# LETTERS TO THE EDITOR

## To the Editor:

In the article titled "Thermodynamics of Wax Precipitation in Petroleum Mixtures" (January, 1996), Lira-Galeana et al. present a multisolid-phase model for predicting wax formation in petroleum mixtures. The authors assume precipitated wax to consist of several solid phases. Each solid phase is described as a pure component or pseudocomponent. A particular component or pseudocomponent $i$ will precipitate if its pure solid state fugacity $f^s_{\text{pure}\,i}$ is lower than the fugacity $f_i^V$ or $f_i^L$ of component $i$ in the mixed vapor or liquid phase.

This representation of wax differs from that selected by other authors (Won, 1986, 1989; Pedersen, 1995; Erickson et al., 1993) who all consider precipitated wax to be one phase in which the entering components form a solid solution.

The new approach is exemplified by comparing experimental and calculated wax precipitation data for binary $n$-alkane mixtures and for eight crude oil mixtures. The binary $n$-alkane mixtures all consists of a heavy $n$-alkane, which is potentially wax forming and a light $n$-alkane which does not form wax but serves as a solvent for the heavy $n$-alkane.

The simulation results for the binary mixtures are, in fact, inappropriate for testing the idea presented in the article that wax should consist of multiple solid phases, each consisting of one pure component. With only one wax forming component present, it is obvious that any wax formed will consist of this component in pure form.

However, the binary mixtures are not our reason for concern, but the application of the concept on crude oil mixtures. The authors have chosen eight North Sea oil mixtures for which Rønningsen et al. (1991) and Pedersen et al. (1991) have published experimental wax precipitation data. The plus fraction is divided into pseudocomponents. The article provides an example (Table 3 in the article) with 15 heptane-plus fractions of which the heaviest four are assumed to be potentially wax forming. Each pseudocomponent contains a range of molecular structures and covers an interval in molecular weight. The wax forming compounds are primarily found among the $n$-alkanes, but even with this limitation, the number of wax forming compounds contained in each of the heaviest pseudocomponents must be expected to be quite high. Nevertheless, the authors assume the mixture presented in their Table 3 to contain a total of only four wax forming components, identical with the four heaviest pseudocomponents. A number of four wax forming compounds has been selected because the authors see four abrupt jumps in the experimental wax precipitation vs. temperature curve for the actual mixture presented by Pedersen et al. (1991). Since other mixtures may have a different number of abrupt jumps, a different number of wax forming pseudocomponents should be selected.

We find the authors' treatment of wax formation in crude oil mixtures unsound. Phase equilibrium calculations on a mixture that contains a very large number of components necessitates grouping into pseudocomponents, and this grouping should be refined to the point where further subgrouping makes no significant change in the calculated equilibrium distribution.

When considering vapor-liquid equilibrium, the equilibrium condition for pseudocomponent $i$ is

$$f_i^L = f_i^V$$

or

$$x_i \phi_i^L = y_i \phi_i^V$$

Suppose now that component $i$ is subdivided equally into two new pseudocomponents, $i1$ and $i2$, with properties very similar to the original component. Then, a new equilibrium calculation will yield

$$x_{i1}\phi_{i1}^L = y_{i1}\phi_{i1}^V, \quad x_{i2}\phi_{i2}^L = y_{i2}\phi_{i2}^V,$$

with

$$\phi_{i1}^L \approx \phi_{i2}^L \approx \phi_i^L, \quad \phi_{i1}^V \approx \phi_{i2}^V \approx \phi_i^V,$$

and

$$x_{i1} = x_{i2} = \frac{1}{2}x_i, \quad y_{i1} = y_{i2} = \frac{1}{2}y_i$$

In contrast for solid/liquid equilibrium with the equilibrium condition

$$x_i \phi_i^L P = f_i^{S,\text{pure}}$$

the subdivision would require that

$$x_{i1}\phi_{i1}^L P = f_{i1}^{S,\text{pure}}$$

$$x_{i2}\phi_{i2}^L P = f_{i2}^{S,\text{pure}}$$

which is incompatible with the condition $\phi_{i1}^L \approx \phi_{i2}^L \approx \phi_i^L$, $f_{i1}^s \approx f_{i2}^s \approx f_i^{s,\text{pure}}$ and $x_{i1} = x_{i2} = (1/2)x_i$. The subdivision essentially reduces the fugacities by a factor of 2 for the liquid phase without affecting the solid phase fugacity, and this leads to a reduction in the wax formation temperature. The approach suggested by the authors therefore will be strongly affected by the manner in which the heavy fractions are grouped, and in the limit where a very large number of components are used to represent the mixture, solid formation becomes impossible.

