LETTERS TO THE EDITOR

To the Editor:

I would like to comment on the article by Nabetani et al. titled "The Effects of Osmotic Pressure and Solute Adsorption on Ultrafiltration of Ovalbumin" (**36,** June 1990, p. 907). The authors, arguing against the use of gel polarization, resistance in series or simple osmotic model, propose the use of a combined osmotic pressure/adsorption resistance model to describe the ultrafiltration of ovalbumin in a cross-flow plate and frame module.

While the model proposed does describe the experimental data reasonably well, it seems odd that there was no attempt to include the effect of a gel layer on ultrafiltration behavior, especially considering that a gel layer was observed during experimentation. In taking such an approach, the authors fell into the common trap of seeing the osmotic and gel models as being exclusive of each other, rather than allowing for the fact that both effects may contribute to the reduction of flux during ultrafiltration.

Nabetani et al. use the following simple equations to describe ultrafiltration behavior.

$$J = k \ln(c_w/c_b) \qquad (1)$$

and

$$J = (\Delta P - \Delta\pi)/(R_m + R_f + R_p) \qquad (2)$$

Equation 1 describes the relationship between flux, mass transfer coefficient and concentrations. Equation 2 describes the relationship between flux, applied pressure, osmotic pressure and any resistance to flow caused by the membrane (R_m), a fouled layer on the membrane surface (R_f), and the concentration boundary layer (R_p). By analogy, it is possible to propose a modified gel model that would take the form

$$J = \Delta P/(R_m + R_f + R_p + R_g) \qquad (3)$$

where R_g is the resistance to flow caused by the gel layer. Both equations could be seen as simplifications of a more "universal" model of the form

$$J = (\Delta P - \Delta\pi)/(R_m + R_f + R_p + R_g) \qquad (4)$$

An estimate of the relative validity of the modified gel and osmotic models can be obtained by calculating the resistance to flow (apart from membrane resistance) in Eqs. 2 and 3 from data measured by Nabetani et al. for the ultrafiltration of 1 wt. % ovalbumin at a cross-flow velocity of 0.805 $m \cdot s^{-1}$. Table 1 shows that the modified gel model is well-behaved compared with the modified osmotic model because the resistance to flow increases with pressure, as would intuitively be expected.

Does this invalidate the modified osmotic model proposed by Nabetani et al.? The answer is "not entirely." The role of osmotic pressure in reducing flux has been demonstrated by many researchers. Inconsistencies in the resistances calculated by the model are probably due partly to an overestimation of the value of the wall concentration from Eq. 1, which ignores the effect of flux and variable solution properties (such as viscosity, density and diffusivity) on the mass transfer coefficient and wall concentration.

Is Eq. 4 a better representation of ultrafiltration behavior? The answer is "yes." The role of fouling and the gel layer in reducing ultrafiltration flux is established well in the literature, and any model should clearly include the effects of these phenomena as well as the effect of osmotic pressure.

What is the best way to model ultrafiltration behavior? The use of Eqs. 1 and 4 is adequate in some cases, but not for all situations. One improvement would be to find a replacement for Eq. 1 that is more appropriate for ultrafiltration. The difficulty of this approach has been discussed by van den Berg and Smolders. Another approach is to solve

Table 1. Resistance to Flow Calculated from Figure 7 of Nabetani et al.

	$(R_f + R_p)$ Modified Osmotic Model Eq. 2, $Pa \cdot s \cdot m^{-1}$			$(R_f + R_p + R_g)$ Modified Gel Model Eq. 3, $Pa \cdot s \cdot m^{-1}$		
ΔP (kPa)	*PO* Membrane	*PS* Membrane	*PAN* Membrane	*PO* Membrane	*PS* Membrane	*PAN* Membrane
100	3.30×10^9	4.06×10^9	3.43×10^{10}	8.83×10^9	1.07×10^{10}	3.73×10^{10}
200	1.49×10^{10}	3.89×10^9	4.82×10^{10}	1.75×10^{10}	1.84×10^{10}	5.13×10^{10}
300	5.43×10^9	1.08×10^{10}	5.49×10^{10}	2.41×10^{10}	2.47×10^{10}	5.82×10^{10}
400	1.49×10^{10}	1.16×10^{10}	6.62×10^{10}	3.38×10^{10}	3.52×10^{10}	6.98×10^{10}

the equations of motion, continuity and mass transport allowing fully for the effects of flux, cross flow, variable solution properties and, if possible, fouling, on the concentration and velocity profiles. One such recent attempt is that of Gill et al.

