# LETTERS TO THE EDITOR

**To the Editor:**

The purpose of this letter is to clarify what we believe are the different molecular phenomena occurring in supercritical fluid (SCF) solutions leading to the unusual and highly useful properties of such mixtures. [Refer to the paper titled "Mean Field Calculations of Thermodynamic Properties of Supercritical Fluids" by Economou and Donohue (p. 1920 in this issue).] We feel that to appreciate the macroscopic behavior, especially to achieve valid correlations and predictions, it is necessary to view these mixtures from a molecular level.

Our attempts to characterize the microscopic behavior began in the early 1980's, when limited evidence was available, including some solubility data. In addition, there were various determinations of very large negative solute partial molal volumes (up to $-20$ L/mol) (Erlich and Fariss, 1969; Erlich and Wu, 1973; Van Wasen and Schneider, 1980; Eckert et al., 1983, 1986), very close to the solvent's critical point, where solvent molar volumes are of the order of 100 $cm^3/mol$. In 1983, we proposed the use of the word "clustering" to describe the observed large, negative solute partial molal volumes (Eckert et al., 1983). The use of this terminology evokes different meanings for different audiences. In the critical phenomena literature, a cluster is a region of space where order parameter fluctuations are correlated. In the chemistry literature, it denotes a tightly-packed, structurally stable aggregate, in which molecules retain their relative positions indefinitely. Furthermore, in the case of SCF's, the same word has been used to describe what in reality are distinct phenomena.

The large solute partial molal properties are a manifestation of critical behavior. They are the result of long-ranged correlations; they grow as a consequence of the divergence of the solvent's compressibility and correlation length, and they influence the sensitivity of solubility to small changes in temperature and pressure. Likewise, the statistical excess number of solvent molecules around a given infinitely-dilute solute molecule, with respect to a uniform distribution at bulk density, diverges at the solvent's critical point. This divergence is due to long-ranged correlations. The use of the word "cluster" in this context (Kim and Johnston, 1987a; Debenedetti, 1987; Debenedetti and Kumar, 1988) can lead to misinterpretations if understood in terms of a close-packed, structurally-stable aggregate of diverging size.

We believe that the term "clustering" more appropriately describes specific, short-ranged effects. What we seek to convey is a picture of local density enhancements in the vicinity of a large solute molecule. It should not be interpreted as a stable aggregate, but as a finite region where the dynamic solvent concentration differs appreciably from the bulk. We shall use the terms "clustering" and "local density augmentation" synonymously.

Subsequently, a great deal of additional work has appeared which is also consistent with this concept of clustering. A variety of spectroscopic studies indicate consistently that the density of an SCF about a solute is augmented significantly over the bulk density (Kim and Johnston, 1987b; Yonker and Smith, 1988; Johnston et al., 1989a; Brennecke et al., 1989, 1990a; Morita and Kajimoto, 1990). As the isothermal compressibility increases, this local effect becomes more pronounced, although it remains finite. The same is true of local compositions of cosolvents (Kim and Johnston, 1987a; Brennecke et al., 1990b). These spectroscopic results would be difficult to represent with any continuum model.

Molecular dynamics (Petsche and Debenedetti, 1989) and integral equation calculations (Wu et al., 1990) show appreciable local density augmentations, although they demonstrate clearly that singularities are due to long-ranged correlations. In addition, large local density augmentations have been calculated from a modified Born equation for SCF water about solute ions (Wood et al., 1981; Flarsheim et al., 1989). Even some kinetic results, such as the photolysis of iodine in SCF ethane, show the effect of solvent clustering (Otto et al., 1984).

Certainly mean field equations can be formulated to account for the observed solubility effects, and such equations are not in any way mutually exclusive with the concept of clustering. In all probability, the design methods for real, multicomponent processes will be cubic equations of state for some time to come. However, for many SCF applications, especially those exploiting cosolvent effects, a molecular view leads to greatly improved understanding and predictability.