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## Reply:

We thank Karen Pedersen and Michael Michelsen for their interest in our work on wax precipitation.

It appears that Pedersen and Michelsen have misunderstood our position. In our multicomponent example, we do not look at the data and then decide how many solid phases are formed. The number of solid phases is decided only by the fugacity criterion: does the fugacity of a component or (pseudocomponent) in the liquid phase exceed that of the solid phase? If so, a solid is formed.

We do not agree with the argument that the manner in which the heavy fractions are grouped would strongly affect the calculated results, because again, there appears to be a misunderstanding. Contrary to Pedersen and Michelsen's erroneous interpretation of our calculations, we do not assume that every "true" component in a pseudocomponent forms a separate solid phase. Using their notation, we do not assume

$$f_{i1}^{s} = f_{i2}^{s} = f_i^{s^{\text{pure}}}$$

Rather, we assume that very similar "true" components $i_1$ and $i_2$ form an ideal solid solution, that is, we assume that for very similar components

$$f_{i1}^{s} = x_{i1} f_i^{s^{\text{pure}}} \quad \text{and} \quad f_{i2}^{s} = x_{i2}^{s} f_i^{s^{\text{pure}}}.$$

Here superscript "pure" refers to "pure" pseudocomponent $i$. In vapor-liquid equilibria, the subdivision of component $i$ into two components $i_1$ and $i_2$ with similar properties to the original component does not change the calculation results. However, in solid-liquid equilibria, when pure solid phases are formed, the subdivision results in inconsistency. The pure solid phase of component $i$ in one case, and two separate pure solid phases of components $i_1$ and $i_2$ do not have the same entropy. There will be an entropy of mixing when the pure solid phases of components $i_1$ and $i_2$ are mixed. In our method, very similar components $i_1$ and $i_2$ are not expected to form separate solid phases.

We also do not agree with Pedersen and Michelsen's comment on binary mixtures. Any binary mixture could form a binary solid. Our calculations show that does not happen for the mixtures considered. While results for binary mixtures offer no proof of our basic hypothesis for ternary or higher mixtures, our studies for binary mixtures were important to us to check the calculation procedure.

Our work is indeed different from that of previous authors who assumed, without experimental verification, that all constituents of a crude form a solid solution. The fundamental spectroscopic studies of Snyder and W. B. Pedersen (referred to in our article), however, indicated to us that, in general, different large paraffins may form their own solid phases. Another clear example is the work of Dorset (1990) who found that precipitation in binary normal alkane mixtures is unstable and segregates into two solid phases; each phase consists primarily of the pure component, provided the chain length difference exceeds a certain value (around 5 for certain conditions). We, therefore, postulated that wax formation is a multisolid process. This assumption is nearer to physical reality than the one made by previous authors. In a recent refinement of the model, the hydrocarbon groups are divided into paraffins (P), naphthenes (N), and aromatics (A) (Pan et al., 1996). The calculated wax composition with the modified model is in agreement with data; the precipitated wax consists primarily of normal paraffins, iso-paraffins, and naphthenes; aromatics do not precipitate.

It seems likely that wax formation is not strictly described by either assumption (one solid solution, or separate solid phase for each component). One practical approach is to characterize the wax-forming constituents, that is, carbon numbers > 15 into pseudocomponents with a carbon interval of 5. This approach has been followed by Pan et al. (1996). The reasoning is based on the work of Dorset. For example, two paraffins with carbon numbers 20 and 21 are miscible in the solid phase but two paraffins with carbon numbers 20 and 26 are not. This limited miscibility is taken into account through the concept of pseudocomponents; a pseudocomponent contains "true" components whose carbon numbers are sufficiently close to form one solid phase.

For binary normal alkanes, the experimental data clearly show that separate solid phases can form. For multicomponent systems and crudes, experimental data are severely limited. In the absence of such experimental data, we believe our results show that the multisolid assumption provides a description of available experimental wax-precipitation data which is better than the single-solid assumption used by previous authors.

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## To the Editor:

Lam et al. (June, 1996) discussed drop-size distributions for four systems showing progressive decreases in size as the stirred dispersions were sampled at times between 1 and 10 h. It was stated that this decrease contradicts the widely held view that the largest drop size $d_{\max}$ becomes constant after about 1–2 h.

