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subject: **Interpretation of Svrcek & Mehrotra data in terms of Dan's mixture model**  
*Intevep S.A., November 17, 1997.*

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## Introduction

In this short note I discuss the solubility data from Svrcek & Mehrotra (1982) and I show how these can be used to derive a solubility relation between gas fraction and void fraction. After a short presentation of the experimental procedure, it is shown how the slopes of the solubility curves obtained by Svrcek & Mehrotra can be used to calculate a solubility constant. Two approaches are used: one based on the volume ratio and the other on the weight fraction. When both approaches are transformed into a pressure-gas fraction relation, it is shown that both approaches do not lead to the same result. However in the most frequently occurring cases, the result is identical.

## The experimental procedure

A more detailed presentation of the experimental set-up and measurement procedures can be found in Svrcek & Mehrotra. I resume in a few words some important points. Bitumen and gas (CO<sub>2</sub>, CH<sub>4</sub> or N<sub>2</sub>) are recombined in a mixing cell. From this mixing cell, live oil is pumped to a sample and expansion cell, which is contained in an oven which keeps the bitumen at a given temperature  $T$ . The pressure  $p$  in the cell is decreased by volume expansion of the cell until atmospheric pressure  $p_1$  and the temperature is increased to  $T_1 = 100^\circ\text{C}$ . We suppose that the pressure  $p_1$  is low enough and the temperature  $T_1$  is high enough so that the quantity of gas that remains in the crude under these conditions can be neglected. The solubility of the gas is then calculated by a material balance in terms of volume of gas per volume of original live crude and in terms of weight percent.. The volume of gas is the volume of measured gas at standard pressure  $p_{\text{ref}} = 760 \text{ mmHg} = 1.013 \text{ Pa}$  and standard temperature  $T_{\text{ref}} = 0^\circ\text{C} = 273.15 \text{ K}$

## Results

We discuss here the results of the dissolution of CO<sub>2</sub>, but the results for the other gases (N<sub>2</sub> and CH<sub>4</sub>) are similar. The volume solubility is shown in Figure 1 in terms of volume of liberated gas per original volume of live oil.

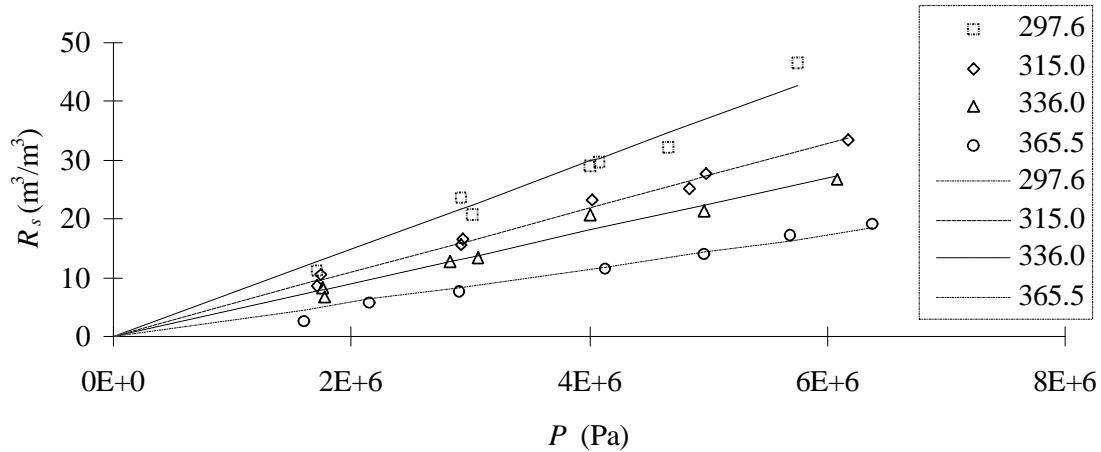


Figure 1 Solubility of  $CO_2$  in Athabasca bitumen in volume of gas (measured at 1.013 Pa and 273.15 K) per volume of live crude, at different temperatures (in K)

This gas is liberated when the pressure is brought back to 1.013 Pa pressure and the temperature is increased to 373.15 K, but its volume is measured at 1.013 Pa and 273.15 K. The straight lines represent linear regressions of a solubility which is supposed proportional to the pressure. The data are not precise enough in order to decide whether at zero pressure still gas remains in the crude or whether at a pressure higher than zero already all the gas has been liberated. Therefore we suppose that zero pressure, the quantity of dissolved gas is zero too.

