeida Xavier, L.C., Park, S.J., Manafi, H., 2001. Asphaltene flocculation and collapse from petroleum fluids. *J. Pet. Sci. Eng.* 32, 217–230.
- Cavett, R.H., 1962. Physical data for distillation calculations—vapor–liquid equilibria. 27th Mid-Year Mtg. API Division of Refining 42 (III), 351–357.
- Edalat, M., Mansoori, G.A., 1988. Buried gas transmission pipelines: temperature profile prediction through the corresponding states principle. *Energy Sources J.* 10, 247–252.
- Edmister, W.C., 1958. *Applied Hydrocarbon Thermodynamics. Part 4: compressibility factors and equations of state.* Gulf Publishing Company Book Division, Houston.
- Escobedo, J., Mansoori, G.A., 1995. Viscometric determination of the onset of asphaltene flocculation: a novel method. *J. SPE Prod. Facilities*, May, 115–118.
- Escobedo, J., Mansoori, G.A., 1997. Viscometric principles of onsets of colloidal asphaltene flocculation in paraffinic oils and asphaltene micellization in aromatics. *SPE Prod. Facilities*, 116–122 (May).
- Espinat, D., 1993. Colloidal structure of asphaltene solutions and heavy-oil fraction studied by small-angle and X-ray scattering. SPE 25187 presented at the SPE Int'l. Symp. Oilfield Chemistry, New Orleans, LA, March 2–5.
- Hirschberg, A., deJong, L.N., Schipper, B.A., Meijer, J.G., 1984. Influence of temperature and pressure on asphaltene flocculation. *SPE J.*, June, 283–293.
- Hu, Y.F., Guo, T.M., 2001. Effect of temperature and molecular weight of *n*-alkane precipitants on asphaltene precipitation. *Fluid Phase Equilib.* (in press).
- Hu, Y.F., Chen, G.J., Yang, J.T., Guo, T.M., 2000. A study on the application of scaling equation for asphaltene precipitation. *Fluid Phase Equilib.* 171, 181–195.
- Huang, S.S., Dyer, S., 1993. Miscible displacement in the Weyburn reservoir: a laboratory study. *J. Can. Pet. Technol.* 32, 42–52.
- Huang, F.H., Li, M.H., Starling, K.E., Chung, F.T.H., 1985. An accurate equation of state for carbon dioxide. *J. Chem. Eng. Jpn.* 18, 490–496.
- Jiang, T.S., Mansoori, G.A., 1985. Asphaltene deposition and its role in enhanced oil recovery miscible gas flooding. *Proceed. of the 3rd European Conf. on Enhanced Oil Recovery*, Rome, Italy, April.
- Kawanaka, S., Park, S.J., Mansoori, G.A., 1988. The role of asphaltene deposition in EOR gas flooding: a predictive technique. SPE Paper#17376. *Proceed. of the SPE/DOE Symp. Enhanced Oil Recovery.* SPE, Richardson, TX.
- Kawanaka, S., Park, S.J., Mansoori, G.A., 1991. Organic deposition from reservoir fluids: a thermodynamic predictive technique. *SPE Reservoir Eng.*, 185–195 (May).
- Kim, S.T., Boudh-Hir, M.E., Mansoori, G.A., 1990. The role of asphaltene in wettability reversal. SPE Paper#20700. *Proceed. of the 65th Ann. SPE Tech. Conf.*, pp. 799–809.
- Leland, T.W., Chappellear, P.S., 1968. The corresponding states principle. A review of current theory and practice. *I&EC Fund.* 60, 15–43.
- Manafi, H., Mansoori, G.A., Ghotbi, S., 1999. Phase behavior prediction of petroleum fluids with minimum characterization data. *J. Pet. Sci. Eng.* 22, 67–93.
- Mansoori, G.A., 1997. Modeling of asphaltene and other heavy organic depositions. *J. Pet. Sci. Eng.* 17, 101–111.
- Mansoori, G.A., Leland, T.W., 1972. Statistical thermodynamics of mixtures (a new version for the theory of conformal solutions). *Faraday Trans. II* (68), 320–344.
- Mansoori, G.A., Patel, V., Edalat, M., 1980. The three-parameter corresponding states principle. *Int. J. Thermophys.* 1 (3), 285–298.
- Massih, A.R., Mansoori, G.A., 1983. Conformal-solution theory of polar fluids: the statistical mechanical basis of shape factors. *Fluid Phase Equilib.* 10, 57–72.
- Park, S.J., Mansoori, G.A., 1988a. Aggregation and deposition of

- heavy organics in petroleum crudes. *J. Energy Sources* 10, 109–125.
- Park, S.J., Mansoori, G.A., 1988b. Organic deposition from heavy petroleum crudes (a fractal aggregation theory approach). *Proceed. of the UNITAR/UNDP 4th Int'l. Conf. on Heavy Crudes and Tar Sands*, Edmonton, Alberta, August.
- Rassamdana, H., Dabir, B., Nematy, M., Farhani, M., Sahimi, M., 1996. Asphalt flocculation and deposition: I. The onset of precipitation. *AIChE J.* 42, 10–22.
- Srivastava, R.K., Huang, S.S., Dyer, S.B., Mourits, F.M., 1995. Quantification of asphaltene flocculation during miscible CO₂ flooding in the Weyburn reservoir. *J. Can. Pet. Technol.* 34, 31–42.
- Vasquez, D., Mansoori, G.A., 2000. Identification and measurement of petroleum precipitates. *J. Pet. Sci. Eng.* 26 (1–4), 49–56.
- Yang, Z., Ma, C.F., Lin, X.S., Yang, J.T., Guo, T.M., 1999. Experimental and modeling studies on the asphaltene precipitation in degassed and gas-injected reservoir oils. *Fluid Phase Equilib.* 157, 143–158.