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Liquid Viscosities of Carbon Dioxide + Hydrocarbons from 310 K to 403 K

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Kinematic viscosities of twelve mixtures made from pentane, hexane, heptane, octane, decane, and carbon dioxide were measured using a rolling ball viscometer. The temperatures ranged from 310 K to 403 K and the pressures from 0.8 MPa to 12 MPa. Kinematic viscosities were converted to absolute viscosities using mixture densities estimated from a modified Rackett equation. Calculated absolute viscosities for the decane + CO_2 system were within 0.5% of the values by Cullick and Mathis. All viscosities of hydrocarbon mixtures and hydrocarbons with CO_2 could be predicted from the Orbey and Sandler correlation with an average absolute deviation of 4.1%. We found that the Lohrenz, Bray, and Clark viscosity correlation cannot be used to estimate the viscosity of the mixtures containing CO_2 with reasonable accuracy.

Introduction

Many reservoirs are underproduced and abandoned when there is still a considerable amount of oil in the rock. Incremental oil recovery from these reservoirs requires secondary and tertiary recovery techniques such as miscible gas injection. The technical and economic viability of CO_2 flooding processes has been established by laboratory and field studies of rock formations and crude oils (Holm and Josendal, 1974; Leung, 1983; Lansangan and Smith, 1993).

A knowledge of the effect of CO_2 upon the properties of a hydrocarbon mixture is essential to evaluate how viscous fingering, gravity segregation, hydrodynamic dispersion, and interfacial tension phenomena affect the local displacement efficiency in a miscible gas flooding process. Traditionally, the oil and gas industry has not devoted ample interest to a detailed evaluation of thermophysical properties and compositions of hydrocarbon fluids. The lack of thermodynamic and physical property data has, in part, led to the design of surface production equipment and reservoir management strategies that were based primarily on empirical correlations that were frequently applied beyond their ranges.

To predict the performance of multiple-contact miscibility processes requires accurate viscosities and densities of the injected solvent, the in-situ fluid, and their mixtures. Mathematical models used to predict the field performance of a carbon dioxide flood employ viscosity correlations based upon CO_2 + hydrocarbon viscosity values where the maximum CO_2 concentration is generally less than 10 mol % (Lansangan and Smith, 1993). However, a CO_2-rich phase having CO_2 concentrations above 50 mol % often is required to achieve profitable oil recoveries. Published viscosity correlations can be off by more than 100% in their predictions and greatly affect the calculated mobilities in the simulation. An incorrect large phase-mobility contrast prediction could result in a conservative oil production estimate. An artificially favorable predicted mobility ratio would result in an excessively optimistic production estimate. Both are artifacts produced largely by improper viscosity, phase density, and phase composition information.

Experimental Methods

A Ruska high-pressure viscometer, model 160, was used. This operates on a rolling-ball principle where the roll time of a 0.6 cm diameter ball is used to determine the viscosities.

The viscometer measures on-line phase viscosities at high pressure and temperature, simulating reservoir conditions. The viscometer requires about 70 cm^3 for complete filling. The method involves a steel ball rolling through the liquid for a precise distance. The viscosity is a function of the time taken to travel this distance, the density difference between the ball and fluid, and a constant. The constant is obtained by calibrating the viscometer with a fluid of known viscosity and density. The viscosity is then calculated from

$$\eta = Kt(\rho_B - \rho_F) \qquad (1)$$

where η is the absolute viscosity, K is the calibration constant determined with standards of known viscosity, ρ_B is the density of the steel ball, ρ_F is the fluid density estimated from the modified Rackett equation, and t is the ball roll time. Two CANNON certified viscosity standards were used for calibration purposes to cover a wide range of viscosity and temperatures. The kinematic and absolute viscosity and the density are reported for these standard fluids at various temperatures.

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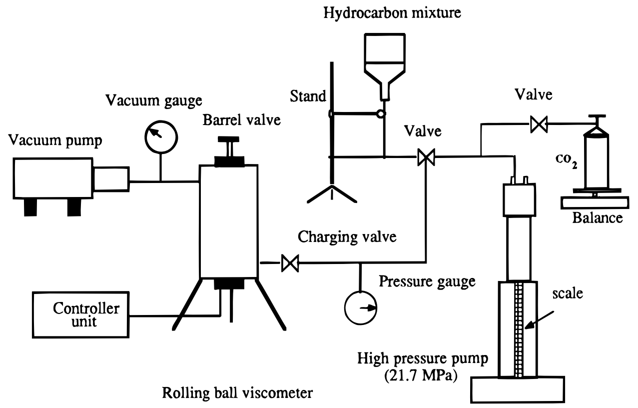

Figure 1. Schematic of the rolling ball viscometer and the charging system.

