Dear Editor,

I thank Dr. Yortsos for his interest in our work. It is clear from the discussion that there is a difference of opinion on the physics of solution gas drive. Our theoretical work carried out in this area has been closely guided by experimental data, oil-field observations, the physics of the process, and the material in the literature.

The main purpose of this response is to clarify certain misconceptions. We divide the essence of the discussion into three main items:
1- Critical Supersaturation Pressure and its Rate Dependency
2- Nature of Bubble Nucleation in Solution Gas Drive
3- Gas Bubble Growth and Critical Gas Saturation Rate Dependency

In the following, each of the above items are discussed.

Critical Supersaturation Pressure and Rate Effect

The critical supersaturation pressure for bubble nucleation at isothermal conditions is defined as the pressure at which the first portion of the gas phase is newly formed. The first portion can in turn be defined as: a) to obtain one nucleus bubble (this definition originates from Volmer2), b) to have a detectable gas volume as we defined in Ref. 2, c) when the bubble nucleation rate exceeds 1 nucleus/cm<sup>3</sup>/sec as defined in the discussion of our work, or d) to form on the average at least one nucleus bubble (Ref. 3). The critical supersaturation pressure predictions based on the above definitions may be substantially different. Since the measurements are very practical with a detectable volume of gas, definition c was adopted in our work.

Fig. R-1 shows the gas fraction vs. (p<sub>b</sub>-p) where, p<sub>b</sub> is the bubblepoint pressure and p is the bulk liquid phase pressure. The x-axis, (p<sub>b</sub>-p), is related to supersaturation; when the amount of the gas phase is very small (detectable gas volume), the x-axis intersection gives the critical supersaturation. Note that as the pressure decline rate increases, the critical supersaturation and supersaturation also increase. These experiments were conducted at a constant rate of pressure decline (Ref. 4).

Fig. R-2 depicts the pressure vs. volume expansion for two different rates of expansion (Ref. 5). Since the fluid used in the experiments is a C<sub>4</sub>/C<sub>10</sub> mixture at pressures away from the critical point, liquid phase volume nearly remains the same after gas evolution. The critical supersaturation pressure is conveniently estimated from the change in the slope of the liquid expansion line (shown by the dashed line). Note that similar to Fig. R-1, the critical supersaturation and the supersaturation increase with an increase in the expansion rate.

Now let us examine the data from Li and Yortsos (Ref. 6). Fig. R-3 portrays the results from three experiments. First, there is no basis to judge the critical supersaturation.
from Li and Yortsos do not. A main conclusion from Yortsos and Parlar (Ref. 7) was that critical supersaturation should be independent of rate even for variations spanning several orders of magnitude.

Contrary to the arguments of the discussion, it is not the definition of the critical supersaturation that leads to the conclusion that critical supersaturation and supersaturation are a weak function of the pressure decline rate; it is unsound physics. We do not agree with the proposition that the critical supersaturation is the supersaturation that is needed to activate a site of mouth width $W$ given by $S_{cr} = p_r - p_{cr} = 2\sigma / W$. From this proposition it is stated that the critical supersaturation pressure is completely independent of rate and it is argued that there is no experimental data to contradict this conclusion. There are plenty of data to prove that the notion of the existence of cavities at the pore walls containing pre-existing or trapped gas to be activated by a supersaturation given by $p_r - p = 2\sigma / W$ does not apply to solution gas drive process. The fact that the above proposition is commonly accepted by others in contexts such as boiling does not make it appropriate for the problem of solution gas drive in porous media. If the above proposition were applicable, then when we change from one fluid mixture to another fluid mixture (both with the same $\sigma$) in a given porous medium, there should be no change in the number of active sites. For a $C_1/C_2$ mixture, and for a crude both with the same $\sigma$, and at the same rate, we observe a vast difference in the number of bubbles (see Ref. 8). We also disagree that critical supersaturation should correspond to the largest cavity. For hydrocarbon mixtures the smallest cavities fit the thermodynamic description; only for pure hydrocarbons the largest cavity is appropriate.