The measured drop-size distributions are welcome. We agree with the statement on p. 1549 that "This clearly indicates that the drops continue to break throughout 8 to 10 h course of the experiments. This stands in direct contrast to the experiments reported in the literature on $d_{\max}$, where it was typically assumed that drop breakage no longer occurred after 1 to 2 h."

However, two matters require comment. First, on p. 1548 the authors wrote "The extent to which drop sizes can dip below $d_{\max}$ is an issue that has not yet been addressed in the literature." However, reference is made on the same page to experiments of Konno et al. (1983) and ourselves (1995) which clearly showed significant decreases up to 5 h and to 24 h, respectively. No citation of other directly relevant work was given, namely Konno and Saito (1987), Konno et al. (1993), and Baldyga and

Bourne (1993). The latter authors were the first to explain that turbulence intermittency can cause the classical theories of Kolmogorov and Hinze to fail (for example, the exponent on the Weber number can be less than $-0.6$). They derived a quantitative model of drop breakup employing a multifractal spectrum of the turbulent energy dissipation rate, which predicts the condition for the smallest value of $d_{\max}$ to be attained.

Secondly, we agree that "similar breakage events occur during the course of the experiment" (p. 1550) and "the nature of drop breakup (distribution of daughter drops) at long times does not differ from the observed at short times" (p. 1552). The statement "Baldyga and Bourne (1995) have proposed, however, that the mechanism of breakup changes at long times" (p. 1552) is not correct and misrepresents our work.

On p. 1548 it is written that we invoked "a change in the breakage mechanism as time progresses—at short times, drops break by average pressure fluctuations, and at long times, they break due to rare but very intense pressure fluctuations." We did not, however, propose a change in mechanism but consistently employed the balance between pressure fluctuations, which arise from velocity fluctuations and disrupt drops, and stabilizing interfacial tension and drop viscosity (see Eq. 12 of Baldyga and Bourne (1993) and Eqs. 95 and 115 of Baldyga and Bourne (1995)). The turbulent events with multifractal exponents close to 1 dominate the breakage for short contact times, giving results very similar to classical solutions based on average stresses. For longer contact times, more violent events having low probabilities are required to cause breakage and a gradual decrease in drop sizes. Using the multifractal representation of the distribution of turbulent energy dissipation rates due to Meneveau and Sreenivasan (1991), the slow but progressive action of highly intermittent pressure fluctuations greatly in excess of their mean value was expressed quantitatively by Baldyga and Bourne (1993, 1995) and compared with drop breakup experiments.

The observed gradual decrease in drop size is not in our opinion due to a mechanistic change in the balance between dispersive and stabilizing forces, but rather to intermittent, highly dissipative bursts of turbulence.

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## Reply:

The intent of our article "Maximum Stable Drop Diameter in Stirred Dispersions" was twofold: 1. to contest the notion of an absolute maximum stable drop size; 2. to show that continuation of breakage proceeds in a quantitatively "similar" way at longer times. The experimental data reveals that the size distributions at various times (1 to 10 h) show self-similar behavior in terms of similarity variables $\zeta = \Gamma(\nu)/\Gamma(\nu_{\text{ref}})$ and $\zeta f'(\zeta)$. The specific choice of similarity variables used here points very strongly to the continued breakage of drops in an identical manner at the times investigated, that is, the daughter drop-size distribution in terms of scaled sizes remains *unchanged* at all times.

In regard to the first issue, it must be admitted that the works of Konno et al. (1983, 1993) and of Baldyga and Bourne (1993, 1995) address the *same* issue and must indeed be credited with finding drops considerably below the classical $d_{\max}$. These references became available to us during the review of our manuscript, and while they were included in our article, comments pertaining to the past literature at large should have been appropriately modified. Clearly, the sentence quoted from our article in the third paragraph of the letter of Baldyga and Bourne needs to be and is retracted. We also thank Baldyga and Bourne for pointing out these references.

The second issue sets, however, the main focus of our article. It is true that Baldyga and Bourne have proposed that the drops initially break by average fluctuations and at later times by intense pressure fluctuations. Although the authors have used a balance of similar forces to explain $d_{\max}$ at short as well as long times, and may thus provide a basis for an argument involving no change in mechanism, we would like to leave them with the following question: Is it reasonable to expect that the breakup of drops at long times by sporadic and very violent fluctuations would produce the *same* daughter drop-size distribution at those obtained at short times? The daughter drop-size distribution has not been an issue in past work. Our work seems to show that the breakage mechanism is "preserved" even at long times.

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