The measuring system consists of a mechanical test assembly and a control unit with solid-state electronic circuitry. The measuring barrel is supported inside a heavy wall, stainless steel, pressure housing. The barrel has a finely honed and lapped cylindrical bore in which a stainless steel ball rolls. A plug containing the barrel seal and a solenoid closes the lower end. When the barrel seal is closed, both ends of the barrel are sealed so that the ball must fall through the fluid in the barrel; if it is open, both ends are open so that the ball rolling can be used for stirring the fluid.

The solenoid holds the steel ball at the top of the barrel, and the ball will not fall until the solenoid current is interrupted. Thus, the human error in timing the ball roll time is eliminated, since the breaking of the solenoid current starts the clock, and the contact made when the ball reaches the end of its travel stops the clock. Rolling times are determined by a digital clock, and the measurements have a repeatability of ±0.1%.

The viscometer is heated with electric heating jackets, and the temperature can be controlled within ±0.2 °C. The pressure can be read with an accuracy of ±0.001 MPa. This equipment is connected to a control unit. Figure 1 shows a schematic of the viscometer and of the fluid charging system.

All hydrocarbons used in this research were from Aldrich Chemical Co. with a minimum purity of 99+%. The water content was less than 0.005%, and the evaporation residue less than 0.0003%. The CO_2 used was certified O_2-free with a minimum purity of 99.99%.

The hydrocarbon mixtures were prepared gravimetrically using a Mettler PM4600 scale (accuracy ±0.01 g). Carbon dioxide was slowly injected into the system using a syringe pump, ISCO 314 N model, with a maximum pressure capacity of 20 MPa. A small cylinder containing CO_2 was placed on a scale to closely monitor the mass delivered. The estimated accuracy in the preparation of the mixtures was better than ±0.01% on a mass basis.

Density Calculation

The pressures used were above the bubble point pressure to ensure that the fluid was in a single phase. This pressure was first estimated using the Soave–Redlich–Kwong EOS to predesign the experiment. The densities were estimated using the modified Rackett equation (Spencer and Adler, 1978), which provides bubble point densities. We assumed that the liquid densities above the saturation pressure do not change substantially from the bubble point density. On the basis of a comparison with the Cullick and Mathis (1984) results for a CO_2 + decane system, the accuracy of this equation was better than ±0.3%. The Rackett equation is not recommended for CO_2 concentrations above 50 mol %, which is the highest concentration used in this work.

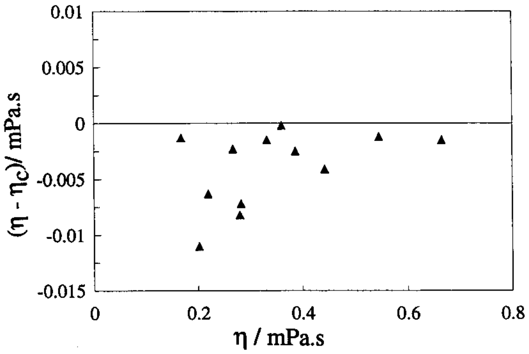

Figure 2. Difference between the viscosities of this work from the viscosities measured by Cullick and Mathis (1984) for decane + CO_2.

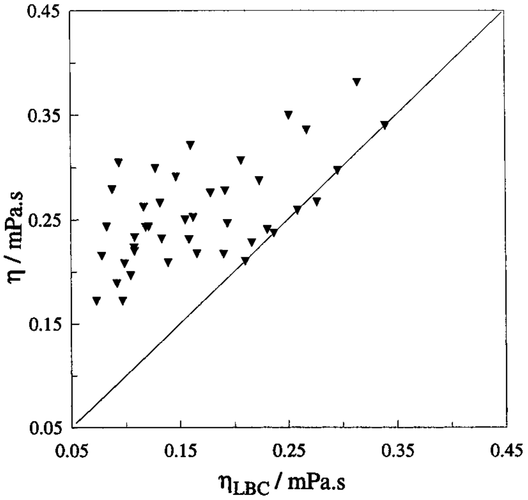

Figure 3. Comparison between measured and predicted viscosities from the LBC (Lohrenz et al., 1964) correlation.