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Reply:

We would like to thank Dr. Wiley for her interest in this work and for taking time to estimate the validity of the osmotic pressure and adsorption resistance model proposed by us.

We also have been thinking that use of Eqs. 1 and 4 is the best way to model ultrafiltration behavior. However, our analysis showed that the effect of the gel-like layer observed on the membrane surface on permeate flux could be neglected and the resistances to permeate flow were caused only by two factors, the membrane itself and solute adsorption. So, we employed a simpler equation similar to Eq. 2, instead of Eq. 4. Further research is under way to confirm the validity of ignoring the effect of the gel-like layer observed on the membrane surface, by directly measuring the resistance of the layer, which will be published later.

We cannot understand the reason why Dr. Wiley thinks that the modified gel model (Eq. 3) is more suitable for description of ultrafiltration behavior than our osmotic pressure and adsorption resistance model. In our model, flux decline is thought to be affected by an increase in the resistance to permeate flow caused by solute adsorption and a decrease in the effective driving pressure caused by the rise in osmotic pressure at the membrane surface. Effects of both of these factors can be estimated independently and be explained physically. So, there is no assumption in the analysis using our model. On the other hand, in the modified gel model, the decrease in flux is thought to be controlled by the resistance caused by fouling and gel-like layer formation. To successfully use this model, the characteristics of the gel-like layer, which is often called "gel," have to be made clear. However, the mechanism of gel-like layer formation and physical properties of the layer (such as an accurate concentration for gelling, specific filtration resistance, compressibility coefficient, and thickness) have not been investigated properly. So, in the analysis by a model similar to the modified gel model, the flux decline, which cannot be explained physically, is usually assumed to be due to the resistance of the gel-like layer. This type of analysis cannot have universal validity. We, therefore, think that our model is better than the modified gel model.

Dr. Wiley pointed out the distribution of values of (R_f+R_p) shown in Table 1, which were obtained by substituting experimental values of flux to Eqs. 1 and 2. Results of her calculations overstate the experimental error, and the distribution has little effect. In fact, Eqs. 1 and 2 describe the experimental data reasonably well, in spite of the distributed (R_f+R_p) values. As for all membranes, averages of the (R_f+R_p) values are in good agreement with the R_a values which are shown in Table 4 in our article and present the resistance due to solute adsorption. This indicates that permeate resistance of the fouling layer is caused only by solute adsorption.

We would like to thank Dr. Wiley for her concern about an overestimation of the wall concentration from Eq. 1, which ignores the effect of flux and variable solution properties such as viscosity, density, and diffusivity on the mass transfer coefficient and wall concentration. In Figure 6 in our article, mass transfer coefficients of three kinds of dextrans measured directly by the velocity variation method were compared with those calculated by the Leveque equation that did not consider the effect of suction flow into the membrane (permeate flux), and our experimental data agreed well with the equation. The values of permeate flux observed during the test by the velocity variation method, 20–25×10^{-6} $m^3\cdot m^{-2}\cdot s^{-1}$, were larger than those obtained during the ultrafiltration of ovalbumin solution. These results indicate that, in the case of our experiment with ovalbumin solution, the effect of flux on mass transfer coefficients is negligible. Effects of variable solution properties on mass transfer coefficients were studied by Nakao et al. (1986). They concluded theoretically that the effects of changes in solution properties, such as viscosity, density, and diffusivity, on the mass transfer coefficient in the concentration polarization layer must be taken into account when the changes were large and the flow in the membrane module was turbulent. However, it was also concluded that the effects could be negligible when the flow in the membrane module was laminar. Therefore, in our analysis the wall concentration was not overestimated.

