A Simple Relation between Solubility Parameters and Densities for Live Reservoir Fluids

Julian Y. Zuo,*,[†] Oliver C. Mullins,[‡] Denise Freed,[‡] and Dan Zhang[†]

DBR Technology Center, Schlumberger, 9450-17 Avenue, Edmonton, Alberta, Canada T6N 1M9, and Schlumberger Doll Research, Cambridge, Massachusetts 02139

A simple equation has been developed for estimating the solubility parameters of live reservoir fluids at elevated pressure and reservoir temperature. The solubility parameters of live reservoir fluids have been simply related to their measured densities by a linear function. The equation has been validated using 45 reservoir fluids covering heavy oil, black oil, volatile oil, and gas condensate with a total of 760 data points. The gas to oil ratio (GOR) range is from (25 to 9369) $m^3 \cdot m^{-3}$, and the American Petroleum Institute (API) gravity varies from (16.6 to 50.2). The pressure ranges from (0.1 to 150.7) MPa, and the reservoir temperature is over a range of (323.9 to 422.0) K. The average absolute deviation of solubility parameters is 0.19 $MPa^{0.5}$ between the new equation and the method proposed by Wang et al. Furthermore, the new equation and the Peng−Robinson equation of state (PR EoS) have been used to calculate solubility parameters, and the results have been compared with the experimental data at pressures up to 30 MPa and 303.15 K for four pure hydrocarbons as well as dead and live oils. The predictions by the new equation and the PR EoS with an average deviation of < 0.5 $MPa^{0.5}$ are within the experimental uncertainty of < 0.8 $MPa^{0.5}$. The results show that the developed equation in this work can be successfully used to approximate the solubility parameters of live reservoir fluids in terms of their measured densities with good accuracy.

Introduction

Asphaltene instability can cause serious asphaltene precipitation or deposition problems in oil production. Asphaltenes are defined as a solubility class, which is the heaviest fraction of oil, insoluble in alkanes such as heptane but soluble in toluene. Asphaltenes are usually dissolved as nanoaggregates in crude oil at reservoir conditions.[1] Sometimes asphaltenes are stably suspended as clusters of nanoaggregates if the asphaltene content in crude oil is high or if the reservoir conditions are at the edge of the asphaltene unstable region.[1] Asphaltenes (or colored asphaltene-like resins) are also dispersed molecularly in condensate where asphaltene contents are very low.[1−3] Above the saturation pressure, a reduction in pressure during oil production causes the density and solubility parameter and, thus, the solvation power of the reservoir fluid for asphaltenes to drop. In contrast, below the saturation pressure, a pressure reduction increases the solvation power due to the liberation of gaseous components. Asphaltene onset boundaries are usually obtained by combining experimental data and thermodynamic models. That is, asphaltene onset envelopes are estimated by a thermodynamic model which has been adjusted to match one or more asphaltene onset point(s).

In the past decades, the Flory−Huggins type of solubility model has been widely used to model asphaltene precipitation in crude oils,[4−6] for example, with the addition of solvents and to screen for potential asphaltene problems during oil production.[7,8] A reservoir fluid can be taken into account as a pseudobinary system consisting of the asphaltene and maltene. The chemical potentials of the asphaltene and maltene can be expressed as[5]

$$\Delta\mu_a = RT\left[\ln \phi_a + \phi_m\left(1 - \frac{v_a}{v_m}\right)\right] + v_a\phi_m^{\,2}(\delta_a - \delta_m)^2 \tag{1}$$

$$\Delta\mu_m = RT\left[\ln \phi_m + \phi_a\left(1 - \frac{v_m}{v_a}\right)\right] + v_m\phi_a^{\,2}(\delta_a - \delta_m)^2 \tag{2}$$

where R, T, δ, v, and ϕ are the universal gas constant, the temperature, the solubility parameter, the molar volume, and the volume fraction, respectively. Subscripts a and m denote the asphaltene and the maltene. Equations 1 and 2 can be employed not only for stock tank oil (STO) but also live reservoir fluids. Because various amounts of light hydrocarbons and nonhydrocarbon gases are dissolved in the hydrocarbon mixtures at high pressure, the solubility parameters of live fluids are dependent on not only temperature and pressure but also the gas to oil ratio (GOR) and compositions. The dissolved gases decrease the solubility parameters of live fluids. This is the reason why gas injection processes may cause asphaltene instability problems.

On the other hand, reservoir connectivity remains the biggest risk factor in deep water development. Reservoir fluid (especially asphaltene) gradients can be used to address reservoir connectivity. In general, different hydrocarbon fluids charge into reservoirs at the ultimate nonequilibrium state. Equilibration then requires a massive fluid flow in the reservoir. Diffusive mixing, which is extremely slow, is likely required in most equilibration processes. A sealing barrier or low transmissivity fault would preclude equilibration. That is, equilibrium asphaltene gradients strongly imply reservoir connectivity. Up to now, there have been no accurate predictive thermodynamic models available in the open literature for modeling asphaltene gradients in oil

---

* To whom correspondence should be addressed. E-mail: yzuo@slb.com.
[†] DBR Technology Center. E-mail: dzhang3@slb.com (D.Z.).
[‡] Schlumberger Doll Research. E-mail: mullins1@slb.com (O.C.M.); freed1@slb.com (D.F.).