Results and Discussion

Table 1 shows the molar composition of the mixtures used in this study. The mixtures of decane + CO_2 were done as a calibration experiment to compare our results with the data published by Cullick and Mathis (1984). Figure 2 shows a deviation plot of the viscosities measured in this work with those of Cullick and Mathis. The agreement is better than 0.5%. Because all the viscosities measured in this work are lower than those reported by Cullick and Mathis, we believe that this could be attributed to volatile impurities in the samples used.

Each viscosity value represents an average of three replicates. The viscometer was rolled for over 10 min to ensure mixing, and after thermal and mechanical equilibrium had been achieved, the viscosity was measured. The ball was allowed to roll back and forth three times; the difference in rolling times was less than ±0.2%.

All measured viscosities were compared with the values predicted from the Lohrenz–Bray–Clark, (LBC) (Lohrenz et al. 1964) viscosity correlation. It has been reported that the correlation does not perform well for crude oil mixtures with CO_2. However, this could be attributed to the characterization scheme for undefined crude oil fractions. We have verified that the correlation deteriorates rapidly as the concentration of CO_2 increases.

Figure 3 compares the measured viscosities with the LBC predicted viscosities. The LBC viscosities are con-

Table 1. Measured Viscosities η and Calculated Densities ρ_c and Viscosities η_c

T/K	P/MPa	ρ/(g·cm^{-3})	η/(mPa·s)	η_c/(mPa·s)	$100(\eta - \eta_c)/\eta$	T/K	P/MPa	ρ/(g·cm^{-3})	η/(mPa·s)	η_c/(mPa·s)	$100(\eta - \eta_c)/\eta$
Butane (1) + Hexane (2) + Decane (3) $x_1 = 0.193, x_2 = 0.193$											
324.260	0.308	0.661	0.381	0.409	−7.300	377.590	0.515	0.616	0.246	0.257	−4.500
342.040	0.377	0.647	0.336	0.344	−2.400	395.370	0.653	0.601	0.217	0.227	−4.600
359.820	0.446	0.632	0.287	0.295	−2.800					AAD/% = 4.3	
Butane (1) + Hexane (2) + Decane (3) + Carbon Dioxide (4) $x_1 = 0.177, x_2 = 0.177, x_3 = 0.56$											
324.260	2.514	0.668	0.350	0.384	−9.700	377.590	2.514	0.622	0.250	0.241	3.600
342.040	2.514	0.653	0.307	0.323	−5.200	395.370	2.514	0.605	0.232	0.213	8.200
359.820	2.514	0.638	0.275	0.277	−0.700					AAD/% = 5.5	
Butane (1) + Hexane (2) + Decane (3) + Carbon Dioxide (4) $x_1 = 0.15, x_2 = 0.15, x_3 = 0.476$											
324.260	4.928	0.678	0.304	0.338	−11.200	377.590	4.928	0.629	0.216	0.214	−0.900
342.040	4.928	0.663	0.279	0.285	−2.200	395.370	4.928	0.612	0.172	0.189	−9.900
359.820	4.928	0.647	0.244	0.245	−0.400					AAD/% = 4.9	
Pentane (1) + Hexane (2) + Heptane (3) + Decane (4) $x_1 = 0.097, x_2 = 0.289, x_3 = 0.103$											
359.820	0.273	0.655	0.266	0.289	−8.600	383.150	0.343	0.634	0.228	0.242	−6.100
377.590	0.308	0.639	0.241	0.252	−4.600	395.370	0.412	0.622	0.217	0.223	−2.800
										AAD/% = 5.5	
Pentane (1) + Hexane (2) + Heptane (3) + Decane (4) + Carbon Dioxide (5) $x_1 = 0.088, x_2 = 0.264, x_3 = 0.094, x_4 = 0.467$											