The theory of rate effect on the critical supersaturation process has been discussed in detail in Ref. 3 for various scenarios.

**Nature of Nucleation in Porous Media**

As discussed above, we reject the proposition that the combination of pre-existing or trapped gas and the supersaturation needed to activate these sites from $S = p_r - p = 2\sigma / W$, describes solution gas drive in porous media. We have also shown that the classical nucleation expression given by

$$J = A \exp\left[-B/S^2\right] \quad \text{(R-1)}$$

does not describe nucleation in porous media in the context of solution gas drive (Ref. 2). In Eq. R-1, $A$ and $B$ are kinetic and thermodynamic parameters, respectively. The parameter $B$ is given by $B = 16\pi\sigma_e^4 / 3kT$, where $\sigma_e$ is an effective specific surface energy of the gas-liquid interface, $k$ is the Boltzmann constant, and $T$ is the
absolute temperature. The specific surface energy is given by \( \sigma_s = \sigma_0^{1/3} \); \( \sigma \) is the surface tension and \( \phi \) may be given by

\[
\phi(\theta) = \frac{1}{4}(2 + 3 \cos \theta - \cos^3 \theta)
\]  

(R-2)

where \( \theta \) is the contact angle at the interfaces (say in the cavity or on a grain). Eq. R-1 describes both the homogeneous and heterogeneous nucleations. From Eq. R-2, the heterogeneous nucleation is thermodynamically favored only when the liquid does not completely wet the rock, as only then \( \phi < 1 \). If gas is the nonwetting phase and oil is the wetting phase in a natural rock, when a nucleus is born, it may not stay in the cavity to grow. It would detach if it is born on the rock surface and move into the pore body. The minimization of Gibbs free energy for the work required to create a nucleus bubble supports this view. In other words, when the liquid completely wets the surface, the cavity cannot hold the gas bubble.

The major theme of our work is that solution gas drive in porous rocks for light oils is of instantaneous nucleation nature; at the critical supersaturation, all the bubbles form and then grow afterwards. This theory had a postulational basis when used in Ref. 2, and its success was demonstrated by describing experimental facts; the experimental verification is overwhelming. In a more recent work, there is solid evidence based on visual observations, that in fact nucleation in porous media is of instantaneous nature (Ref. 8). We observed the instantaneous formation of bubbles on the surface of a rock in a special high pressure visual coreholder around the critical supersaturation pressure for a 35 API crude and for a C1/C3 mixture. Fig. R-4 shows the sketches of bubble growth and expansion (details are provided in Ref. 8).

![Image](Fig. R-4 - Bubble formation and growth on the rock surface at volume expansions of 1.2 and 2.1 cm³ (from Ref. 8).)

In the discussion, it is interpreted that instantaneous nucleation which was introduced to model the solution gas drive experiments is the same as homogeneous nucleation. This interpretation is invalid. Eq. R-1 describes both homogeneous and heterogeneous nucleation and the rate of bubble nucleation, \( J \), is related to supersaturation. On the other hand, for instantaneous nucleation, the supersaturation that follows after bubbles' formation, does not contribute to further bubble formation.

The introduction of instantaneous nucleation greatly simplifies the description of pressure-volume relationship at nonequilibrium conditions. The number of bubbles is the only unknown. In our work, a very simple theory was used to obtain the bubble density from the pressure-volume data. The estimated bubble density from the instantaneous nucleation model increases as the rate of pressure decline increases. Theoretical analysis by Haves, Dawe, and Evans and visual observations in Ref. 8 show that as the rate of pressure decline increases the bubble density also increases which is in support of our work.

We offer a theory which describes the laboratory observations and has direct experimental support (Ref. 2). The results from the work cited in the discussion are often in disagreement with various experimental observations.