10.1021/je100155d

reservoirs, although some successful work has been done on modeling asphaltene phase behavior.[4−9,11,12] It is required to include a gravity term when modeling reservoir fluids travel downhole because large vertical offsets are routinely encountered. For gravity, size counts. Without knowing the molecular or colloidal size of asphaltenes, modeling asphaltenes in reservoirs is precluded and is reduced to fitting with pseudocomponents. In particular, cubic equations of state (EoS's) are all variants of the van der Waals EoS. Also, the van der Waals EoS is derived from the ideal gas law. The cubic EoS's are developed for gas−liquid equilibria and were never intended to handle solids, let alone complex solids such as asphaltenes. In spite of this, the cubic EoS's have been used in commercial software to handle asphaltene phase behavior and gradients. The issue is that a lot of adjustable parameters such as molecular weight, size, and interaction parameters were utilized in the EoS and they cannot be used to discern reservoir connectivity using equilibrium asphaltene gradients. Therefore, a thermodynamic model[2,3] was developed for the modeling of equilibrium asphaltene distributions in oil columns by combining the Flory−Huggins type of solubility model[4−6] with the gravitational contribution. A detailed discussion of the theoretical treatment of asphaltenes in reservoirs can be found elsewhere[2,3] and is beyond the scope of this paper. Here, the key results are simply listed in a heuristic manner. In a general sense, there are three terms that control the distribution of (suspended) asphaltenes in crude oils: gravity, solubility, and entropy. All three terms depend on the asphaltene particle size which is from recent advances in asphaltene science.[1] The entropy term acts to disperse the asphaltenes throughout the oil column. Its magnitude is not that large. Naturally, the entropy term is larger for more numerous but smaller asphaltene particles at a given asphaltene mass fraction. The gravity term requires knowledge of the molecular and/or colloidal size of asphaltenes in the reservoir crude oil as well as the density contrast. The solubility term for asphaltenes is heavily dependent on the GOR where variations of the solubility parameters of live reservoir fluids with depth play a very important role.

Therefore, the solubility parameters of live reservoir fluids are crucial for the analysis of asphaltene gradients in oil reservoirs during formation evaluation. Moreover, this new approach aids in understanding processes involving reservoir fluids in geologic time that give rise to tar mats and bitumen impregnated core. In eqs 1 and 2, the most important parameters are the solubility parameters of the maltene and asphaltene, which are usually determined by matching asphaltene onset (and/or other) experimental data simultaneously. Doing this might result in unrealistic solubility parameter values in mathematic regression. In contrast, the pressure−volume−temperature (*PVT*) reports give us a great deal of information on the phase behavior of reservoir fluids at different pressures and formation temperatures. This information can be employed to compute the solubility parameters of reservoir fluids. Once a method is generalized to estimate the solubility parameters of live fluids, the solubility parameters and/or molar volume (size) of asphaltenes can be adjusted to match the experimental data. As a result, the solubility parameters of live fluids are at least reasonable. Similar treatments are also utilized for the analysis of asphaltene gradients in oil reservoirs. In other words, a single formalism is used to treat both asphaltene gradients and phase behavior in the reservoir. Once variations of oil solubility parameters, GOR (compositions) with depth, and asphaltene solubility parameters are obtained, the particle size of asphaltenes can be determined by corresponding thermodynamic modeling of downhole fluid analysis (DFA) measurements of asphaltene (color) gradients in oil columns. Consistency is checked with these observations and analysis as well as with known asphaltene science for asphaltene molecules, nanoaggregates, or clusters of nanoaggregates.[1−3] If discrepancies are found, then reservoir fluid dynamics are likely and can be determined. This information can be used to delineate reservoir connectivity or compartmentalization, which is the greatest risk factor in deepwater−oil production. Therefore, the solubility parameters of live reservoir fluids are vital in the Flory−Huggins type of solubility model.

The solubility parameters of STO have been related to the STO refractive indices and/or densities measured at ambient conditions.[9−11] Estimating the solubility parameters of live fluids at downhole reservoir conditions requires fluid *PVT* properties which are usually measured in laboratories and calculated by EoS's after matching the experimental *PVT* data.[4,5] However, fluid *PVT* properties may not be available, or they may be only partially available, such as knowing GOR and densities of live fluids at high pressure in DFA measurements. Therefore, a simple method is highly demanded for the estimation of the solubility parameters of live fluids under formation conditions. In this paper, a simple equation has been proposed to compute the solubility parameters of live reservoir fluids. The developed equation associates the solubility parameters of live fluids only with their densities measured in *PVT* laboratories or by DFA tools.