359.820	2.514	0.645	0.278	0.272	2.200	383.150	2.514	0.624	0.231	0.228	1.300
377.590	2.514	0.629	0.252	0.237	6.000	395.370	2.514	0.612	0.209	0.210	−0.500
										AAD/% = 2.5	
Pentane (1) + Hexane (2) + Heptane (3) + Decane (4) + Carbon Dioxide (5) $x_1 = 0.075, x_2 = 0.225, x_3 = 0.08, x_4 = 0.397$											
359.820	4.928	0.625	0.243	0.241	0.800	383.150	4.928	0.604	0.197	0.202	−2.500
377.590	4.928	0.608	0.219	0.210	4.100	395.370	4.928	0.592	0.172	0.187	−8.700
										AAD/% = 4.0	
Pentane (1) + Decane (2) $x_1 = 0.288$											
354.260	0.239	0.649	0.334	0.337	0.900	389.820	0.446	0.618	0.237	0.254	−7.200
365.930	0.308	0.639	0.297	0.305	−2.700	401.480	0.515	0.607	0.210	0.234	−11.400
377.590	0.377	0.629	0.259	0.278	−7.300					AAD/% = 5.9	
Pentane (1) + Decane (2) + Carbon Dioxide (3) $x_1 = 0.258, x_2 = 0.655$											
354.260	2.514	0.628	0.321	0.318	0.900	389.820	2.514	0.592	0.243	0.239	1.600
365.930	2.514	0.617	0.291	0.287	1.400	401.480	2.514	0.579	0.223	0.221	0.900
377.590	2.514	0.605	0.266	0.262	1.500					AAD/% = 1.9	
Pentane (1) + Decane (2) + Carbon Dioxide (3) $x_1 = 224, x_2 = 0.553$											
354.260	4.928	0.634	0.299	0.279	6.700	389.820	4.928	0.597	0.208	0.211	−1.400
365.930	4.928	0.621	0.262	0.253	3.400	401.480	4.928	0.585	0.189	0.195	−3.200
377.590	4.928	0.611	0.233	0.231	0.900					AAD/% = 3.1	
Decane (1) + Carbon Dioxide (2) $x_1 = 0.849$											
310.930	6.996	0.727	0.665	0.658	1.100	373.150	6.996	0.677	0.332	0.345	−3.900
344.20	6.996	0.701	0.442	0.441	0.200	403.150	6.996	0.651	0.267	0.275	−3.000
										AAD/% = 2.1	
Decane (1) + Carbon Dioxide (2) $x_1 = 0.699$											
310.930	6.996	0.733	0.546	0.546	−0.050	373.150	6.996	0.675	0.280	0.289	−3.200
344.260	6.996	0.703	0.386	0.368	4.700	403.150	6.996	0.649	0.220	0.231	−5.000
										AAD/% = 3.2	
Decane (1) + Carbon Dioxide (2) $x_1 = 0.495$											
310.930	6.996	0.749	0.360	0.395	−9.700	373.150	10.443	0.684	0.202	0.214	−5.900
344.260	6.996	0.712	0.282	0.268	5.000	403.150	11.822	0.651	0.168	0.173	−3.000
										AAD/% = 5.9	

sistently lower than the measured values, and the differences can be as high as 100%. The second correlation was from the recently published work by Orbey and Sandler (1993). We selected their procedure because it is simple and more accurate than many current models (Amin and Maddox, 1980; Barrufet and Iglesias-Silva, 1993; Mehrotra, 1981), including the more complicated methods based upon corresponding states (Ely and Hanley, 1981).

The one-fluid approach was used to evaluate the viscosity of the hydrocarbon mixture with mixing rules defined for the parameters of the model. Since the viscosity correlations for CO_2 are different from those of the hydrocarbons, the multifluid approach was used to evaluate the effect of CO_2 on the viscosity of the mixture. These steps consisted of (1) evaluating the viscosity of the hydrocarbon mixture at atmospheric pressure and selected temperature, (2) correcting for pressure, (3) evaluating the viscosity of CO_2, and (4) using a mixing rule to provide the mixture value.