The temperatures are an average of the exact temperatures in each point of the same curve. These temperatures display a variation of less than 1 K around the mean temperature.

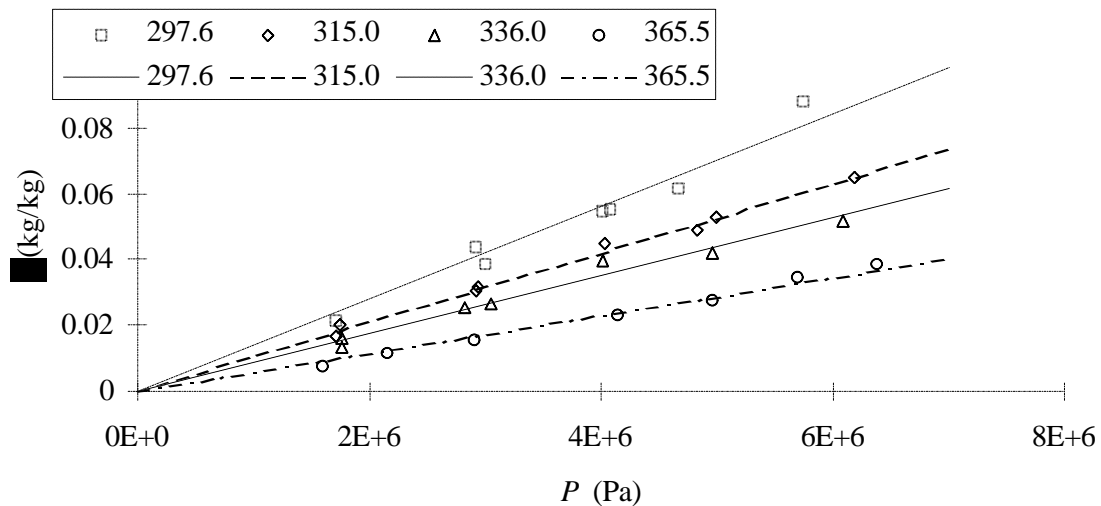


Figure 2 Solubility of  $CO_2$  in Athabasca bitumen in weight fraction, at different temperatures (in K)

In Figure 2 the same data are represented, but now in terms of weight fraction. The data are again fitted by straight lines through the origin, although, as we will see later, this does not lead to the same solubility relation as the one that can be obtained from Figure 1.

The slopes of the linear regressions of volume solubility and weight solubility are given in Table 1.

| $T$ (K) | slope $R_s$ ( $\text{Pa}^{-1}$ ) | slope $\xi$ ( $\text{Pa}^{-1}$ ) |
|---------|----------------------------------|----------------------------------|
| 297.6   | $1.40 \cdot 10^{-8}$             | $7.43 \cdot 10^{-6}$             |
| 315.0   | $1.05 \cdot 10^{-8}$             | $5.47 \cdot 10^{-6}$             |
| 336.0   | $8.76 \cdot 10^{-9}$             | $4.49 \cdot 10^{-6}$             |
| 365.5   | $5.78 \cdot 10^{-9}$             | $2.88 \cdot 10^{-6}$             |

Table 1 Slopes of solubility graphs

### Gas fraction-pressure relation from volume solubility

According to the linear regression in Figure 1, we can model the solubility expressed in volumes ratios as

$$(R_s)_{pref, Tref}^{p, T} = K_V p \quad (1)$$

where  $(p, T)$  are the condition at which this quantity of gas is dissolved and  $(p_{ref}, T_{ref})$  are the conditions in which it is expressed. The volume ratio  $R_s$  can be written as

$$(R_s)_{pref, Tref}^{p, T} = (V_g)_{pref, Tref}^{p, T} / V_l \quad (2)$$

where  $(V_g)_{pref, Tref}^{p, T}$  is the volume of gas which is dissolved at conditions  $(p, T)$ , measured at conditions  $(p_{ref}, T_{ref})$  and  $V_l$  is the original volume of live oil before depressurisation. It is supposed that the liquid can be treated as incompressible since we are mainly interested in live oils below their bubble point. Under these conditions, when the pressure is lowered, the creation of volume by gas coming out of solution is much larger than that by liquid depressurisation.

According to the ideal gas law (for convenience we assume its applicability valid, although any other equation of state connecting the gas pressure and density could be used as well)

$$(V_g)_{pref, Tref}^{p, T} = \frac{N(p, T)RT_{ref}}{p_{ref}} \quad (3)$$

where  $N(p, T)$  is the number of moles of gas dissolved at  $(p, T)$  and  $R$  is the gas constant. Note that although  $V_g$  depends on the reference conditions,  $N$  does not.

