DETERMINATION OF CO_2 MINIMUM MISCIBILITY PRESSURE USING SOLUBILITY PARAMETER

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ABSTRACT

Gas injection process is one of the most efficient Enhanced Recovery Methods. A key parameter of a gas injection project is the Minimum Miscibility Pressure (MMP), the pressure which the efficiency of the local displacement comes close to 100%. Based on the concept of solubility parameter and having as independent variables only saturation pressure and oil temperature, a methodology was developed to calculate the MMP for pure CO_2 with good results.

INTRODUCTION

The gas injection above the Minimum Miscibility Pressure (MMP) is a large used resource to improve the oil recovery from reservoirs. The MMP is the lowest pressure for the development of miscibility through multiple contacts with specific oil at reservoir temperature. The reservoir which the process is applied must be operated in or above the MMP developing miscibility for multiple contacts [1]. Experimental determination of the MMP is slow and expensive; therefore, new methods have been developed based on equation of state and empirical correlations

Equation of state is useful to calculate the reservoir fluid phase behavior, but it is necessary to adjust its parameters to fit lab experiments. These experimental data are obtained from PVT measurements: the constant composition expansion (CCE); differential liberation (DL); swelling tests. Therefore this systematic becomes costly due to the necessary experiments for its application.

The determination of the MMP through correlations is based on sets of experimental data, and is limited to the range of available data. The independent variables are the temperature and, some intrinsic oil characteristics like composition, heavy fraction density, etc. Empirical correlations researchers disagree about influence of oil characteristics in the MMP. The error is important, when comparing the MMP experimental with the calculated ones. It is possible to conclude that the correlation is restricted to the range of experimental data used in its generation.

Lange [2] has developed a procedure for calculating the MMP based on the difference between the oil and gas solubility parameter. Practical experiments conducted in the CEPGN (Petroleum and Natural Gas Study Center of Salvador University - UNIFACS) have shown unsatisfactory results when applying this methodology.

This work presents a new methodology to calculate the MMP for pure CO_2 based on the concept of solubility parameter. The independent variables are the saturation pressure and the reservoir temperature. The independent variables are very well known for any reservoir; therefore, no additional experimental data is necessary.

MMP DETERMINATION USING THE LANGE PROCEDURE

The solubility parameter δ, originates in regular solution theory for mixtures of nonpolar liquids developed by Hildebrand and Scatchard [3]. The solubility parameter of a pure compound is defined as

$$\delta = \left(\frac{\Delta H' - RT + PV}{V} \right)^{0,5} \qquad \textbf{(1)}$$

where V is the molar volume, ΔH' is residual enthalpy .

Two substances with same solubility parameters δ_1 and δ_2 must be soluble in each other in accordance with the general rule: solubility is favored by chemical and structural similarity. As soon as the difference between δ_1 and δ_2 increases, the dissolution capacity decreases.

Lange [2] presented a simplified correlation to estimate the oil solubility parameter (δ_o) from the average molecular weight of the oil M and its temperature T:

$$\delta_o = 0{,}01.M + 6{,}54 - 0{,}01.(T - 25) \qquad \textbf{(2)}$$

According to Lange [2], the correspondence between the MMP and the difference between solubility parameters can be transformed into a useful tool for MMP determination through the following method:

- the gas solubility parameter (solvent) is determined in some pressures using equation (3) - developed for Giddings *et al.* [4] that is an extension of solubility parameter for supercritical fluids

$$\delta_g = 0{,}326 (P_c)^{0,5} \left(\frac{\rho_r}{\rho_{r(liq)}} \right) \qquad \textbf{(3)}$$

where δ_g is gas solubility parameter in $(\mathrm{cal/cm^3})^{0,5}$; P_C the critical pressure in psia; ρ_r the reduced density, defined as ρ/ρ_c, where ρ is the density and ρ_c is the critical density; $\rho_{r(liq)}$ the gas reduced density at boiling point, considered constant and equal to 2,66. Lange [2] has used literature data of ρ, ρ_c and P_c;

- The oil solubility parameter is determined in the temperature of interest through the equation (2);
- The MMP is the pressure in which: $\left| \delta_o - \delta_g \right| \approx 3{,}0 \left(\frac{cal}{cm^3} \right)^{0,5}$

The difference between the solubility parameters reflects the chemical similarity of the injected gas and the oil, which can determine, in last instance, the gas capacity (solvent) to promote a small interfacial tension with the oil. Then smaller difference between solubility parameters of the liquid and gaseous phases means more miscibility between fluids.

Practical experiments conducted in the CEPGN (Petroleum and Natural Gas Study Center of Salvador University - UNIFACS) have shown unsatisfactory results when applying this procedure.