Cosolvent effects in SCF's of factors of 2–5 are now commonplace, even with very small amounts of additive. Recently effects greater than two orders of magnitude have been reported (Johnston et al., 1989b; Foster, 1990). These are brought about by very specific and short-ranged interactions between solute and cosolvent and suggest the possibility of a large local composition augmentation. If such a phenomenon does exist, and we can measure and control it by judicious choices of cosolvents, it certainly raises exciting possibilities of tailoring SCF solutions for specific separations and even chemical reactions.

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## Reply:

We agree with many of the points made in the above letter by J.F. Brennecke, P.G. Debenedetti, C.A. Eckert, and K.P. Johnston, particularly their last. However, we disagree on three issues.

First, we disagree with the authors that "in the chemistry literature, it (a cluster) denotes a tightly-packed, structurally-stable aggregate in which molecules retain their relative positions indefinitely." We believe that most people view a cluster as "tightly-packed," but *not* structurally-stable. Certainly in the literature on nucleation, where the term is used extensively, clusters are dynamic entities that grow and shrink rapidly.

Second, we disagree that "appreciable local density augmentations . . . are due to long-ranged correlations." McGuigan and Monson (1990) have made integral equation calculations in the critical region similar to those cited, but found that "the physical effects associated with the divergence of $\bar{V}_2^\infty$ are due to the development of long-range correlations in the solvent and not to drastic changes in the local structure about the solute."

Finally, the authors state, "mean field equations can be formulated to account for the observed solubility effects, and such equations are not in any way mutually exclusive with the concept of clustering." However, mean field theory precludes the existence of clusters. Therefore, since mean field theory shows that large partial molar properties are a consequence of the compressibility in the critical region, these large partial molar properties *cannot* be a consequence of clustering as suggested in the papers quoted in our article.

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## To the Editor:

In a recent paper titled "Initial Condition for Population Balance in an MSMPR Crystallizer" by Rojkowski (April 1990, p. 630), the author argued that the correct initial condition to the population balance equation for an MSMPR crystallizer with size-distributed nucleation, size-dependent growth, and negligible attrition and agglomeration is

$$Gn|L_n = 0 \qquad (1)$$

where $L_n$ is the smallest size of nuclei ($L_n \geq 0$). The author pointed out that at the size exactly $L_n$, the crystal input due to growth is zero as the growth process did not populate at the smallest nuclei size ($L_n$). To satisfy the conservation of the overall number of crystals over the entire size range ($L_n$, $\infty$), *viz.*, the total number of nuclei added by birth in an MSMPR crystallizer ($B_T V$) equals that of product crystals leaving the crystallizer ($N_T q$). He intuitively guessed that Eq. 1 must be the proper initial condition. He then discussed the concept of population density of nuclei at the moment of birth to show that

$$b(L_n) = n_n(L_n)/\tau$$
$$= \frac{d[G(L_n)n(L_n)]}{dL} \qquad (2)$$

in order to satisfy Eq. 1 [$n(L_n) = 0$ when $G(L_n) > 0$]. He also indicated that it was the derivative which determined the birth function in close proximity of the size $L_n$. The algebraic form of the population balance equation relating birth function at any size to population density and derived previously on the basis of negligible contribution due to growth should be valid for nongrowing particles, since the product population density is the sum of these two densities. Equalities in Eq. 2 are valid numerically at $L = L_n$ only because of suggested process constraints. Birth rate function characterizing the addition of new crystals by birth for a system to particle continuum at any point should depend on process conditions and environment.

The population density function derived usually from the measured raw data of size analysis is discontinuous (or analytic) at the lower bound, *viz.*, the size $L_n$. The author invoked several types of population density functions [$n(L)$, $n_n(L)$, $n^*(L)$, $n_p(L)$], all of which are difficult to determine empirically. The MSMPR constraint requiring the identical and continuous population densities for the crystallizer contents and the product is difficult to visualize satisfactorily. The smallest nucleus size, $L_n$, is the additional process parameter added to the process description and difficult to assign *a priori*. Equation 1 with $L_n = 0$ has been used by Randolph and his coworkers (Youngquist and Randolph, 1972; Randolph and Cise, 1972; Randolph and Sikdar, 1976). The identity in his Eq. 5 is valid only in the limiting case of $dL \rightarrow 0$. The proper initial condition should be

$$nG|L_{n^-} = 0; \quad nG|L_{n^+} = B(L_n) \qquad (3)$$

The population balance approach provides a predictive multidimensional particle distribution theory which can be effectively used for both process simulation and identification problems. It is important to recognize that both crystal nucleation and growth are rate processes, and a careful definition of the rate concept is essential at the outset. One does not measure process rates directly, but only arrives at their values by some combination of measurement and theory. The overall nucleation rate usually determined from the change in number concentration per unit time is rather difficult to evaluate precisely and reliably because of the difficulty associated with the measurements.