Substitution of (2) and (3) in (1) leads to

$$N(p, T) = \frac{p_{ref} V_l K_V}{RT_{ref}} p$$

We assume that above the bubble point pressure  $\tilde{p}$ , the quantity of dissolved gas does not vary anymore with the pressure. At the bubble point we denote  $N(\tilde{p}) = \tilde{N}$ . The difference between the number of moles in solution at the bubble point and the number of moles is

solution at a pressure  $p$ , is the also the number of moles that will be present as a free gas at pressure  $p$ , so

$$N_g = \tilde{N} - N = \frac{p_{ref} V_l K_V}{RT_{ref}} (\tilde{p} - p) \quad (4)$$

This molar quantity of gas also follows the ideal gas law, so that the volume of free gas at that temperature  $T$  and pressure  $p$

$$V_g = \frac{N_g RT}{p} \quad (5)$$

Substitution of (4) then gives the gas-liquid ratio

$$\frac{V_g}{V_l} = \frac{Tp_{ref} K_V}{T_{ref} p} (\tilde{p} - p)$$

This gas-liquid ratio can be expressed in a void fraction  $\phi$  as

$$\frac{V_g}{V_l} = \frac{\phi}{1 - \phi} \quad (6)$$

so that by combination of the two precedent equations

$$\gamma \frac{\phi}{1 - \phi} = \tilde{p} \frac{\tilde{p} - p}{p} \quad (7)$$

where

$$\gamma \equiv \frac{T_{ref} \tilde{p}}{Tp_{ref} K_V} \quad (8)$$

Equation (7) can be simplified in the following cases:

- a) small pressure drop  $\tilde{p} / 2 \ll p < \tilde{p}$
- b) small gas fraction  $\phi \ll 1$

If (a) is satisfied then

$$\gamma \frac{\phi}{1 - \phi} = \tilde{p} - p \quad (9)$$

if (b) is satisfied

$$\frac{\gamma}{\tilde{p}} \phi = \frac{\tilde{p} - p}{p} \quad (10)$$

and if both of them are satisfied

$$\gamma \phi = \tilde{p} - p \quad (11)$$

The last situation is also realised when  $\phi \ll 1$  and  $\gamma \geq O(1)$ . The latter says that the solubility has to be relatively small, shall both conditions be satisfied.

### Gas fraction-pressure relation from mass solubility

According to Figure 2, expressed in mass fractions we obtain

$$\xi = K_m p \quad (12)$$

The mass fraction is defined as

$$\xi = \frac{m_{gd}}{m_{gd} + m_{lp}} \quad (13)$$

where  $m_{gd}$  and  $m_{lp}$  are the masses of dissolved gas and pure liquid per unit volume. Supposing that the liquid density is constant, and neither a function of dissolved gas concentration, nor of pressure through compressibility effects, we can write  $\rho_l = m_{lp}$ . The mass density of gas equals the molar density multiplied by the molar mass  $M_g$ , so that (13) can be written as

$$\xi = \frac{NM_g}{NM_g + \rho_l V_l}$$

The same number of moles  $N$  that is measured at reference conditions, was dissolved at pressure  $p$ .  $N$  can be written, using (12)

$$N = \frac{\rho_l V_l K_m}{M_g} \frac{p}{1 - K_m p}$$

Defining  $N_g$  in a way similar to that in the previous section

$$N_g = \frac{\rho_l V_l K_m}{M_g} \left( \frac{\tilde{p}}{1 - K_m \tilde{p}} - \frac{p}{1 - K_m p} \right)$$

and by (5)

$$\gamma' \frac{V_g}{V_l} = \frac{\tilde{p}}{p} \left( \frac{\tilde{p}}{1 - K_m \tilde{p}} - \frac{p}{1 - K_m p} \right)$$

with

$$\gamma' \equiv \frac{\tilde{p} M_g}{RT \rho_l K_m} = \frac{\rho_g}{\rho_l K_m} \quad (14)$$

where

$$\rho_g \equiv \frac{\tilde{p} M_g}{RT}$$

is the gas density at the bubble point pressure. In most situations,  $\rho_g \ll \rho_l$  so that also  $\gamma' \ll 1/K_m$ , which in the following we will assume applicable.