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To the Editor:

The third article published by Hounslow (1990b) in the *AIChE J.* is concerned with estimation of nucleation, growth and aggregation rates from steady-state experimental population density data from an MSMPR crystallizer. In all his articles (Hounslow et al., 1988; Hounslow 1990a,b), the author transformed the conventional birth and death functions expressed in terms of volume as the internal coordinate to the length-based form to use the classical population balance approach in terms of crystal size. In the first two, the author developed a numerical discretization scheme using the basic definition of rate processes to determine the rate of change of specific crystal number in an interval and subsequently the principle of superimposition of discretized description of each rate process. It is an attempt to arrive at a semi-empirical recurrence relation such that both the rates of change of crystal number and volume be identical to those predicted by the moment transformation of the population balance equation. Although many of his illustrations show that the analytical and numerical results for crystal number concentration including the variation of the first four moments are in close agreement, it is necessary to point out that the equations derived are configuration-specific. With increased number of model parameters, it will be difficult to rely on this approach as it uses only average point values to adjust the solution.

In all these articles, the moment transformation of the population balance with this modification of transforming length-based birth and death functions allowed him to define the closed set of moments only when $j/3$ is an integer. Consequently, his approach in the third article (1990b) relied on using only two moments equations (zeroth and third moments) to characterize the model parameters. Both the chemical reaction engineering and crystallization literature are replete with studies using the moments analysis for parameter characterization. It is well known that only lower-order moments should be considered, since the parameters determined from higher moments have large uncertainties (see, for example, Redke, 1971; Tavare, 1989). The growth rates defined from Eq. 20 in the third article (1990b) will certainly have large uncertainty. With the author's formulation, it is rather difficult to analytically evaluate the other moments and hence the coefficient of variation based on population distribution. The empirical relation in his Eq. 19 (see also his Figure 3) derived from his numerical solution provides the third relation and may not always be satisfactory. To calculate the coefficient of variation based on population distribution moments were evaluated numerically from the discretized solution. Although the author ensures small error ($<0.1\%$) in population distribution, the uncertainty in higher-order moments is usually large due to tail effects (Tavare and Garside, 1986). The definition of the index of aggregation is satisfactory to an aggregating system in only an MSMPR configuration. It is also important to note that the parameter estimate B_0 is not the true nucleation rate of the system.

Table 1. Summary of Parameter Estimates (Nickel Ammonium Sulfate, Run B23, Tavare et al., 1985)

Technique	$B_0 \times 10^{-9}$ No./L·h	G μm/h	$\beta_0 \times 10^{9}$ L/No.·h	$B_0/G \times 10^{-6}$ No./μm·L
Liao and Hulbert Model (1976)				
Marquardt Algorithm	0.65	131	90	5.0
Moments Analysis	0.45	150	150	3.0
Hounslow Approach (1990a,b)				
Speed-Up Package (?)	1.7	388	800	4.3
Moments Analysis	1.4	389	801	3.5

The Liao and Hulburt (1976) model, based on the length-conserving population balance equation, provides the analytical solution and set of algebraic moment equations, both of which can be used easily to determine parameter estimates (G, B_0 and β_0). The growth rate in this case is defined from the ratio of first to zeroth moment. The first moment equation for $j=0$ (Eq. 7) is the same for both of the models. The parameter estimates derived from a set of population density data (Tavare et al., 1985) for nickel ammonium sulfate from a CMSMPR crystallizer at steady state using two approaches are summarized in Table 1. The results from moments techniques compare favorably with those derived using optimization procedures that are most accurate. The resulting difference between the two approaches are due primarily to different moments ratios used in the growth rate determination and different functionality of index of aggregation with coefficient of variation based on population distribution (Eqs. 19 and 31 in his third article, 1990b). Most previous studies indicated that the moments technique is not very satisfactory for model discrimination.

