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subject: Some points about Dan's mixture model
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Introduction

Some recent information. We are working on a publication of Dan's model and there are still some doubts about the derivation of equilibrium solubility. I am going to present the present form of the derivation and then I am going to explain the doubts.

There is a second point which is very important. Some people think that foamy oils are foams, at high gas fractions¹ (typically as high as 70 or 80 % in situ) with associated Plateau borders and that foamy oil reservoirs display some foam threshold. That is to say, there is a minimum pressure draw down below which the reservoir does not display the typical characteristics of foamy oil reservoirs.

Other people tend to think that foamy oils do not foam inside the reservoir and that the gas fractions are low (lower than 25%). They only start foaming at very low pressures, e.g. close to the well head. But in the reservoir no Plateau borders are created and it is just a bubbly mixture. Marangoni effects might play a role, but only when bubbles coalesce, in inhibiting coalescence.

This is an important issue as well and I would like to know your opinion on this.

The derivation of equilibrium solubility.

The model is based on experimental evidence. Svrcek & Mehrotra measure the volume of gas which comes out of a live oil at pressure p and temperature T when its pressure is lowered to a reference pressure p_{ref} and when its temperature is altered to a reference temperature T_{ref} . We denote the volume of gas that then comes out of solution as \hat{V}_g . The original volume of live oil when it was at pressure p , is called V_l . They observe that

$$p - p_0 = \hat{\gamma} \hat{V}_g / V_l \quad (1)$$

where p was the original pressure of the live oil, p_0 is a constant and $\hat{\gamma}(T)$ is a function of temperature.

We are going to change this solubility curve a little bit by admitting that above a pressure \tilde{p} , which we call the bubble point pressure, no more gas was available to dissolve in the oil. We also assume that at this pressure the volume of gas that can come out in Svrcek & Mehrotra's experiment is $\tilde{V}_g = \hat{V}_g(\tilde{p})$. So then (1) can be written as

$$\tilde{p} - p = \hat{\gamma}(\tilde{V}_g - \hat{V}_g) / V_l \quad (2)$$

The gas fraction ϕ is defined as

¹ I am going to use interchangeably the terms "gas fraction", "void fraction" and "gas saturation". The "critical gas saturation" is thus the same as the "critical gas fraction".

$$\phi = \frac{\Omega_g}{\Omega_g + V_l} \quad (3)$$

where

$$\Omega_g = \tilde{V}_g - \hat{V}_g \quad (4)$$

From (3),

$$\Omega_g = V_l \frac{\phi}{1 - \phi} \quad (5)$$

So that, combining (2), (4) and (5), we obtain

$$\tilde{p} - p = \hat{\gamma} \frac{\phi}{1 - \phi} \quad (6)$$

For $\phi \ll 1$, this simplifies to

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

which is the solubility relation that we had before.

This says thus: take the reciprocal of the slope of the graphs of Svrcek & Mehrotra; This gives you $\hat{\gamma}$ and then equation (6) tells you how the gas fraction in a PVT cell varies with the pressure.

Question about this derivation

I have the following question about this derivation. According to this derivation, it does not matter whether Svrcek & Mehrotra do their experiments at 1 atmosphere, 2 atmospheres, at 50°C, or 100°C, it is all the same. If you lower the pressure far enough so that most of the dissolved gas comes out, then you are measuring the volume that gives you the correct solubility.

Let us argue now in terms of the number of moles. If you lower the pressure far enough then a number N of moles comes out of solution. If we are at reference pressure p_{ref} and reference temperature T_{ref} , then this number of moles correspond to a volume (assuming that the ideal gas law applies) of

$$\hat{V}_g = NRT_{ref} / p_{ref} \quad (8)$$

If Svrcek and Mehrotra would do their experiment at another reference pressure and temperature (p_2, T_2) , where we assume that this pressure would also be low enough so that nearly all the dissolved gas would come out, then the measured volume of gas would be

$$\hat{V}_{g2} = NRT_2 / p_2 \quad (9)$$

which of course can be very different from the volume in (8). For example, even if $T_{ref} = T_2$, and we assume that $p_{ref} = 14.7$ psi, $p_2 = 7.35$ psi and the bubble point pressure $\tilde{p} = 1400$ psi, so that the difference in gas coming out of solution between the different reference pressures can be neglected, then still we would measure at the second reference pressure a volume of gas which is twice as high! This shows that the graphs of Svrcek and Mehrotra and the slopes of the curves, *do* depend on the references pressure and temperature.

So if you know that Svrcek & Mehrotra measure that, when the pressure of the live oil is lowered from the bubble point pressure \tilde{p} to the reference pressure p_{ref} , a volume of \tilde{V}_g comes out, then you know as well (assuming applicability of the ideal gas law) that this corresponds to

$$\tilde{N} = \frac{p_{ref} \tilde{V}_g}{RT_{ref}} \quad (10)$$

moles. Equally, if you would have been lowering the pressure, not from the bubble point pressure, but from some lower pressure p , then you would measure a volume \hat{V}_g , which corresponds to

$$\hat{N} = \frac{p_{ref} \hat{V}_g}{RT_{ref}} \quad (11)$$

moles.