By substitution of (6)

$$\gamma' \frac{\phi}{1 - \phi} = \frac{\tilde{p}}{p} \left( \frac{\tilde{p}}{1 - K_m \tilde{p}} - \frac{p}{1 - K_m p} \right) \quad (15)$$

Again some simplified cases appear, depending on the following two constraints

- a) small pressure drop  $\tilde{p}/2 \ll p < \tilde{p}$
- b) small gas fraction  $\phi \ll 1$

If only (a) is satisfied

$$\gamma' \frac{\phi}{1 - \phi} = \frac{1}{1 - K_m \tilde{p}} (\tilde{p} - p)$$

which is similar to (10) if  $K_m \tilde{p} \ll 1$ ; If only (b) is satisfied

$$\gamma' \phi = \frac{\tilde{p}}{p} \left( \frac{\tilde{p}}{1 - K_m \tilde{p}} - \frac{p}{1 - K_m p} \right)$$

which is similar to (10) if  $K_m \tilde{p} \ll 1$ , and if both are satisfied

$$\gamma'\phi = \tilde{p} - p \quad (16)$$

which is similar to (11).

### Comparison between the two approaches

To show that the approaches of the preceding paragraphs are equivalent, we calculate the values of  $\gamma / \tilde{p}$  and  $\gamma' / \tilde{p}$  for the data from Svrcek & Mehrotra (1982). This involves the same calculations as Svrcek & Mehrotra carried out in their reporting. Therefore it is not surprising that we will find  $\gamma = \gamma'$ .

| $T$ (K) | $K_V$ (Pa <sup>-1</sup> ) | $K_m$ (Pa <sup>-1</sup> ) | $\rho_l$ (kg·m <sup>-3</sup> ) | $\gamma / \tilde{p}$ | $\gamma' / \tilde{p}$ |
|---------|---------------------------|---------------------------|--------------------------------|----------------------|-----------------------|
| 297.6   | $1.40 \cdot 10^{-8}$      | $7.43 \cdot 10^{-6}$      | 1041                           | 1.22                 | 1.22                  |
| 315.0   | $1.05 \cdot 10^{-8}$      | $5.47 \cdot 10^{-6}$      | 1015                           | 1.57                 | 1.57                  |
| 336.0   | $8.76 \cdot 10^{-9}$      | $4.49 \cdot 10^{-6}$      | 1005                           | 1.79                 | 1.79                  |
| 365.5   | $5.78 \cdot 10^{-9}$      | $2.88 \cdot 10^{-6}$      | 984                            | 2.56                 | 2.55                  |

Table 2 Solubility data from Svrcek & Mehrotra (1982) and calculated coefficients  $\gamma / \tilde{p}$  and  $\gamma' / \tilde{p}$

The results are reported in Table 2. The liquid density is an average of the different pressures, but the deviation of the average is never more than approximately 1%. The values of  $\gamma / \tilde{p}$  are obtained using (8), using  $T_{ref} = 273.15$  and  $p_{ref} = 1.013 \cdot 10^5$ . The values of  $\gamma' / \tilde{p}$  are calculated by (14), using  $M_g = 4.40 \cdot 10^{-2}$  kg·mole<sup>-1</sup>.

The preceding calculations show that the earlier proposed relations

$$\frac{\gamma}{\tilde{p}} = \frac{T_{ref}}{Tp_{ref}K_V} = \frac{M_g}{RT\rho_l K_m} = \frac{\rho_g}{\rho_l K_m \tilde{p}}$$

are coherent with the calculations and the results reported by Svrcek & Mehrotra.

In view of the preceding results, we propose to define a dimensionless reciprocal solubility constant by replacing  $\gamma / \tilde{p}$  by  $\gamma$ , which is only a function of the live crude oil and does not depend on the bubble point pressure. The solubility relation then become

$$\gamma \frac{\phi}{1-\phi} = \frac{\tilde{p} - p}{p}$$

simplifying, for small pressure drops  $\tilde{p} / 2 \ll p < \tilde{p}$ , to

$$\gamma \tilde{p} \frac{\phi}{1-\phi} = \tilde{p} - p$$

for small gas fractions,  $\phi \ll 1$ , to

$$\gamma \phi = \frac{\tilde{p} - p}{p}$$

and for small pressure drops and small gas fractions

$$\gamma \tilde{p} \phi = \tilde{p} - p$$

### Literature references

Svrcek W.Y., Mehrotra A.K., 1982, "Gas solubility, viscosity and density measurements for Athabasca bitumen", *J. Can. Petrol. Tech.*, July-August: 31-38.