The author points out that the coefficient of variation based on population distribution is a satisfactory statistic to evaluate the aggregation parameter from only one set of experimental data. It is necessary to point out that calculated coefficients of variation from classical-size analysis data usually show large scatter around theoretically-calculated values. The index of aggregation defined as the difference between unity and the ratio of number of crystals leaving the crystallizer to that nucleated and evaluated from calculated population-based coefficient of variation of observed size analysis does not necessarily reflect the percentage (or degree) of agglomerates determined from physical examination of the product crystals (Nyvlt, 1985; Zumstein and Rousseau, 1989). Third moment of crystal-size distribution with respect to size should not be affected by volume-conserving agglomeration process. An internal consistency check on mass balance, i.e., similar values of magma densities calculated from solution concentrations and observed weight of product crystals, is usually satisfactory in most experiments. Magma density calculated from process description and kinetic relations appears in good agreement in this case with the measured value; generally it may have relatively large error.

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Reply:

The points made in Dr. Tavare's letter may be grouped under three headings: comments on the discretized population balance (DPB), comments on the population balance for aggregating systems, and the interpretation of the data of Tavare et al. (1985).

Comments on the DPB

Dr. Tavare describes the DPB as "a semi-empirical recurrence relation." It is, in fact, explicit in rate of change of particle numbers and is deduced from theoretical, rather than experimental, arguments. Rather than being "configuration-specific," it is as general as the continuous population balance, from which it is deduced. It has been used to describe batch, semibatch, steady-state continuous and dynamic continuous systems.

Population balance for aggregating systems

There seems little doubt that the simplest realistic model for a crystallizing system, in which there is significant aggregation, includes a size-independent linear rate of growth and a volume-conserving aggregation mechanism. One of the characteristics of the population balance so formed is that it is extremely cumbersome when written using particle length as the internal coordinate, as is apparent in Eqs. 1, 2 and 3 of the article under discussion. The birth term may be much simplified if volume is used as the internal coordinate; in which case, however, the growth term acquires a nonconstant coefficient. This complexity is doubly significant in the context of this letter. First, it was the reason that Hulburt and Katz (1976) chose to propose an approximate length-conserving model for aggregation: such an approach simplifies the birth term and allows an analytical solution. Secondly, it gives rise to the limited set of moments available analytically. This last restriction is inherent in the population balance and does not stem from any modification or transformation made by me.

Interpretation of the data of Tavare et al. (1985)

Dr. Tavare points out that using the length-conserving model of Liao and Hulbert (1976), analytical expressions for all of the moments and indeed the population density function may be deduced. This allows him to use a nonlinear optimization technique to fit that model to his data with all the associated statistical accuracy that such a technique can deliver. But, aggregation in crystallizing systems is most assuredly *not length-conserving*. Under conditions of constant particle density and porosity, crystal aggregation *must be volume-conserving*. Even allowing that aggregates have a slightly higher porosity than single crystals, one would expect a fractal index (Amal et al., 1989) of only a little less than 3. One must conclude that Tavare et al. have fitted an approximate model with great accuracy. On the other hand, the approach adopted in the article under discussion is to fit an exact model with as much accuracy as is warranted by the experimental data. Figure 1 of the article shows calculated size distributions with a tenfold variation in the fraction of particles aggregated. The method described in the article is certainly accurate enough to determine which line best describes the experimental data—beyond that point, there is little hope of further refining the values of the estimated parameters with any statistical significance.

Finally, I do not propose that the analysis of one set of data is sufficient evidence to suggest that this approach may always be used for parameter estimation. Rather, I believe I showed that the full, volume-conserving population balance can be solved in a dimensionless form and, as a separate issue, that the data of Tavare et al. are described well by the full population balance.

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To the Editor:

In a recent article titled "Thermodynamics of Lewis Acid-Base Mixtures" by Economou et al. (December 1990, p. 1851), the authors analyzed various possible analytical approximations to the equation of state for a mixture of compounds forming self-associates as well as cross-associates. The authors concluded that the approximation proposed by Anderko (1989a) was not accurate for mixtures of amphoteric and basic or acidic components. The purpose of this letter is to clarify the differences between the models employed by Economou et al. (1990) and Anderko (1989), which in some cases preclude direct comparison of analytical approximations.