**Critical Gas Saturation and Rate Effect**

First, we do not yet have a model for the critical gas saturation, \( S_{gc} \), that can honor available experimental observations. We also believe that \( S_{gc} \) is generally small in the range of 0.5 percent at low enough rates. Experimental data reveal that \( S_{gc} \) increases as the rate of pressure decline increases. One could qualitatively explain the increase in \( S_{gc} \) from the rate effect due to an increase in the number of bubbles, i.e., increase in bubble density.

In our work on pressure-volume evolution at nonequilibrium conditions, a constant shape factor was used to partly include the effect of growth in porous media. This is a crude approach; a network-based model decorated with sound physics would be the preferred approach. However, the shape-factor approach was useful to proceed and to test the major issues of nucleation in porous media. We also assumed that the bubble density in the solution gas drive process is very low compared to the number of the pores—orders of magnitude smaller. This, we believe is a good assumption for light oils and an excellent assumption for model fluids.

We do not agree with results presented in Fig. D-3 of the discussion. This figure is presented as evidence that critical gas saturation estimated from the instantaneous nucleation is independent of the rate. The rate of pressure decline affects the bubble density at the critical supersaturation while the results presented in Fig. D-3 are based on the assumption that bubble density is constant and is independent of rate; another misconception which adds to the confusion.
AUTHOR'S REPLY TO DISCUSSION OFPRESSURE ANDVOLUME EVOLUTION DURING GAS PHASE FORMATION IN SOLUTION GAS DRIVE PROCESS

On the reproducibility and the effect of rate, there is too much speculation; the return to nucleation with pre-existing or trapped gas and constant supersaturation to activate the sites is also unnecessary. The work, whether theoretical analysis or experimental data of the type reviewed in the discussion unfortunately ignores the literature. The issue of reproducibility was addressed in Ref. 5 and was concluded that the results were reproducible (see Conclusion No. 1).

In conclusion, the hydrocarbon fluid mixture itself has an important effect on the evolution of gas phase in porous media. The effect cannot be described by surface tension and the rate of pressure decline alone. This, we believe is the most fascinating aspect of studying the efficiency of solution gas drive in porous media. It seems that the thermodynamics and the thermodynamic stability of new phase formation in porous media for hydrocarbon mixtures have to be developed further to study nucleation in porous media. We hope to publish our work on the subject in the future.

Nomenclature

\[ A = \text{kinetic constant of the classical nucleation rate expression} \]
\[ B = \text{thermodynamic constant of the classical nucleation rate expression} \]
\[ J = \text{nucleation rate, number of bubbles (volume-time)} \]
\[ k = \text{Boyle-Mariotti constant} \]
\[ p = \text{pressure in the bulk liquid phase} \]
\[ p_s = \text{buublepoint pressure} \]
\[ p_{cr} = \text{critical supersaturation pressure} \]
\[ p_e = \text{equilibrium gas phase pressure} \]
\[ S = \text{supersaturation} \]
\[ S_{cr} = \text{critical supersaturation} \]
\[ S_g = \text{gas saturation} \]
\[ S_{cr} = \text{critical gas saturation} \]
\[ T = \text{absolute temperature} \]
\[ W = \text{poro mouth width} \]

Greek Letters

\[ \sigma = \text{surface tension} \]
\[ \sigma_s = \text{specific surface energy} \]
\[ \phi = \text{defined by Eq. R-2} \]
\[ \theta = \text{contact angle} \]

References


Abbas Firoozabadi, SPE, is senior scientist and director at the Reservoir Engineering Research Institute, 845 Page Mill Rd., Palo Alto, CA, 94304, email: AF@rerinat.org. His current research focus include equilibrium, nonequilibrium and irreversible thermodynamics, and multiphase flow in fractured and layered media. Firoozabadi was a visiting professor in the Petroleum and Geosystems Engineering department at the University of Texas-Austin in the Fall of 1996. He holds a BS degree from the Abadan Institute of Technology and MS and PhD degrees from the Illinois Institute of Technology, all in gas engineering.