The conventional MSMPR crystallizer theory relates nucleation rate as

$$B = n^o G \qquad (4)$$

where $n^o$ is the population density of nucleus size crystals and $G$ usually is the ensemble average value. Equation 4 assumes that the size of all the embryo-size crystals is vanishingly close to zero and that the experimental data to zero size must be extrapolated. As long as the linear relationship of the population density plot is observed over the entire range, the estimates will not affect. Should the assumption of zero size be correct, $n^o$ will tend to be infinity and linearity of the population density plot cannot be guaranteed. This will invalidate Eq. 4 and will make it difficult to determine the nucleation rate. The linear extrapolation however provides a practical solution. The nonlinearity in the population density plot cannot be treated by the linear first-order equation. Several modifications have been suggested to account for it in the crystallization literature.

## Notation

$B(L)$ = nucleation rate at $L$, no./m$^3$ · s
$B_T$ = total nucleation rate, no./m$^3$ · s
$b(L)$ = birth function of nuclei at $L$, no./m$^4$ · s
$G(L)$ = overall linear growth rate at $L$, m/s
$L_n$ = minimum size of nuclei, m
$N_T$ = total number of crystals per unit volume of suspension, no./m$^3$
$n(L)$ = population density of crystals, no./m$^4$
$n_n(L)$ = population density of nuclei at birth, no./m$^4$
$n_p(L)$ = product population density, no./m$^4$
$q$ = volumetric flowrate of suspension, m$^3$/s
$V$ = crystallizer volume, m$^3$
$\tau$ = mean residence time, s

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## Reply:

Dr. Tavare insists that the initial condition

$$G(L)\, n(L)\,_{|L_n = o} = 0 \qquad (1)$$

to the population balance equation for an MSMPR crystallizer with size-distributed nucleation, size-dependent growth, and negligible attrition and agglomeration, that is,

$$d(G\, n) + \frac{n(L)}{\tau}\, dL = b(L)\, dL \qquad (2)$$

is intuitive and incorrect. He maintains that the proper initial condition should be

$$Gn_{|L_n^-} = 0; \; Gn_{|L_n^+} = B(L_n) \qquad (3)$$

Unfortunately, *his* Eq. 3 appeared to be *Deus ex machina* and was not supplemented by any physical explanation nor checking. I cannot agree with the above thesis by any means and I will try again to prove that the opposite is true: the fact that Eq. 1 is correct, not Eq. 3, will be verified in two ways. The notation and references are the same as in the Letter to the Editor written by Dr. Tavare.

First, I would like to stress again that identity 1 was obtained from the integral constraint resulting from the conservation of the overall number of crystals over the entire size range ($L_n$, $\infty$). This is the safest tool for deriving an initial condition for poorly defined boundary. Let us check first the validity of Dr. Tavare's initial condition, *his* Eq. 3, in the same way.

Integrating Eq. 2 gives

$$G(\infty)\,n(\infty) - G(L_{n^+})\,n(L_{n^+}) + \frac{1}{\tau}\int_{L_n^+}^{\infty} n(L)\,dL = \int_{L_n^+}^{\infty} b(L)\,dL \qquad (4)$$