Existing Models for Solubility Parameters of Dead and Live Oils

The molar refraction (R_m) of a pure substance can be given by the Lorentz−Lorenz equation

$$R_m = F_{RI}\frac{M}{\rho} \quad \text{and} \quad F_{RI} = \frac{n^2 - 1}{n^2 + 2} \tag{3}$$

where F_{RI}, M, n, and ρ are the function of the refractive index, the molar mass, the refractive index, and the mass density, respectively. Vargas et al.[11,23] obtained the one-third rule for 229 dead crude oils all over the world in the API range of (9.9 to 41.3) ° API (API = 141.5/SG − 131.5, where SG is the specific gravity), which implies the function of the refractive index divided by the mass density is a constant which is equal to 1/3,

$$F_{RI}\frac{1}{\rho} = \left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{1}{\rho} = \frac{R_m}{M} = \frac{1}{3} \tag{4}$$

Because the molar refraction is nearly independent of temperature and pressure, the one-third rule can be applied over a wide range of temperature and pressure. Wang and Buckley proposed a linear relation between the solubility parameter and the function of the refractive index for dead crude oils at 20 °C[5]

$$\delta_{STO}/\text{MPa}^{0.5} = 52.042F_{RI} + 2.904 \tag{5}$$

Applying the one-third rule to eq 5, the STO solubility parameters can be expressed as a linear function of the STO mass density at $T = 15.6$ °C and $p = 101.325$ kPa

$$\delta_{STO}/\text{MPa}^{0.5} = 17.347\rho_{STO}/\text{g}\cdot\text{cm}^{-3} + 2.904 \tag{6}$$

Correra et al. developed similar correlations for the STO solubility parameters in terms of the STO mass density based on about 170 dead crude oils from several Italian and African fields[10]

$$\delta_{\mathrm{STO}}/\mathrm{MPa}^{0.5} = 13.181\rho_{\mathrm{STO}}/\mathrm{g \cdot cm^{-3}} + 6.3583 \qquad (7)$$

It can be seen that the coefficients in eq 6 are different from those in eq 7. The difference might be caused by the different oil databases used for developing both correlations. It is noted that eq 7 was developed only using Italian and African oils. To compare both correlations, STO solubility parameters at different densities were calculated. The differences of STO solubility parameters between the calculations by eqs 6 and 7 ($\Delta\delta_{\mathrm{STO}}/\mathrm{MPa}^{0.5}$) are −0.538, −0.122, 0.295, and 0.712 at $\rho_{\mathrm{STO}}/\mathrm{g \cdot cm^{-3}}$ = (0.7, 0.8, 0.9, and 1.0) corresponding to API gravity of (71, 45, 26, and 10) °API, respectively. The differences are reasonable in a density range of interest.

Live oil can be treated as a mixture of STO and flashed gas. Buckley et al. proposed an equation to estimate the function of the refractive index for live oils using the volume average mixing rule based on one unit volume of STO[4]

$$(F_{\mathrm{RI}})_{\mathrm{LiveOil}} = \frac{1}{B_o}(F_{\mathrm{RI}})_{\mathrm{STO}} + 1.34 \cdot 10^{-6}\frac{R_s}{B_o}\left(\frac{F_{\mathrm{RI}}}{C}\right)^{0}_{\mathrm{gas}} \qquad (8)$$

where C, B_o, and R_s are the molar concentration (in $\mathrm{mol \cdot cm^{-3}}$), the formation volume factor (FVF in $\mathrm{m^3 \cdot m^{-3}}$), and the GOR (in $\mathrm{m^3 \cdot m^{-3}}$), respectively, which can be obtained from fluid *PVT* reports. The factor $1.34 \cdot 10^{-6}$ in the second term on the right side of eq 8 converts R_s from $\mathrm{m^3 \cdot m^{-3}}$ to $\mathrm{mol \cdot cm^{-3}}$. The ratio of F_{RI}/C is the molar refraction of the flashed gas mixture.

Substituting eq 5 into eq 8 and rearranging it, the expression is given by[6]

$$\delta_{\mathrm{LiveOil}}/\mathrm{MPa}^{0.5} = \frac{1}{B_o}\delta_{\mathrm{STO}}/\mathrm{MPa}^{0.5} + 2.904\left(1 - \frac{1}{B_o}\right) + 6.964 \cdot 10^{-5}\frac{R_s}{B_o}\sum x_i R_{mi} \qquad (9)$$

where R_{mi} and x_i are the molar refraction and the mole fraction of light component i in the solution gas, respectively. To obtain eq 9, it is assumed that eq 5 is valid even for live oils.

If no refractive index measurements are available, eq 6 can be utilized to calculate the solubility parameters of dead crude oils, which is used in this work. The molar refraction of the light ends can be approximately computed by[6]

$$R_{\mathrm{mLight}} = \sum x_i R_{mi} = -15.9\left(\frac{x_{\mathrm{C1-C3}}}{x_{\mathrm{C1-C6}}}\right) + 23.0 \qquad (10)$$

where $x_{\mathrm{C1-C3}}/x_{\mathrm{C1-C6}}$ is the mole ratio of group C_1-C_3 in group C_1-C_6. At a high GOR (e.g., > 356 $\mathrm{m^3 \cdot m^{-3}}$), eq 10 may not be accurate enough. As a result, the molar average is used to estimate the molar refraction of the solution gas. The molar refractions of light components at ambient conditions are given in Table 1. Once the *PVT* data and mole fractions of the solution gas components are available, the molar refraction of the solution gas mixture can be calculated.

