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II. Applications to the Calculation of Swelling Factors of CO_2—Crude Oil Systems

In an earlier ~~article~~, a Corresponding States Method was presented for predicting the saturated liquid densities of both pure components and mixtures. The method is based on the known saturated liquid densities of two reference fluids and requires the critical properties and acentric factors of the pure components as input parameters. ~~We~~ use the method here to calculate the swelling factors of CO_2-crude oil mixtures using CO_2 and *n*-dodecane as the reference fluids. The critical properties and acentric factors of the crude oils were estimated from their API gravities and Watson K-factors. Using only one adjustable coefficient to characterize each CO_2-crude oil system, swelling factors were calculated to within 0.5% of their experimental values. The single adjustable coefficient is linearly related to the boiling point of the crude.

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SCOPE

The use of carbon dioxide for tertiary oil recovery from petroleum reservoirs is receiving increasing attention. One of the characteristics of carbon dioxide is that it promotes swelling. The extent of the expansion or swelling is measured by the "swelling factor," and these are used to calculate other properties of interest in enhanced oil recovery. Swelling factors are directly related to the saturated liquid densities of CO_2-crude oil mixtures, and we recently proposed a method for calculating saturated liquid densities.

That method is basically an extension of the three-parameter corresponding states principle of Pitzer and co-workers, and uses the properties of two (nonspherical) reference fluids. The method has been used to calculate very accurate values of the saturated liquid densities of LNG mixtures published previously and is extended here, using different reference fluids and different reference equations, to calculate saturated liquid densities, and hence swelling factors, of CO_2-crude oil mixtures. The method can be extended to mixed gas-crude oil systems, and to other thermodynamic properties.

CONCLUSIONS AND SIGNIFICANCE

Described here is an analytic method for calculating saturated liquid densities, and hence swelling factors, of CO_2-crude oil systems, which are of interest in enhanced oil recovery. The method uses an extension of Pitzer's three-parameter corresponding states principle, based on two reference fluids chosen so that their properties are close to the key components of interest. The method gives extremely accurate predictions of the saturated liquid densities of LNG mixtures (Teja 1980), when the critical properties and acentric factors of the components are known.

When the critical properties and acentric factors have to be estimated, as in the case of crude oils in CO_2-crude oil mix-

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tures, the method gives good agreement with experimental data, provided a single binary interaction coefficient is used to characterize each CO_2-crude oil system. The single binary interaction coefficient is linearly related to the boiling point of the crude oil, and this results in a valuable means of extending the predictions to other crudes. The method is not restricted to CO_2-crude oil mixtures and can be easily extended to mixed gas-crude oil systems.

This study also provides a means of generalizing empirical equations, such as the modified Rackett equation used here, to components not used in the fitting procedure and to mixtures.

Enhanced oil recovery from reservoirs has recently received much attention. Among the commonly used methods for secondary and tertiary oil recovery are: water flooding, immiscible gas displacement, miscible fluid displacement, in situ combustion and heat injection. A method that is gaining in popularity is that of injecting CO_2 gas. Holm and Josendal (1974) list the following advantages of using CO_2 as an oil recovery agent: it promotes swelling, it reduces oil viscosity, it increases oil density, it is highly soluble in water, it exerts an acidic effect on rock, it can vaporize and extract portions of the crude, and it is transported chromatographically through the porous rock.

In another study, Holm (1976) compared the use of CO_2 as a miscible solvent with other solvents, including propane, gas enriched with light hydrocarbons, high pressure gas, and solvents which are mutually soluble in both oil and water. The main advantages of CO_2 over the others are that it achieves miscible displacement at pressures of only 1,100—3,000 psia (7,585-20,685 kPa) and that it is applicable to reservoirs which have been depleted of their gas and LPG components.