By definition

$$B_T \equiv \int_{L_n^+}^{\infty} b(L)\,dL; \qquad B(L) = \int_{L_n^+}^{L} b(L)\,dL \qquad (5)$$

and

$$N_T \equiv \frac{1}{\tau}\int_{L_n^+}^{\infty} n(L)\,dL \qquad (6)$$

Note that taking $L_n$ as the lower limit of integration would be equally proper because $G(L)$, $b(L)$ and $n(L)$ functions are assumed to be continuous. Substituting Eqs. 3, 5 and 6 to Eq. 4, assuming that $b(L_n)$ is finite (which is the case for size-distributed nucletion) and noting that the term $G(\infty)\,n(\infty)$ vanishes, yields

$$0 - B(L_n) + N_T/\tau = B_T; \qquad N_T/\tau = B_T \qquad (7)$$

Thus, one obtains from Eq. 7 that

$$B(L_n) \equiv 0 \qquad (8)$$

while the right-side equality in *his* Eq. 3 suggests that this "point" nucleation rate is nonzero. Thus, the initial condition proposed by Dr. Tavare is incorrect numerically because

$$n(L_n^+) = n(L_n) = 0 \qquad (9)$$

Secondly, the size-distributed nucleation rate $B(L)$ is discrete, in fact. The number of crystals in a cubic meter of suspension, however, is in the order of billion. Thus, one can safely assume that this function is continuous in the size range $L_n$, $\infty$. Dr. Tavare can write that the left limit $B(L_n^-) = 0$, since there is a physical constraint, but more formally the function $B(L)$ is not defined at this point. The apparently strange identity 8 becomes evident when one considers the limit of the right part of Eq. 5,

$$\lim_{\Delta L \to 0} \int_{L_n}^{L_n+\Delta L} b(L)\,dL \equiv B(L_n) = B(L_n^+) = 0 \qquad (10)$$

Equation 10 is valid under the assumption that the boundary value of the birth function $b(L_n)$ is greater or equal to zero, but is finite. It is quite different with the classical MSMPR crystalizer case, in which nucleation process is assumed to occur only at size exactly equal to $L_n$. In this case, the birth function is no longer continuous because

$$b(L_n) = B_T\,\delta(L - L_n) \qquad (11)$$

Thus, it is the so-called pseudofunction (distribution). From the known property of the Dirac delta pseudofunction $\delta(L)$, it results

$$\lim_{\Delta L \to 0} \int_{L_n}^{L_n+\Delta L} b(L)\,dL \equiv B(L_n) = B_T > 0; \quad B(L_n^+) = 0 \qquad (12)$$

Thus, in the classical case as mentioned in my paper, the population density of the nucleus-size crystals $n(L_n^+)$ is finite, because the population density of nuclei at birth $n_n$ is infinite at point $L_n$ but zero at point $L_n^+$. The value of $n(L_n)$ is not defined. In the case of size-distributed nucleation, the first function is zero at point $L_n$ because the latter is finite at the same point.

The correct initial condition, Eq. 1, can be expressed equally well in the form resembling Eq. 8, that is,

$$B(L_n) \equiv 0 = G(L_n)\,n(L_n) \qquad (13)$$

because

$$n(L_n) \equiv 0 \qquad (14)$$

as it has been deduced in my paper—not intuitively but from the integral constraint 4. The nucleation rate $B(L)$, however, is the reason (forcing function) of the crystallization process in an MSMPR crystallizer, while the population density $n(L)$ is its result (reply function). An initial condition for any ordinary differential equation should concern the value of the reply function, not of the forcing function. According to this formalism, the initial condition (Eq. 14) appears to be "*better*" than Eq. 13.

I must also correct Dr. Tavare's understanding that Eq. 1 has been used by Randolph and his coworkers. They have employed only the generally untrue assumption

$$b(L) \simeq n(L)/\tau \qquad (15)$$

instead. Only in their last paper (Randolph and Sikdar, 1976), Eq. 1 was employed (see discussion under their Eq. 9), but its justification quite differs from that in my paper. They comment: "If secondary nuclei are created at a finite size, then the particle flux at zero size, $Gn_{|L=0}$, is zero." Thus, the generally valid Eq. 1 was evident for them (that time) in such a specific case only.

I must agree with Dr. Tavare that my Eq. 5 is valid only in the limiting case of $dL \to 0$. I also agree that the product $nG_{|L-} = 0$, but it does not exist physically.

Finally, I would like to thank Dr. Tavare for his remarks. He forced me to think over the problem once again.

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