Table 1. Molar Refraction of Light Components at T/K = 298.15 and p/kPa = 101.325

component	$R_m/\mathrm{cm^3 \cdot mol^{-1}}$	ref
N_2	4.43	NPL[13]
CO_2	6.66	Besserer and Robinson[14]
H_2S	10.73	NPL[13]
C_1	6.575	Achtermann and Hong[16]
C_2	11.26	Hadrich[15]
C_3	15.97	Hadrich[15]
C_4	20.6	Hadrich[15]
C_5	25.35	Hadrich[15]
C_6	29.85	Hadrich[15]

Wang et al. tested and verified eq 9 for 27 live oil samples in their practical screening method (ASphaltene InStability Trend, ASIST) for potential asphaltene destabilized problems in oil reservoirs,[6] which dramatically improved the accuracy of asphaltene instability predictions. Kraiwattanawong et al. proposed similar equations for the solubility parameters of live fluids using fluid *PVT* properties and the EoS.[17]

A New Equation for Solubility Parameters of Live Fluids

The Lorentz−Lorenz equation (eq 3) can be rearranged as

$$F_{\mathrm{RI}} = \frac{R_m}{M}\rho \qquad (11)$$

As mentioned by Wang,[9] the molar refraction (R_m) is nearly independent of temperature and pressure. Now, if it is assumed that the molar refraction (R_m) is independent of temperature and pressure, then the function of the refractive index (F_{RI}) is a linear function of density for a specified fluid provided that its composition is fixed. Moreover, if every crude oil is treated as a pseudocomponent in a single phase (for instance, above the saturation pressure), the ratio (R_m/M) is supposed to be a constant, which is the one-third rule validated by Vargas et al.[11,23] for a great number of dead oils. The one-third rule is also supposed to be valid for live fluids because the ratio (R_m/M) is assumed to be independent of temperature and pressure and equal to 1/3. Therefore, eq 6 can be extended to live fluids at any conditions as well if the assumption mentioned previously is valid. Consequently, the new equation for solubility parameters is just to extend eq 6 simply to live oils

$$\delta/\mathrm{MPa}^{0.5} = 17.347\rho/\mathrm{g \cdot cm^{-3}} + 2.904 \qquad (12)$$

Equation 12 is now used for estimating solubility parameters of both STO and live oils in terms of corresponding density. The new equation must be verified for live oil at high pressure.

Validation of the New Equation for Solubility Parameters of Live Fluids

To validate the new equation for the solubility parameters of live reservoir fluids at high pressure, the *PVT* data for 45 different fluids were used from heavy oil, black oil, near critical volatile oil to gas condensate. The GOR range is from (25 to 9369) $\mathrm{m^3 \cdot m^{-3}}$. STO density changes from (0.779 to 0.955) $\mathrm{g \cdot cm^{-3}}$ (API gravity varies from (16.6 to 50.2) °API). The pressures are varied from (0.1 to 150.7) MPa ((14.7 to 15 326) psi), and the reservoir temperatures cover a range of (323.9 to 422.0) K ((123.4 to 300.0) °F). The typical complete *PVT* tests were conducted for these 45 fluids. The *PVT* experiments consist of the single stage flash, constant composition expansion (CCE), differential liberation (DL), and separator testing. On the basis of the *PVT* data, the solubility parameters of the 45 live fluids above and below saturation pressure at reservoir conditions were calculated by use of eq 9. On the other hand, the solubility parameters were estimated by means of eq 12 in terms of the measured densities.

The solubility parameters calculated by eqs 9 and 12 versus densities are illustrated in Figure 1 for these 45 fluids. It can be seen that the solubility parameters increase linearly with an increase in live fluid densities. It is known that an increase in GOR causes a reduction in densities as well as solubility parameters. The correlated linear function (dotted line) based

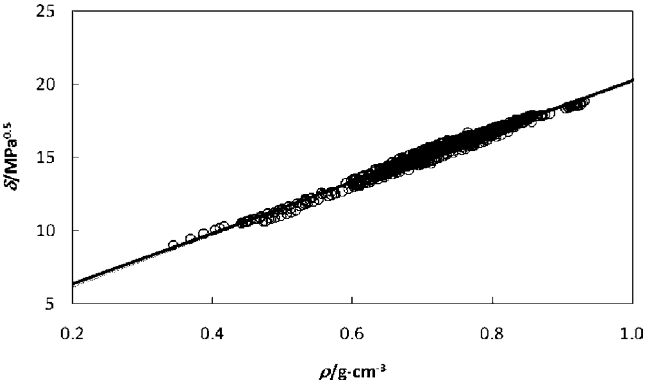

Figure 1. Solubility parameters versus density for 45 live fluids: ○, calculated by eq 9; —, calculated by new equation of eq 12; ••••, a linear correlation obtained from the values calculated by eq 9 ($\delta = 17.717\rho + 2.6273$; $R^2 = 0.9821$). A linear relationship was found between the solubility parameter and the density.