Interest using CO_2 to enhance oil recovery processes has led to performance prediction methods which can be applied to specific reservoirs (de Nevers 1964). However, the use of these performance methods requires a knowledge of the solubility, swelling and viscosity properties of CO_2-crude oil mixtures at reservoir conditions. Simon and Graue (1965) correlated the available solubility data from several sources, including their own experimental data, for a variety of crude and refined oils between 110 and 250°F (316-394 K) and pressures up to 2,376 psia (16,383 kPa). These data were used to develop graphical correlations for predicting CO_2 solubility, fluid swelling and viscosity of CO_2-crude oil mixtures.

There are several disadvantages in using Simon and Graue's work. First, the correlations are in graphical form and are therefore inconvenient for computer calculations. Further, several graphs must be used before arriving at a particular value of a property. Second, the correlations are empirical, and therefore subject to errors when extrapolated beyond the range of crudes covered in the study (i.e., when extrapolated beyond Watson K-factors of 11.0-12.4). Finally, the correlations cover pure CO_2 injection only. In practice, the injected CO_2 (whether commercial or from recycling in the oil recovery process) is likely to be mixed with other gases (N_2, CH_4), and there is no a priori means of extending Simon and Graue's work to mixed gases.

An extended Corresponding States Method for saturated liquid densities proposed earlier (Teja 1980) can easily be applied to the calculation of swelling factors in CO_2-crude oil systems given the average boiling point or Watson K-factor and specific gravity of the crude and the known properties of two reference substances. The method has the advantage of being completely analytical and easy to use. In addition, good agreement with experiment can be obtained with a suitable choice of reference fluids to represent key components. And, the method can handle multicomponent gas-crude oil mixtures, provided the binary interaction coefficients are available.

THE CORRESPONDING STATES METHOD

When CO_2 dissolves in oil, there is an increase in liquid volume. The volume of the oil and dissolved CO_2 at saturation temperature and pressure, divided by the volume of the oil (without CO_2 at the same temperature but at atmospheric pressure) is defined as the swelling factor. Elementary algebraic manipulation yields the definition:

$$\text{Swelling Factor} = \frac{\rho^s\,[\text{oil at } T]}{\rho^s\,[\text{sat. oil} + CO_2 \text{ at } T]} \times \frac{1}{1 - x_{CO_2}} \tag{1}$$

where the numerator is the molar density of the oil at the given (saturation) temperature and the denominator contains the molar density of the oil saturated with CO_2 at that temperature. x_{CO_2} is the mole fraction of CO_2 in the mixture CO_2 + crude oil. Thus, if an equation is available for saturated liquid densities (of mixtures), then swelling factors can easily be calculated. Such an equation was proposed earlier (Teja 1980) and is an extended form of Pitzer's three-parameter corresponding states principle

$$\frac{V}{RT_c/P_c} = \frac{V^{(r1)}}{RT_c^{(r1)}/P_c^{(r1)}} + \frac{\omega - \omega^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}} \left\{ \frac{V^{(r2)}}{RT_c^{(r2)}/P_c^{(r2)}} - \frac{V^{(r1)}}{RT_c^{(r1)}/P_c^{(r1)}} \right\} \tag{2}$$

where V is the molar volume and ω is Pitzer's acentric factor. The superscripts $(r1)$ and $(r2)$ refer to the (known) properties of two reference fluids which are chosen so that they are typical of the components of interest. The equation may also be written as

$$\frac{Z_c}{\rho_R} = \frac{Z_c^{(r1)}}{\rho_R^{(r1)}} + \frac{\omega - \omega^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}} \left\{ \frac{Z_c^{(r2)}}{\rho_R^{(r2)}} - \frac{Z_c^{(r1)}}{\rho_R^{(r1)}} \right\} \tag{3}$$

so that if expressions are available for the reduced saturation densities (as functions of reduced temperature) of two reference substances, then the saturated liquid density of any substance can be calculated at any temperature, using only the critical properties and acentric factor of that substance.