So at a pressure \tilde{p} we have \tilde{N} moles of dissolved gas and at a pressure p , we have \hat{N} moles of dissolved gas. If we suppose that at pressure \tilde{p} no free gas is available and the gas fraction is zero, then lowering the pressure in a live oil from \tilde{p} to p liberates a number of moles equal to

$$N = \tilde{N} - \hat{N} = \frac{p_{ref}}{RT_{ref}} (\tilde{V}_g - \hat{V}_g) \quad (12)$$

Combining this with the data from Svrcek & Mehrotra, according to equation (2)

$$N = \frac{p_{ref} V_l}{RT_{ref} \hat{\gamma}} (\tilde{p} - p) \quad (13)$$

This number of moles corresponds at the pressure p to a volume of

$$V_g = \frac{NRT}{p} = \frac{p_{ref} T V_l}{T_{ref} \hat{\gamma}} \frac{\tilde{p} - p}{p} \quad (14)$$

The gas fraction, that is the same gas fraction which enters in the continuity equation, is defined as

$$\phi \equiv \frac{V_g}{V_g + V_l} \quad (15)$$

Substituting (14) in (15) the gas fraction is shown to be related to pressure as

$$\phi = \frac{\frac{p_{ref} T}{T_{ref} \hat{\gamma}} \tilde{p} - p}{\frac{p_{ref} T}{T_{ref} \hat{\gamma}} (\tilde{p} - p) + p} \quad (16)$$

So this replaces equation (6) in the actual formulation.

In some cases equation (16) can be simplified. If we suppose that

$$\frac{\tilde{p} - p}{p} \ll \frac{T_{ref} \hat{\gamma}}{p_{ref} T} \quad (17)$$

then (16) simplifies to

$$\phi = \frac{p_{ref} T}{T_{ref} \hat{\gamma}} \frac{\tilde{p} - p}{p} \quad (18)$$

and its validity criterion (17) is then simply that the gas fraction has to be low $\phi \ll 1$.

When we also assume that

$$\frac{\tilde{p} - p}{p} \ll 1$$

then we can replace the pressure in the denominator of (18) with \tilde{p} and we obtain

$$\tilde{p} - p = \gamma \phi \quad (19)$$

where

$$\gamma \equiv \hat{\gamma} \frac{T_{ref} \tilde{p}}{T p_{ref}} \quad (20)$$

Equation (19) is thus only valid when two assumptions are verified:

1. The gas fraction has to be small $\phi \ll 1$
2. The pressure has to be close to saturation pressure $\tilde{p} / 2 \ll p < \tilde{p}$

Equation (19) is almost the same as the original equation (7), with one difference: the solubility in (7) is $\hat{\gamma}$ and the solubility in (19) is γ . The difference between the two is not just a small correction factor but some order of magnitude. For example, if $T = T_{ref}$, $\tilde{p} = 1400$ psi and $p_{ref} = 14.7$ psi, then $\gamma \approx 100 \hat{\gamma}$. So it is important to know whether the actual modelling is all right or whether the doubts are justified.

The procedure to obtain the coefficient γ is then: take the slope from the data of Svrcek & Mehrotra. This is $\hat{\gamma}$. Multiply this with the ratio $\tilde{p} T_{ref} / p_{ref} T$ and you obtain some reciprocal solubility constant γ , which is really constant and does not depend on how and at what conditions Svrcek & Mehrotra did their experiments.

To foam or not to foam

To be honest about this point, I have actually not enough time to support my opinion on this point. I am just going the present two different ideas of which I like the second. I even think that the first is wrong. I let it up to you to come up with supplementary evidence which supports your own opinion.

Idea A

The characteristic of foamy oils is that during pressure draw down of the reservoir a foam is created. That seems logical, that is why they are called oily foams. This foam is a foam in the traditional sense, that is to say that the gas fraction (gas saturation) has to be higher than approximately 73%. The bubbles in the foam are thus closely packed together and Plateau borders are formed between them. Surfactant molecules tend to stabilise this foam by Marangoni effects. A critical gas saturation does not exist in foamy oils, at least not if the residence time of the foam in the reservoir and tubing is smaller than its life time, which is nearly always the case.

There is also a foaming threshold. That means that below a certain critical pressure draw down, the characteristics of foamy oils do not appear.

According to Dan's saying, Brij Maini likes this idea. That is what appears from his paper with Sarma (Maini & Sarma, 1994)

Idea B

“Foamy oil” is a term which is a little bit unluckily chosen because foamy oils are not foams at all. They only foam when the pressure gets very low, for example close to the well head. But in the reservoir they are just a bubbly mixture with low gas fractions, lower than 25% and in many cases even lower than 10%. Most heavy oils have a critical gas saturation of 25% above which they form continuous gas, just as light oils do at a lower pressure. If this happens, then the primary recovery is achieved. This is what Maini says as well, in his 1996 paper (Maini, 1996). Plateau borders and close packed spheres, it is all nonsense, in the reservoir it does not exist.

There is one typical thing about foamy oil: bubbles do not coalesce as easily as in light oils and therefore all the gas that gets out of solution stays in the oil and helps by its volume growth at decreasing pressure, to push the oil out of the reservoir. Two possible reasons might be given for the fact that bubbles do not coalesce so easily in foamy oil.

1. The viscosities are higher in foamy oils than in light oils
2. Foamy oils might contain surface active molecules which inhibit the coalescence of bubbles.

I think that the second idea is correct. Dan would probably rather go for the first. What is your opinion on these matters? Do you have any experimental evidence which helps decide between the two ideas or generate a third idea which is different from these two?

Literature references

- Maini B.B., Sarma H., 1994, “Role of Nonpolar foams in production of heavy oils”, *Advances in Chemistry Series*, **242**: 405-420.
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