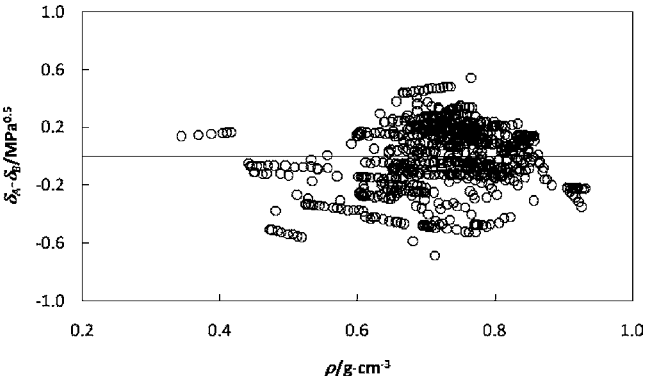

Figure 2. Deviations of solubility parameters ($\delta_A - \delta_B$) versus density for 45 live fluids: ○, solubility parameter differences ($\delta_A - \delta_B$) between the calculations by eqs 9 and 12. The bias is −0.01 MPa$^{0.5}$. The deviations are within ± 0.7 MPa$^{0.5}$, which is close to a typical experimental uncertainty of < 0.8 MPa$^{0.5}$ using the internal pressure approach.

Table 2. Summary of the Results for 45 Reservoir Fluids from Heavy Oil to Gas Condensate[a]

oil #	R_s m^3·m^{-3}	API	p_{max} MPa	N_P	AAD MPa$^{0.5}$	AARD
1	25.1	16.6	55.3	17	0.24	1.28
2	30.1	26.4	41.4	13	0.09	0.50
3	31.3	25.7	41.4	17	0.12	0.69
4	34.7	30.3	55.2	16	0.18	1.06
5	51.8	30.6	105.7	24	0.14	0.85
6	57.5	34.4	58.6	19	0.06	0.36
7	58.1	33.8	20.7	11	0.14	0.84
8	60.7	35.5	82.8	17	0.46	2.97
9	69.8	22.1	27.6	15	0.45	2.74
10	76.4	24.9	55.2	16	0.07	0.39
11	111.0	32.9	34.5	16	0.09	0.54
12	127.0	42.3	34.5	12	0.16	1.05
13	130.4	22.8	93.1	21	0.10	0.57
14	142.3	28.8	41.4	12	0.18	1.14
15	144.8	27.3	68.9	21	0.14	0.88
16	149.6	35.5	55.3	21	0.08	0.54
17	153.2	35	100.1	26	0.17	1.08
18	166.3	22.9	103.5	17	0.18	1.09
19	167.8	26.3	69.1	18	0.27	1.71
20	172.9	37.8	100.1	19	0.41	2.69
21	176.0	32	96.5	18	0.25	1.59
22	178.8	29.8	93.1	17	0.10	0.63
23	184.7	25.2	96.5	20	0.15	0.97
24	203.2	35.2	58.6	23	0.25	1.70
25	204.8	34.7	93.1	19	0.15	1.01
26	213.4	30	100.0	16	0.14	0.90
27	213.4	30.1	86.0	14	0.08	0.49
28	222.3	39.4	55.2	17	0.20	1.39
29	222.6	33.1	100.0	15	0.22	1.43
30	230.6	30.3	101.1	17	0.21	1.41
31	238.5	27.9	100.1	16	0.20	1.27
32	253.3	29.7	100.0	16	0.05	0.34
33	261.5	33.3	102.8	19	0.22	1.51
34	281.9	28.8	100.0	19	0.06	0.43
35	298.5	33.9	100.0	18	0.24	1.74
36	351.0	39.2	65.6	24	0.22	1.57
37	404.6	36.4	82.7	22	0.19	1.35
38	405.4	50.2	51.7	14	0.48	3.90
39	441.9	35.4	83.1	20	0.30	2.37
40	513.3	35	100.0	10	0.33	2.48
41	712.4	40.5	48.3	12	0.12	0.94
42	746.6	42	89.7	22	0.12	0.98
43	890.3	41.1	100.1	9	0.41	3.71
44	3319.8	43.2	68.9	6	0.16	1.62
45	9375.3	46.8	69.1	9	0.23	2.89
sum				760	0.19	1.31

[a] AAD = $(1/N_P)\ \sum_i|\delta_{Ai} - \delta_{Bi}|$ and AARD = $(1/N_P)\ \sum_i|(\delta_{Ai} - \delta_{Bi})/\delta_{Ai}|\cdot 100$.

on the values calculated by eq 9 is very close to that computed by eq 12 (solid line). The correlation coefficient is about 0.98.

Figure 2 shows the deviations of solubility parameters between the calculations by eqs 9 and 12 as a function of density for live reservoir fluids. The deviations are within ± 0.7 MPa$^{0.5}$. As mentioned by Verdier et al.,[18] a typical experimental uncertainty for solubility parameter measurements using the internal pressure approach is < 0.8 MPa$^{0.5}$.