Equation (3) can be extended to mixtures via the van der Waals one-fluid model, whereby the reduction of temperature and density (or volume) is carried out by means of pseudocritical properties:

$$T_{cm} V_{cm} = \sum_i \sum_j x_i x_j T_{cij} V_{cij} \tag{4}$$

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \tag{5}$$

$$\omega_m = \sum_i x_i \omega_i \tag{6}$$

$$Z_{cm} = \sum_i x_i Z_{ci} \tag{7}$$

These equations can be used with Eqn. (3) to obtain the saturated liquid densities of mixtures, if values can be assigned to the cross-parameters T_{cij} and V_{cij} $(i \neq j)$. The mixing rules used in the earlier study on LNG mixtures were retained in this study and are given by

$$V_{cij} T_{cij} = (T_{cii} V_{cii} T_{cjj} V_{cjj})^{0.5} \tag{8}$$

$$V_{cij} = \eta_{ij} (V_{cii}^{1/3} + V_{cjj}^{1/3})^3 / 8 \tag{9}$$

As shown in the earlier study, only one adjustable coefficient η_{ij} is sufficient to characterize each binary system.

TABLE 1. CONSTANTS FOR THE REFERENCE FLUIDS

Constant	CO_2	n-$C_{12}H_{26}$
Critical temp., $T_c(K)$	304.21	658.26
Critical press., $P_c(MPa)$	7.379	1.824
Critical compressibility, Z_c	0.2742	0.2376
Acentric factor, ω	0.225	0.562
Rackett constant, $Z_{(r)}$	0.27275	0.24692

TABLE 2. CRUDE IDENTIFICATION

Crude oil	SG	$T_b(K)$
A	.951	707.92
B	.858	606.36
C	.858	669.04
D	.944	710.78
E	.976	785.54
F	.984	704.52
G	.894	720.81
H	.988	773.09
I	.945	731.81

C. and F. were refined oils. The rest were crude oils.

The application of Eqns. (3)-(9) to any defined mixture at a given temperature requires only the properties of two reference substances and the critical properties and acentric factors of all components (or pseudo-pure-components) in the mixtures as will be described below.

APPLICATION TO CO_2—CRUDE OIL MIXTURES

The method outlined above has been used to obtain swelling factors in CO_2-crude oil mixtures, with equations for saturated liquid densities for two suitable references. CO_2 and n-dodecane were chosen as the reference substances in all calculations presented below. CO_2 is obviously a key component in CO_2-crude oil systems, and n-dodecane is an n-alkane with a large acentric factor for which an accurate expression for the saturated liquid density was available.

The saturated liquid densities of CO_2 and n-dodecane were represented as functions of reduced temperature by the modified Rackett equation of Spencer and Adler (1978)

$$\frac{Z_c^{(r)}}{\rho_R^{(r)}} = Z_{(r)}^{\{1 + (1 - T_R)^{2/7}\}} \tag{10}$$

where the single constant $Z_{(r)}$, the values of the critical properties, and acentric factors for each reference are given in Table 1. These were obtained from the work of Spencer and Adler (1978) and from Reid et al. (1977).

In extending Eqns. (3)-(9) to CO_2-crude oil mixtures, the mixtures are treated as binary systems, with the crude regarded as a pseudo-pure component. A major problem here is that each crude is a mixture of various hydrocarbons, and the composition of these hydrocarbons is unknown and varies from crude to crude. Adequate characterization of crude oils is therefore necessary as a first step. Attempts at this were made as early as 1935, by Watson et al. Their characterization factor is called "Watson K factor" or the "UOP characterization factor." It is defined as the mean average boiling point raised to the one-third power, divided by the specific gravity of the crude.