For a binary mixture containing an amphoteric component M (e.g., an alcohol) and a basic component B (e.g., a ketone), Economou et al. take into account the self-association reaction for the amphoteric component:

$$M_i + M = M_{i+1} \qquad (1)$$

and the cross-association reaction:

$$M_i + B = M_iB \qquad (2)$$

A similar scheme is proposed for amphoteric (M) and acidic (A) components. It is assumed that the molecule B has only one interaction site so that once one B species is added, no further cross-association can occur in that end of the chain, where B is located.

In Anderko's (1989) model, the self- and cross-association reactions are defined by:

$$(M_iB_j)M + M(M_kB_l) = (M_iB_j)M - M(M_kB_l) \qquad (3)$$

and

$$(M_iB_j)M + B(M_kB_l) = (M_iB_j)M - B(M_kB_l) \qquad i,j,k,l = 0, \ldots, \infty, \qquad (4)$$

respectively (cf. Eqs. 1a–1c in Anderko's (1989) article. It is assumed that B has two interaction sites and subsequently the B monomer can be situated in the middle as well as at the ends of the associated chain. This makes the number of possible associated structures much larger than in the case of Eqs. 1-2. Similarly, for a mixture containing one basic and one acidic component, more than one association reaction is allowed for. In short, Anderko's model is a generalization of the continuous linear association model for all possible self- and cross-association reactions.

There is no sufficient experimental evidence that would suggest which scheme, Eqs. 1-2 or Eqs. 3-4, is more probable. However, it should be noted that many Lewis bases, such as ketones, have two lone pairs of electrons on the oxygen atom, thus providing two possible basic interaction sites. If association mechanisms other than hydrogen bonding, such as charge-transfer complexes or clustering due to strong dipole-dipole interactions, are also taken into account, the extended continuous association schemes such as Eqs. 3-4 are even more plausible.

The differences in the association models affect the material balances that have to be solved in conjunction with an equation of state. Thus, an analytical approximation to the equation of state for the model (Eqs. 3-4) cannot be expected to be accurate for the model (Eqs. 1-2).

Additionally, analytical approximations to the equation of state containing two amphoteric components (e.g., two alcohols) need some comments. In this case, the models of Economou et al. (1990) and Anderko (1989) are very similar except that Economou et al. separately treat the cross-association reactions M(acidic) + N(basic) and M(basic) + N(acidic). Economou et al., following an earlier work of Ikonomou and Donohue (1988), approximated the ratio of the total number of moles n_T to the analytical (superficial) number of moles n_o for a mixture of n amphoteric components as:

$$\frac{n_T}{n_o}=\sum_{i=1}^{n}\frac{2x_i}{1+\sqrt{1+4K_{ii}RT/v}} \qquad (5)$$

where K_{ii} is the self-association constant for the ith amphoteric component. If inert components are also present, a sum of their mole fractions $\Sigma\, x_k$ should be added to the righthand side of Eq. 5. Economou et al. (1990) found that Eq. 5, coupled with the PACT EOS, yielded a somewhat better approximation for binary alcohol + alcohol mixtures than the equation proposed by Anderko (1989):

$$\frac{n_T}{n_o}=\sum_{i=1}^{n}\frac{2x_i}{1+\sqrt{1+4RT\left(\sum_{j=1}^{n}K_{ij}x_j\right)/v}}+\sum_{k=1}^{r}x_k \qquad (6)$$

where K_{ij} ($i \neq j$) is the cross-association contant between components i and j. The differences between Eqs. 5 and 6 can be easily compensated by using an effective constant K_{ij} differing slightly from the default value $K_{ij}=\sqrt{K_{ii}K_{jj}}$. In fact, it was shown (Anderko, 1989) that K_{ij} was the only adjustable binary parameter needed to accurately represent the data for various mixtures. However, a more important difference between Eqs. 5 and 6 is observed when only one associating compound is present. In this case, only Eq. 6 reduces to the exact analytical solution:

$$\frac{n_T}{n_o}=\frac{2x_1}{1+\sqrt{1+4RTK_{11}x_1/v}}+\sum_{k=1}^{r}x_k \qquad (7)$$

whereas Eq. 5 for $n = 1$ misses the x_1 factor in the denominator. This behavior is of utmost importance when equilibria in ternary mixtures such as alcohol(1) + alcohol(2) + hydrocarbon are to be calculated. If a model is to be successful for ternary and multicomponent mixtures, it should be consistent with models for all binary pairs (e.g., alcohol(1) + alcohol(2), alcohol(1) + hydrocarbon, alcohol(2) + hydrocarbon). Anderko (1989) demonstrated the effectiveness of Eq. 6 for several ternary systems containing components of different chemical nature. Therefore, it is believed that Eq. 6 is a better approximation than Eq. 5 when applied to multicomponent mixtures.

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Reply:

Regarding Dr. Anderko's comments on the approximate solutions used for the material balance expressions for a binary mixture of amphoteric components (components that have one acidic bonding site and one basic bonding site per molecule), we agree with most of his points, particularly the distinction he makes between the treatment of cross-association in the two derivations and the fact that there may not be sufficient experimental data to distinguish the models. We also agree with his statements about the apparent generality of his approximation for multicomponent mixtures. However, a clarification of the reasons for the conclusions made in our article is warranted.

In our article, chemical theory was used to account explicitly for hydrogen bonding interactions, and the resulting expressions were incorporated into the perturbed-anisotropic-chain theory (PACT). The resulting equation, the acid-base PACT (ABPACT), is a closed-form equation of state. For a binary mixture of amphoteric components, chemical theory reduces to the following expressions for the mole fractions of the monomers of the two components, W_1 and W_2, and the ratio of the true number of moles to the superficial number of moles, n_T/n_0:

$$x_1=\frac{W_1}{(1-a_1W_1)^2}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} i a_{12}W_1^iW_2^j \qquad (1)$$

$$x_2=\frac{W_2}{(1-a_2W_2)^2}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} j a_{12}W_1^iW_2^j \qquad (2)$$

$$\frac{n_T}{n_0}=\frac{W_1}{1-a_1W_1}+\frac{W_2}{1-a_2W_2}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}a_{12}W_1^iW_2^j \quad (3)$$

where x_1 and x_2 are the mole fraction of the two components, $a_1=K_1RT/v_0$, $a_2=K_2RT/v_0$, $a_{12}=\overline{K}(RT/v_0)^{i+j-1}$, K_1 and K_2 are the equilibrium constants for the self-association, $\overline{K}$ is the equilibrium constant for the solvation, and v_0 is the molar volume of the system. Equations 1 and 2 form a system of two algebraic equations with two unknowns, W_1 and W_2; n_T/n_0 can be obtained from Eq. 3 after Eqs. 1 and 2 have been solved. However, Eqs. 1 and 2 are nonlinear algebraic equations, and no analytic solution has been found yet. Since the numerical solutions of the two equations is computationally intensive, various approximate solutions have been proposed (Ikonomou and Donohue, 1988; Anderko, 1989).

Recently, Panayiotou (1990) proposed approximate expressions for W_1 and W_2 that are similar to the expressions proposed by Ikonomou and Donohue (1988) and Anderko (1990). However, his expression for n_T/n_0 is different due to an approximation he uses to decouple the infinite series of Eqs. 1 and 2.