The results are also summarized in Table 2. The GOR (R_s), API gravity, maximum pressure (p_{max}), number of data points (N_p), average absolute deviation (AAD), and average absolute relative deviation (AARD) are listed in different columns of Table 2.

The AAD is 0.19 MPa$^{0.5}$ (the bias of the deviations is −0.01 MPa$^{0.5}$), and the AARD is 1.31 % (the bias is −0.09 %) for 45 reservoir fluids with a total of 760 data points. From the analyses mentioned previously, it can be seen that the predictions of solubility parameters by eq 12 are in good agreement with those by eq 9 for live reservoir fluids. Consequently, the solubility parameters of live fluids can be estimated by means of the measured live fluid densities. This new equation simplifies the estimation of the solubility parameters of live fluids with no requirements for measuring GOR, formation volume factors, compositions of light ends, and so forth. This simplification makes an analysis of DFA asphaltene gradients and fluid profiling in oil columns in real time possible. This is because there are no complete *PVT* data available for DFA measurements in real time and especially no formation volume factors at downhole conditions. In this case, eq 9 is not applicable. In contrast, eq 12 can be applied because DFA measures live fluid density downhole in real time.

Figure 3 shows typical solubility parameters as a function of pressure at reservoir temperatures for four live oils from heavy oil to near critical volatile oil. Since the near critical volatile oil with a GOR of 746.6 m^3·m^{-3} (4192 scf·STB^{-1}) consists of relatively high acid gases of H_2S and CO_2, a somewhat higher difference was found between eq 9 and the new equation of eq 12. However, the results are still in accord. The solubility parameters of live fluids decrease with a pressure decrease from the reservoir to the bubble points (in a single phase region). This is because fluid expanding leads to decreasing interactions among molecules (particles). Below the bubble point, the dissolved gas escapes from the oil and causes an increase in the solubility parameters of live fluids with a pressure reduction because gas has low solubility parameters. The densities of live fluids have the same behavior as solubility parameters. Below

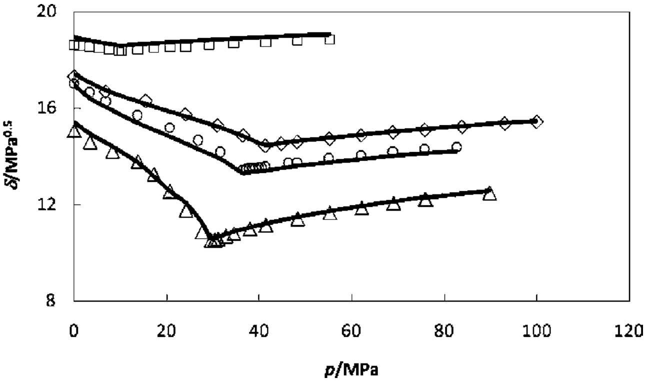

Figure 3. Typical solubility parameters of live fluids as a function of pressure at reservoir temperatures: —, calculated by new equation of eq 12; □, calculated by eq 9 for R_s/m^3·m^{-3} = 25; ◇, calculated by eq 9 for R_s/m^3·m^{-3} = 253; ○, calculated by eq 9 for R_s/m^3·m^{-3} = 405; △, calculated by eq 9 for R_s/m^3·m^{-3} = 747. Higher GOR fluids have larger variations of solubility parameters with pressure.

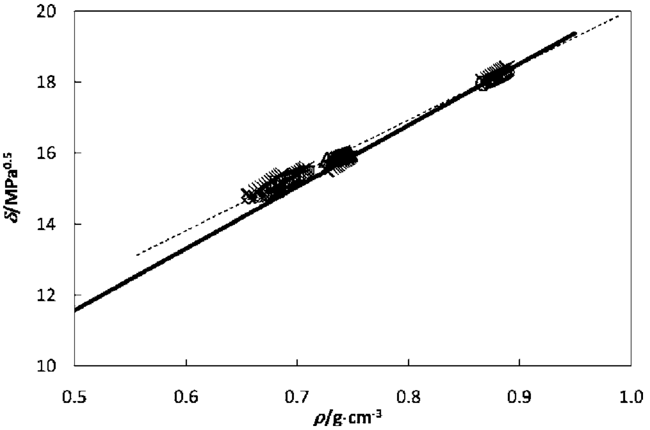

Figure 4. Comparison of solubility parameters of pure hexane, heptane, decane, and toluene at high pressures up to 30 MPa and 303.15 K: —, calculated by the new equation of eq 12; ×, calculated by the PR EoS; ---, a linear regression from the values calculated by the PR EoS ($\delta = 15.599\rho + 4.4475$; $R^2 = 0.9858$); ◇, experimental data[18] for hexane; □, experimental data[18] for heptane; △, experimental data[18] for decane; ○, experimental data[18] for toluene. Both the new correlation and the PR EoS are in good agreement with the experimental data.

the saturation pressure, the larger the GOR varies, the higher the increase of the solubility parameters and densities with pressures is. In contrast, if pressure is above the saturation pressure, the higher GOR and the greater compressibility the fluids have, the larger the reduction of the solubility parameters and densities with pressures is.