Before Eqn. (3) can be used for the crude, however, values must be obtained for its hypothetical critical properties, and acentric factor given the specific gravity and the boiling temperature or the Watson K factor. This problem was studied by Kesler and Lee (1976) when they correlated the enthalpy of crude oil fractions. Kesler and Lee used the available crude data on enthalpies to estimate the apparent critical properties of each crude as a function of its specific gravity and average boiling temperature. They obtained the following relationships for the critical temperature and pressure

$$T_c = 341.7 + 811\ SG + (0.4244 + 0.1174\ SG)\ T_b + (46690 - 326230\ SG)/T_b \tag{11}$$

$$\ln P_c = 8.3634 - \frac{0.0566}{SG} - \left(0.24244 + \frac{2.2898}{SG} + \frac{0.11857}{SG^2}\right) \times 10^{-3} T_b + \left(1.4685 + \frac{3.648}{SG} + \frac{0.47227}{SG^2}\right) \times 10^{-7} T_b^2 - \left(0.42019 + \frac{1.6977}{SG^2}\right) \times 10^{-10} T_b^3 \tag{12}$$

Kesler and Lee also correlated the acentric factor of each crude as a function of its 'Watson K factor' and the reduced boiling temperature, $T_{br} (= T_b/T_c)$ as

$$\omega = -7.904 + 0.1352\ K - 0.007465\ K^2 + 8.359\ T_{br} + (1.408 - 0.01063\ K)/T_{br} \quad (\text{for } T_{br} > 0.8) \tag{13}$$

and

$$\omega = \frac{\ln P_{br} - 5.92714 + 6.09648 T_{br}^{-1} + 1.28862 \ln T_{br} - 0.169347\ T_{br}^6}{15.2518 - 15.6875\ T_{br}^{-1} - 13.4721 \ln T_{br} + 0.43577\ T_{br}^6} \quad (\text{for } T_{br} < 0.8) \tag{14}$$

where $P_{br} = 14.7/P_c$ and T_c, P_c are calculated from Eqns. (11) and (12). Hence, given the boiling point or Watson K-factor and specific gravity of any crude, its critical temperature, critical pressure and acentric factor can be estimated for use with any corresponding states method. The critical compressibility of a given crude was estimated in this study using

$$Z_c = 0.2905 - 0.085\ \omega \tag{15}$$

and hence the critical volume was calculated from

$$V_c = Z_c R T_c / P_c \tag{16}$$

Watson K factors (calculated from viscosities) and specific gravities of the crudes studied in this paper have been reported by Simon and Graue (1965). The average boiling point of each crude was calculated from this data using the relationship

$$T_b = (\text{Specific Gravity} \times \text{Watson K factor})^3 \tag{17}$$

RESULTS AND DISCUSSION

Measurements on 39 different CO_2-crude oil mixtures were reported by Simon and Graue (1965). The mixtures included nine different oils (seven crudes and two refined oils) whose properties are listed in Table 2. Using these properties and Eqns. (11)-(16), we can calculate the critical properties and acentric factors of the crude oils. These critical properties, in turn, used with Eqn. (3), estimate the densities of the crude oils at various temperatures.

Equations (3)-(9) were then used to estimate the densities of mixtures of CO_2-crude oil at the same temperatures (given the