A NEW METHODOLOGY TO CALCULATE THE MMP

Using oil temperature and boiling point, and 28 oil samples (25 from published publications and 3 proprietary samples) a correlation was developed to calculate the oil solubility parameter:

$$\delta_{ocorrel} = \frac{a \cdot (P_{Sat})^b}{c \cdot T^d} \tag{4}$$

where:

$a = 4{,}8979256$; $b = -0{,}019744107$; $c = 0{,}463561$; $d = 0{,}30616709$;

T – reservoir temperature (°K), divided by 100;

P_{Sat} – oil saturation pressure (atm), divided by 10.

To evaluate the correlation it was accomplished a comparison between the values obtained by the correlation - equation (4) - and the value from a more accurate solubility parameter, supplied by an equation of state. The equation Soave-Redlich-Kwong (SRK) – Soave [5] was selected.

The calculation of the oil solubility parameter was realized with the equation (1) with the residual enthalpy ΔH' and the molar volume V obtained by the equation of state SRK, expressed as:

$$P = \frac{R.T}{V-b} - \frac{a(T)}{V.(V+b)} \tag{5}$$

For mixtures, the classic mixture rules have used:

$$a = \sum_i \sum_j z_i . z_j (a_i . a_j)^{1/2} . (1 - K_{ij}) \qquad b = \sum_i z_i b_i \tag{6}$$

where z_i is the component molar fraction. The pure components parameters a_i and b_i are described in terms of critical temperature Tc, critical pressure Pc, acentric factor w and Kij are the binary interaction parameters.

The residual enthalpy expression for the SRK equation is explicit by:

$$\Delta H' = \ln\left(1 + \frac{b}{V}\right) . \frac{1}{b} . \left[a - \frac{da}{dt}.T\right] + R.T - Z.R.T \tag{7}$$

where V is the molar volume, Z is the compressibility factor and :

$$\frac{da}{dT} = \sum_i \sum_j z_i . z_j . (1 - K_{ij}) . \frac{d}{dT}\left[(a_i . a_j)^{0.5}\right] \tag{8}$$

To calculate ΔH' and V the critical temperature Tc, critical pressure Pc, acentric factor w of each component and the interaction parameter Kij must be known. For the defined components, pure components parameters are known, however for the TBP fractions and

TBP residue is necessary characterization procedures. In this in case Pedersen *et al* [6] characterization have used in simulator SPECS (Technical University of Denmark).
The comparison between solubility parameter obtained by Eq.(4) and by equation of state SRK have given very good results (average error of 6,82%): from 28 oils evaluated only for two oils the results was not so good, for 21 oils the error was less than 5%, for 3 oils the error was between 5 and 10%.
The target of this study was the MMP calculation. Further evaluations detected the need an additional correction factor to be applied to oil solubility parameter to calculate MMP. The adjusted functional form for correction factor (G) is given by:

$$G = d \cdot \left[\left(P_{Sat}{}^{e} \right) \cdot \left(T^{f} \right) \right] \tag{9}$$

where:

$d = 8{,}875152$; $e = 0{,}168489$; $f = -1{,}67852$;
T – reservoir temperature (°K), divided by 100;
P_{Sat} – oil saturation pressure (atm), divided by 10.

Therefore the next step is CEPGN criterion determination to calculate the MMP. This criterion is explicit by:

$$\delta_{gcorrel} = G \cdot \left(\delta_{ocorrel} \right)^{-0,5} \tag{10}$$

With the oil temperature and its saturation pressure the correction factor (G), and the oil solubility parameter $\delta_{ocorrel}$ are obtained. With the CEPGN criterion Eq (10), the value $\delta_{gcorrel}$ is obtained. The MMP is the pressure in which, in the gas temperature, the solubility parameter corresponds to $\delta_{gcorrel}$. To calculate the gas solubility parameter the Eq. (3) is employed and an equation of state or literature data are used to calculate the gas density ρ
An efficient supercritical fluid solubility parameter calculation is associated with the quality of the pressure-volume-temperature description of the fluid. According to Shim [7], an efficient CO_2 equation of state is Reynolds equation [8], given by:

$$\begin{aligned} P = {} & \rho^2.M1 + \rho^3.M2 + \left[\left(\rho^3.M3 + \rho^5.M4 \right) \exp\left(-A20.\rho^2 \right) \right] + \\ & + \rho.R.T + \rho^4.(A9.T + A10) + \rho^5.(A11.T + A12) + \rho^6.A13 \end{aligned} \tag{11}$$

where T is the temperature in °C, P is the pressure in atm, ρ density in g/ cm^3 and other parameters are temperature function.