The viscosity of the hydrocarbon mixture at atmospheric pressure is calculated as

$$\ln\left(\frac{\eta}{\eta_{\mathrm{ref}}}\right) = k\left[-1.6866 + 1.4010\left(\frac{T_{\mathrm{B}}}{T}\right) + 0.2406\left(\frac{T_{\mathrm{B}}}{T}\right)^2\right] \quad (2)$$

where k is evaluated as

$$k = 0.143 + 0.00463(T_{\mathrm{B}}/\mathrm{K}) - 4.05 \times 10^{-6}(T_{\mathrm{B}}/\mathrm{K})^2 \quad (3)$$

The mixing rule used for the normal boiling point T_{B} was a cubic average,

$$T_{\mathrm{B,mix}} = [\sum_{i=1}^{nh} x_i T_{\mathrm{B},i}{}^3]^{1/3} \quad (4)$$

where nh is the number of hydrocarbon components in the mixture and all mole fractions x_i are renormalized by excluding CO_2. The pressure correction, regardless of temperature, is

$$\ln(\eta(P)/\eta(P^*)) = \exp(0.98 \times 10^{-5}(P/\mathrm{MPa})) \quad (5)$$

Orbey and Sandler (1993) provide a piecewise correlation for the viscosity of CO_2 to cover the range from gas, dense gas, saturated liquid, and liquid. At subcritical temperatures and pressures less than the saturation pressure, a constant value of viscosity is suggested:

$$\eta_{\mathrm{CO_2}} = 0.015\ \mathrm{mPa{\cdot}s} \quad (6)$$

For subcritical temperatures and at the saturation pressure,

$$\eta^{\mathrm{sat,l}}_{\mathrm{CO_2}}(T)/\mathrm{mPa} = -0.2127 + 83.05/(T/\mathrm{K}) \quad (7)$$

At pressures above the saturation pressure,

$$\eta^{\mathrm{l}}_{\mathrm{CO_2}}(T,P)/(\mathrm{mPa{\cdot}s}) = \eta^{\mathrm{sat,l}}_{\mathrm{CO_2}}(T)/(\mathrm{mPa{\cdot}s}) + 0.0017[(P - P_{\mathrm{sat}})/\mathrm{MPa}] \quad (8)$$

For supercritical temperatures and at atmospheric pressure, the following equation is used,

$$\mu^{\mathrm{g}}_{\mathrm{CO_2}}(T, P = 0.1\ \mathrm{MPa})/(\mathrm{mPa{\cdot}s}) = 0.00197 + 4.4 \times 10^{-5}(T/\mathrm{K}) \quad (9)$$

while for pressures above the atmospheric pressure,

$$(\mu^{\mathrm{g}}_{\mathrm{CO_2}}(T,P) - \mu^{\mathrm{g}}_{\mathrm{CO_2}}(T, P = 0.1\ \mathrm{MPa}))/(\mathrm{mPa{\cdot}s}) = 0.00502 - 1.02 \times 10^{-5}(T/K)(P/\mathrm{MPa}) \quad (10)$$

For the CO_2 vapor pressure, the equation by Angus et al. (1976) was used. The viscosity for the mixture is then evaluated as

$$\eta_{\mathrm{mix}} = x_{\mathrm{hc}}\eta_{\mathrm{hc}} + x_{\mathrm{CO_2}}\eta_{\mathrm{CO_2}} \quad (11)$$

The original parameters of the Orbey and Sandler equations were used.

Table 1 gives the viscosity and density as a function of temperature and pressure, the viscosity predicted using the Orbey and Sandler (1993) correlation, and the difference from this model. The density was calculated from the modified Rackett equation. The average absolute deviation (AAD/%) indicated at the bottom of the table is evaluated from

$$\mathrm{AAD/\%} = \left[\sum_{i=1}^{N}\left|\frac{(\eta - \eta_{\mathrm{p}})}{\eta}\right|_i\right]\frac{100}{N} \quad (12)$$

with N being the number of data points. The overall AAD/% for the 54 values is 4.1%, with the largest value being 5.9% for the mixture which contained the largest CO_2 concentration (50 mol %).

Conclusions

The viscosities for some well-defined hydrocarbon + CO_2 mixtures have been measured, and on the basis of a comparison with published values, the technique is sufficiently accurate for engineering calculations. Thus, the technique may be well suited for crude oil systems.

The percent average absolute deviation (AAD/%) of our results compared with the Orbey and Sandler model indicates that the model is sufficiently accurate for most engineering applications. LBC correlation, however, deteriorates rapidly as the concentration of CO_2 increases.

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