TABLE 3. CALCULATED AND EXPERIMENTAL VALUES OF SWELLING FACTORS FOR CO_2-CRUDE OIL MIXTURES

Oil	Mix	T(°K)	P(MPa)	x_{CO2}	SW. Fac_{exp}	SW. Fac_{calc}	Dev. %
A	1	316.5	2.000	0.196	1.025	1.024	−0.10
(η_{12}=	2		3.17	0.294	1.039	1.039	0.
1.008)	3		5.45	0.455	1.092	1.081	−1.01
	4		13.10	0.667	1.245	1.226	−1.53
	5	366.5	7.85	0.423	1.070	1.081	1.03
	6		16.28	0.625	1.196	1.211	0.42
B	1	344.3	3.22	0.235	1.048	1.046	−0.19
(η_{12}=	2		5.94	0.380	1.104	1.095	−0.81
1.086)	3		8.90	0.531	1.193	1.187	−0.50
	4		14.06	0.675	1.370	1.377	0.51
C	1	266.5	3.18	0.313	1.053	1.047	−0.57
(η_{12}=	2		6.15	0.495	1.112	1.101	−0.99
1.020)	3		10.58	0.667	1.220	1.229	0.74
	4		16.38	0.717	1.303	1.304	0.08
D	1	322.1	3.25	0.299	1.040	1.042	0.19
(η_{12}=	2		6.87	0.508	1.116	1.103	−1.16
1.006)	3		10.31	0.632	1.202	1.188	−1.16
	4	394.3	3.78	0.215	1.031	1.033	0.19
	5		7.75	0.366	1.072	1.069	−0.28
	6		9.65	0.430	1.092	1.092	0
	7		15.80	0.571	1.163	1.175	1.03
E	1	322.1	2.78	0.251	1.024	1.030	0.59
(η_{12}=	2		5.23	0.457	1.051	1.055	0.38
0.912)	3		10.71	0.669	1.148	1.148	0
	4		12.29	0.677	1.163	1.155	−0.69
F	1	322.1	3.57	0.283	1.049	1.049	0
(η_{12}=	2		7.69	0.498	1.129	1.128	−0.09
1.06)							
G	1	327.6	3.80	0.356	1.052	1.061	0.85
(η_{12}=	2		7.54	0.555	1.128	1.128	0
0.996)	3		10.62	0.658	1.205	1.205	0
	4		16.00	0.708	1.252	1.267	1.20
H	1	327.6	2.76	0.251	1.013	1.030	1.68
(η_{12}=	2		9.20	0.584	1.117	1.113	−0.36
0.948)	3		12.80	0.650	1.159	1.159	0
I	1	335.9	5.65	0.418	1.068	1.069	0.09
(η_{12}=	2		10.15	0.598	1.152	1.150	−0.17
0.986)	3		15.17	0.681	1.232	1.232	0
	4	366.5	4.96	0.328	1.049	1.052	0.29
	5		11.59	0.553	1.133	1.133	0.

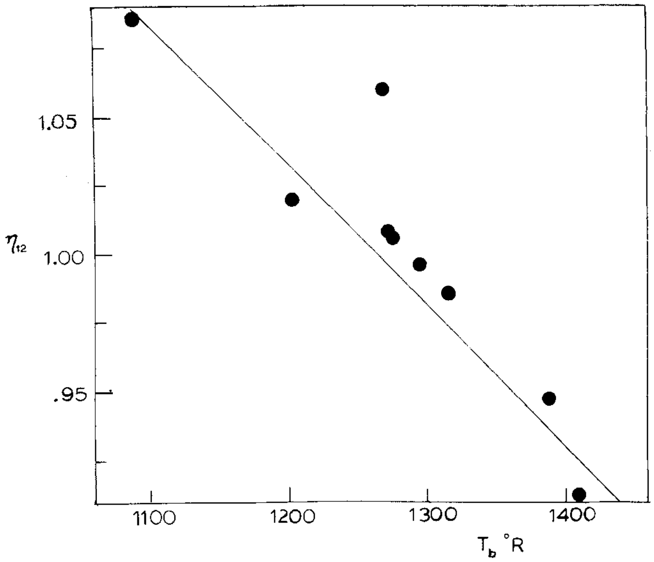

Figure 1. The binary interaction coefficient η_{12} for CO_2-crude oil mixtures as a function of the average boiling temperature of the crude.

solubility of CO_2 in the crude oil at those temperatures).* The two calculated densities were then used in Eqn. (1) to obtain the swelling factors of CO_2-crude oil mixtures.

Experimental and calculated swelling factors are tabulated in Table 3. Very good agreement can be obtained between experimental and calculated values, provided a single binary interaction coefficient is used to characterize each CO_2-crude oil mixture. The overall average absolute deviation for the 39 data points was 0.48% and the maximum deviation was 1.68%. This compares favorably with an average absolute deviation of 0.5% and a maximum deviation of 2.6% for Simon and Graue's graphical correlation.