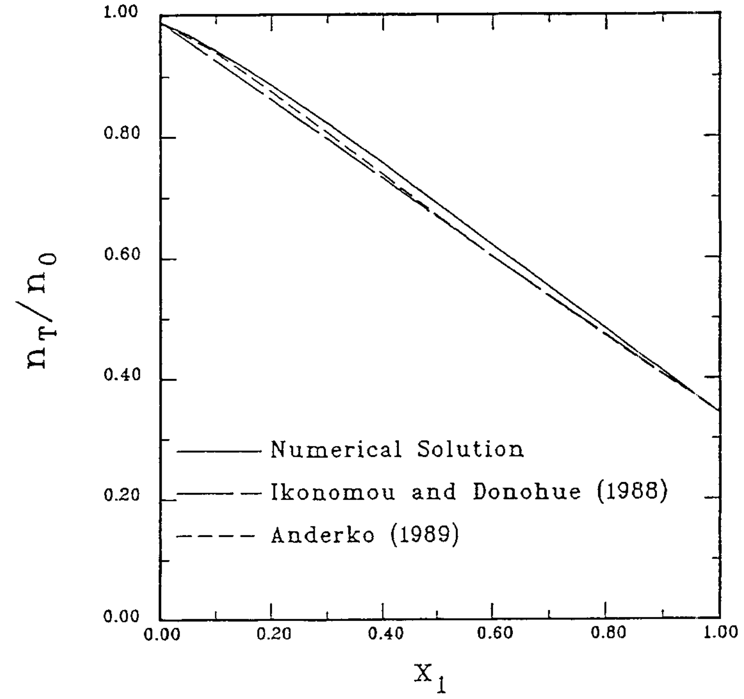

Figure 2. **n_T/n_0 vs. x_1 for a binary mixture of a strong amphoteric component and a weak amphoteric component from the numerical solution, the Ikonomou and Donohue approximation, and Anderko approximation.**

In Economou et al. (1990), we compared the approximate solutions of Ikonomou and Donohue (1988) and Anderko (1989) with experimental data. While the Anderko approximation is more appealing phenomenologically, the Ikonomou and Donohue approximation was found to be in better agreement with the experimental data than the Anderko approximation for the systems studied. Recently, Suresh and Elliott (1991) applied both approximations to their equation of state for associating components and also obtained the result that the Ikonomou and Donohue approximation was in better agreement with the experimental results for phase equilibria for most of the systems examined.

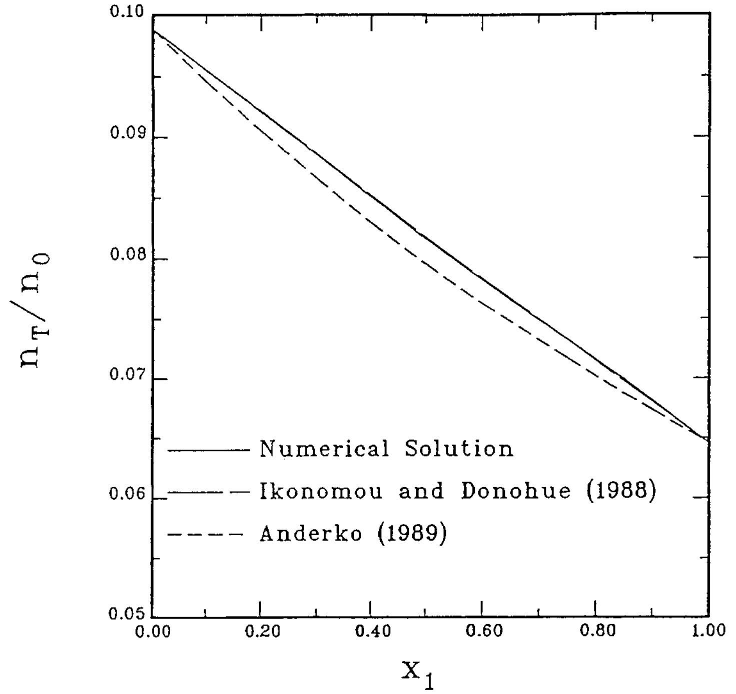

Figure 1. **n_T/n_0 vs. x_1 for a binary mixture of strong amphoteric components from the numerical solution, the Ikonomou and Donohue approximation, and Anderko approximation.**