To validate the new equation further, the experimental data of solubility parameters at pressures up to 30 MPa and 303.15 K for some pure hydrocarbons and dead and live oils measured by Verdier et al.[18] were used for comparison. At the same time, the Peng−Robinson equation of state (PR EoS)[19,20] with the Peneloux volume translation[21] was also utilized for comparison. The characterization procedure of Zuo and Zhang[22] was employed to characterize the single carbon number and plus fractions of dead and live oils in the EoS calculations. Four pseudocomponents were employed to represent C_{7+} fractions.

Figure 4 compares the results calculated by the new equation of eq 12 and the PR EoS with the experimental data at pressures up to 30 MPa and 303.15 K for pure hexane, heptane, decane, and toluene.[18] The AADs of the solubility parameters calculated by the new equation and the PR EoS for the four pure hydrocarbons are 0.22 and 0.15 MPa$^{0.5}$, respectively. The predictions by both methods are comparable and within the experimental uncertainty (< 0.8 MPa$^{0.5}$). The PR EoS is slightly better at lower pressure, while the new equation is somewhat better at higher pressure. The results indicate that the new equation can be used to estimate solubility parameters of pure hydrocarbons at high pressure with good accuracy.

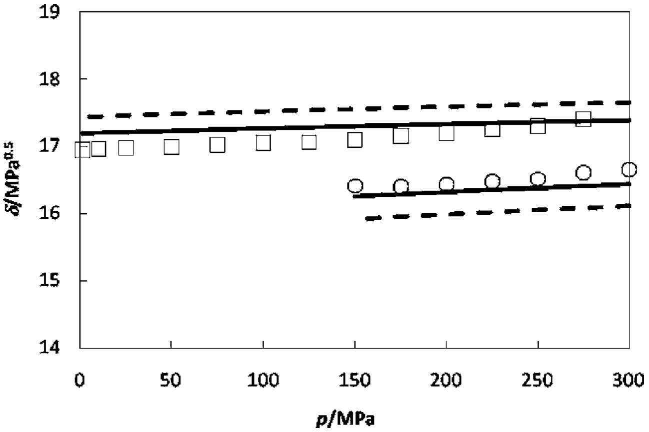

Figure 5. Comparison of solubility parameters of dead oil 1 and live oil 1 at high pressures up to 30 MPa and T/K = 303.15: —, calculated by the new equation of eq 12; ---, calculated by the PR EoS; ○, experimental data[18] for dead oil 1; □, experimental data[18] for live oil 1. The new equation is better than the PR EoS because the latter is dependent on fluid characterization procedures, while the former depends only on fluid densities.

Figure 5 compares the results calculated by the new equation of eq 12 and the PR EoS with the experimental data at pressures up to 30 MPa and 303.15 K for dead oil 1 and live oil 1.[18] The AADs of the solubility parameters calculated by the new equation and the PR EoS for the dead and live oils are 0.17 and 0.45 MPa$^{0.5}$, respectively. Again, the predictions by both methods are within the experimental uncertainty (< 0.8 MPa$^{0.5}$). The new equation is better than the PR EoS for oils. This might be because the PR EoS method is, to a certain extent, sensitive to characterization of a single carbon number and plus fractions of reservoir fluids. As mentioned by Verdier et al., the PR EoS gave an average deviation of 4.9 MPa$^{0.5}$ in calculating oil solubility parameters in terms of the characterization procedure given in their paper.[18] The results show that the new correlation can be utilized to calculate solubility parameters for live reservoir fluids with good accuracy.

Conclusions

The solubility parameters of live reservoir fluids have been found to be a linear function of their densities measured at high pressures and formation temperatures. The new equation has been validated using 45 reservoir fluids from heavy oil, black oil, and volatile oil to gas condensate with a total of 760 data points. Good agreement has been achieved between the calculations with the new equation and the correlation proposed by Wang et al. based on fluid *PVT* properties. In addition, the new equation and the PR EoS with the Peneloux volume translation have been used to calculate solubility parameters, and the results have been compared with the experimental data at pressures up to 30 MPa and 303.15 K for four pure hydrocarbons, a dead oil and a live oil. The predictions by the new equation and the PR EoS are within the experimental uncertainty and comparable. However, the new equation is better than the PR EoS for reservoir fluids because the latter is dependent on fluid characterization procedures, while the former depends only on fluid densities. The results indicate that the new equation can be used to estimate solubility parameters for reservoir fluids at low and high pressures with good accuracy.

Note Added after ASAP Publication: This paper was published on the Web on May 4, 2010. Changes were made to the text, and reference 23 was added. The revised paper was reposted on June 15, 2010.