In addition to the computational advantages of the present analytical method, the method has the further advantage that the single binary interaction coefficient used in the calculations varies linearly with the boiling temperature of the crude (Figure 1). The method can therefore be interpolated and extrapolated (with caution) to any particular crude whose average boiling point or Watson K-factor and specific gravity are known. There is also the important advantage that the method is not restricted to binary mixtures and can be extended to mixed gas-crude oil systems using binary coefficients only.

No theoretical reason for the correlation of the binary interaction coefficient η_{12} with the boiling point of the crude is offered here. We note only that similar correlations between binary interaction coefficients and critical properties (and therefore boiling temperatures via Eqns. 11-16) have been obtained for other hydrocarbon systems (Teja 1978), and therefore the present correlation is not unusual. The single value, which does not apparently fall on the line (Figure 1), is associated with a refined oil (F), where only two data points were available. If a value of η_{12} from the straight line is used to obtain the swelling factors for these two data points, the average error for these points increases to about 2%, which is still quite satisfactory.

Experimental saturation pressures are also reported in Table 3. These were not used directly in any calculations as discussed above, but are shown merely to demonstrate the range of pressures considered here. It should also be added that CO_2-heavy hydrocarbon mixtures sometimes exhibit liquid phase separations, so that not all compositions need be possible at a given temperature.

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NOTATION

K = Watson or UOP characterization factor
P = pressure
R = gas constant
SG = specific gravity
T = thermodynamic temperature
V = volume
x = mole fraction
Z = compressibility; constant in Rackett equation

Greek Letters

η = binary interaction coefficient
ρ = density
ω = acentric factor

Superscripts

$r1$ = reference fluid 1
$r2$ = reference fluid 2

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*It should be noted that the saturated liquid density of mixtures is a function of composition and reduced temperature only. Thus, pressure does not appear explicitly in the calculations but implicitly via its effect on the CO_2 solubility.

Subscripts

b = boiling point value
c = critical value
calc = calculated value
exp = experimental value
i,j = components i,j
(r) = reference
R = reduced value

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Modelling Flow Pattern Transitions for Steady Upward Gas-Liquid Flow in Vertical Tubes

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Models for predicting flow pattern transitions during steady gas-liquid flow in vertical tubes are developed, based on physical mechanisms suggested for each transition. These models incorporate the effect of fluid properties and pipe size and thus are largely free of the limitations of empirically based transition maps or correlations.

SCOPE

When gas-liquid mixtures flow in a conduit, the two phases may distribute in a variety of patterns. The particular pattern one observes depends on the flow rates, the fluid properties and the tube size. Figure 1 shows the expected patterns for a 5.0 cm diameter vertical pipe, flowing water and air at low pressure. Heat and mass transfer rates, momentum loss, rates of back mixing and residence time distributions all vary greatly with flow pattern. Given the existence of any one pattern, it is possible to model the flow so as to predict the important process design parameters. However, a central task is to predict which flow pattern will exist under any set of operating conditions as well as the flow rate pair at which transition between flow patterns will take place.

Many two-phase flow pattern maps have been proposed. Most of these have been based primarily on experiments and thus were limited to the conditions near those of the measurements. It is the objective of this work to suggest physically based mechanisms which underlie each transition and to model the transitions based on these mechanisms. The results are applicable for a wider range of properties and conduit sizes than would be expected from empirically determined transitions.

CONCLUSIONS AND SIGNIFICANCE

Models are developed to predict the transition boundaries between the four basic flow patterns for gas-liquid flow in vertical tubes: bubble, slug, churn and dispersed-annular. It is suggested that churn flow is the development region for the slug pattern and that bubble flow can exist in small pipes only at high liquid rates, where turbulent dispersion forces are high. Each transition is shown to depend on the flow rate pair, fluid properties and pipe size, but the nature of the dependence is different for each transition, because differing mechanisms control. The theoretical predictions are in reasonably good agreement with a variety of published flow maps based on data.

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