RESULTS

In order to validate the CEPGN methodology several samples from Recôncavo Basin were used. The data were obtained from experimental tests in CEPGN. For confidentiality reasons, the saturation pressure and temperature data are not supplied. The results can be seen in Table 1. The tested oils were not used for correlation development.

The results in Table 1 show that the methodology is good enough for tested oils, with different range of saturation pressure and reservoir temperature. For a better visualization, the MMP values are presented in Figure 1, showing the correlation quality

Table 1- Percentile error between experimental and predicted MMP with CEPGN methodology

Oil	MMP exp (psia)	$\delta_{ocorrel}$ (cal/cm^3)^{0,5}	$\delta_{gcorrel}$ (cal/cm^3)^{0,5}	MMP calc (psia)	Error %
1	2025	7,2990	3,449	1883,11	7,01%
2	2450	7,0209	4,899	2424,26	1,05%
3	2800	6,9250	5,547	2834,00	1,21%
4	3450	6,8712	5,952	3204,39	7,12%
5	4150	6,8121	6,435	3822,09	7,90%
6	2550	7,0130	5,338	2432,50	4,61%
7	2850	6,9709	5,636	2627,72	7,80%
8	3150	6,9174	5,892	2936,94	6,76%
9	2350	7,1753	4,233	2027,82	13,71%
10	3650	6,7235	4,774	3558,62	2,50%
11	4050	6,6502	5,271	4077,05	0,67%
12	3550	6,7970	4,970	3303,68	6,94%
13	3250	6,8750	5,172	3008,70	7,42%
14	3450	6,7448	5,653	3770,05	9,28%
15	2650	6,8662	4,811	3001,18	13,25%

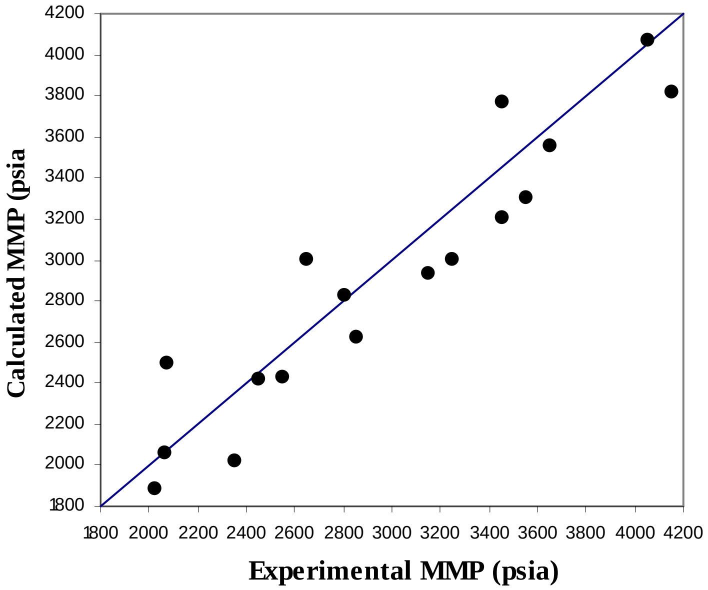

Figure 1 – Comparison between experimental MMP and calculated MMP with CEPGN methodology

CONCLUSION

An alternative methodology was created for MMP evaluation. Using oil temperature and its saturation pressure as independent variables, a methodology was developed for 28 samples (25 from published publications and 3 proprietary samples). Experimental MMP for new 15 proprietary samples were used to validate the methodology. The following points have been considered as relevant:

- It is possible to obtain oil solubility parameter using an equation of state. The necessary information is: the molar composition, the molecular weight of the C_7^+ fraction, temperature and the saturation pressure. Two tools are necessary: the material characterization and the computational program development, since is not possible to calculate the oil solubility parameter in the commercial simulators;
- gas solubility parameter (CO_2) can be calculated with good accuracy by using the Reynolds equation of state [8] to calculates the density of CO_2 and the Giddings equation [4] to calculate gas solubility parameter;

oil solubility parameter calculated, based on an empirical correlation presented by Lange [2], was not appropriate;

- Lange procedure to calculate MMP, where MMP is the pressure in which the difference between oil and gas solubility parameter is around 3 $(cal/cm^3)^{0,5}$, was not appropriate;
- a new empirical correlation was developed (CEPGN correlation) to calculate oil solubility parameter, having as independent variables oil saturation pressure and temperature;
- a CEPGN methodology was developed to calculate MMP based on oil solubility parameter and a correction factor (G).

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