Literature Cited

(1) Mullins, O. C. The Modified Yen Model. *Energy Fuels* **2010**, *24*, 2179–2207.
(2) Freed, D. E.; Mullins, O. C.; Zuo, J. Y. Equilibrium Distributions of Asphaltenes in the Presence of GOR Gradients. *Energy Fuels* **2010**, submitted.
(3) Zuo J. Y.; Freed, D. E.; Mullins, O. C.; Zhang, D. *Interpretation of DFA Color Gradients in Oil Columns Using the Flory-Huggins Solubility Model*, Paper SPE #130305. To be presented at SPE International Oil & Gas Conference and Exhibition, Beijing, China, June 8−10, 2010.
(4) Buckley, J. S.; Hirasaki, G. J.; Liu, Y.; Von Drasek, S.; Wang, J. X.; Grll, B. S. Asphaltene Precipitation and Solvent Properties of Crude Oils. *Pet. Sci. Technol.* **1998**, *16* (3−4), 251–285.
(5) Wang, J. X.; Buckley, J. S. A Two-Component Model of the Onset of Asphaltene Flocculation in Crude Oils. *Energy Fuels* **2001**, *15*, 1004–1012.
(6) Wang, J. X.; Creek, J. L.; Buckley, J. S. *Screening for Potential Asphaltene Problems*, Paper SPE #103137. Presented at the 2006 SPE Annual Technical Conferences and Exhibition, San Antonio, TX, USA, Sept 24−27, 2006.
(7) Creek, J. L.; Wang, J.; Buckley, J. S. Verification of Asphaltene-Instability-Trend (ASIST) Predictions for Low-Molecular-Weight Alkanes. *SPE Prod. Oper.* **2009**, *5*, 360–367.
(8) Wang, J. X.; Buckley, J. S. *An Experimental Approach to Prediction of Asphaltene Flocculation*, Paper SPE# 64994. Presented at the 2001 SPE International Symposium on Oilfield Chemistry, Houston, TX, USA, Feb 13−16, 2001.
(9) Wang, J. X. Predicting Asphaltene Flocculation in Crude Oils. Ph.D. Thesis, New Mexico Institute of Mining and Technology, Socorro, NM, 2000.
(10) Correra, S.; Merlini, M.; Di Lullo, A.; Merino-Garcia, D. Estimation of the Solvent Power of Crude Oil from Density and Viscosity Measurements. *Ind. Eng. Chem. Res.* **2005**, *44*, 9307–9315.
(11) Vargas, F. M.; Gonzalez, D. L.; Creek, J. L.; Wang, J. X.; Buckley, J.; Hirasaki, G. J.; Chapman, W. G. Development of a General Method for Modeling Asphaltene Stability. *Energy Fuels* **2009**, *23*, 1147–1154.
(12) Wang, J. X.; Buckley, J. S. Asphaltene Stability in Crude Oil and Aromatic Solvents - The Influence of Oil Composition. *Energy Fuels* **2003**, *17*, 1445–1451.
(13) *Kaye & Laby Online Tables of Physical & Chemical Constants,2.5.7 Refractive Index of Gases*, 16th ed.; National Physical Laboratory: Teddington, U.K., 1995. http://www.kayelaby.npl.co.uk/general_physics/2_5/2_5_7.html.
(14) Besserer, G. J.; Robinson, D. B. Refractive Indices of Ethane, Carbon and iso-Butane. *J. Chem. Eng. Data* **1973**, *18* (2), 137–213.
(15) Hadrich, J. The Lorentz-Lorenz Function of Five Gaseous and Liquid Saturated Hydrocarbons. *Appl. Phys.* **1975**, *7*, 209–213.
(16) Achtermann, H. J.; Hong, J. Refractive Index and Density Isotherms for Methane from 273 to 373 K and at Pressure up to 34 MPa. *J. Chem. Eng. Data* **1992**, *37* (4), 414–418.
(17) Kraiwattanawong, K.; Fogler, H. S.; Gharfeh, S. G.; Singh, P.; Thomason, W. H.; Chavadej, S. Thermodynamic Solubility Models to Predict Asphaltene Instability in Live Crude Oils. *Energy Fuels* **2007**, *21*, 1248–1255.
(18) Verdier, S.; Duong, D.; Andersen, S. I. Experimental Determination of Solubility Parameters of Oils as a Function of Pressures. *Energy Fuels* **2005**, *19*, 1225–1229.
(19) Peng, D.-Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.
(20) Peng, D.-Y.; Robinson, D. B. *The characterization of the heptanes and heavier fractions for the PGA Peng-Robinson Programs*; GPA Research Report RR-28, 1978.
(21) Peneloux, A.; Rauzy, E.; Freze, R. A Consistent Correction for Redlich-Kwong-Soave Volumes. *Fluid Phase Equilib.* **1982**, *8*, 7–23.
(22) Zuo, J. Y.; Zhang, D. *Plus Fraction Characterization and PVT Data Regression for Reservoir Fluids near Critical Conditions*, Paper SPE #64520 Presented at SPE Asia Pacific Oil and Gas Conference and Exhibition, Brisbane, Australia, Oct 16−18, 2000.
(23) Vargas, F. M.; Chapman, W. G. Application of the one-third rule in hydrocarbon and crude oil systems. *Fluid Phase Equilib.* **2010**, *290*, 103–108.

Received for review February 11, 2010. Accepted April 26, 2010.

JE100155D