Here, we examine only the hydrogen bonding expressions and we compare the two approximations with the numerical solutions for two hypothetical systems. In Figure 1, n_T/n_0 is plotted as a function of the mole fraction of component 1, x_1. In these calculations, K_1 is 0.56 and K_2 is 0.23 (these values correspond to the equilibrium constants for methanol and *i*-propanol at 25°C). RT/v_0 was set equal to 400 (this corresponds to a liquid-phase value for the volume at 25°C). As shown in Figure 1, Ikonomou and Donohue's approximation is almost identical with the numerical solution, whereas Anderko's approximation deviates somewhat from the numerical solution. Similar results also were obtained for W_1 and W_2. The differences between the two approximations result in the differences in phase equilibria calculations as shown in Figure 1 of Economou et al. (1990). Though there are advantages to the Anderko approximation, these results clearly show that the Ikonomou and Donohue approximation is better for this kind of mixture.

In Figure 2, K_1 is 0.56 and K_2 is 10^{-3}, so that component 2 is a very weak self-associating component. RT/v_0 was set equal to 10 corresponding to a vapor-phase value for the volume at 25°C. Note the difference in the scale of the Y-axis between the two figures. In Figure 2, although both approximations are in reasonable agreement with the numerical solution, Anderko's approximation is closer to the numerical solution. This is because as K_2 becomes lower, the system of the two amphoteric components eventually becomes an amphoteric-diluent mixture. For this type of mixture, Anderko's expression reduces to the exact analytic solution, whereas Ikonomou and Donohue's approximation does not. For an amphoteric-diluent mixture, however, the material balances can be solved analytically and no approximate solution is needed.

An important difference, however, between the two approximations is that only Anderko's approximation reduces to the analytic solution for the amphoteric-diluent system if one sets $K_2=\bar{K}=0$. As noted in his letter, this is important in multicomponent mixtures of alcohols and diluents where an approximate solution should describe correctly all the constituent binary systems. One, then, is faced with a choice as to which is most important in a multicomponent mixture containing amphoteric molecules and diluents. On the one hand, the approximation of Ikonomou and Donohue gives more accurate results for amphoteric-amphoteric binary mixtures. On the other, the Anderko approximation is more accurate for amphoteric-diluent binary mixtures. Though the Anderko approximation is more phenomenologically appealing, it is not apparent which will give better results.

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To the Editor:

In applying fractional Brownian motion (FBM) theory to a stochastic analysis of three-phase fluidized beds (**36**, p. 1528, October 1990), Fan et al. illustrated the reproducibility of the Hurst exponent by ten experiments, pertaining to Figure 8c, and repeated under identical experimental conditions (Table 3).

The mean of $H = 0.925$ with a standard deviation of 0.0428 is the figure of merit of reproducibility in the case of $U_g = 0.0129$ m/s and $U_\ell = 0.076$ m/s, with probe no. 2. In Figure 8b, we find $H = 0.96$ at the same U_g, but at $U_\ell = 0.056$ m/s.

Let us test the assumption that the measurements reported in Figures 8b and 8c are statistically indistinguishable, i.e., the hypothesis that the true mean of H is 0.96 in Figure 8c, against the counterhypothesis that the true mean is less than 0.96 (since the sample mean in Table 3 is 0.925). Assuming that the measurement errors are normally distributed with zero expectation, in the absence of any statement by the authors concerning their experimental error structure, the test statistic of the hypothesis is computed as $t = (0.925 - 0.960)/(0.0428/\sqrt{10}) = -2.586$. Given that the critical values of the T distribution are $-1.833(\alpha = 0.05)$ and $-2.821(\alpha = 0.01)$ at a degree of freedom of $10 - 1 = 9$, it follows that the hypothesis of the true mean in Table 3 being 0.96 can be rejected only at a significant, but not at a highly significant, level of confidence.

This finding raises the question whether, from other experiments reported without reproducibility information, one could expect that similar hypotheses made about the means of the Hurst exponent would not be found rejectable statistically even at a significant level of confidence and perhaps with uncomfortably high P values. If it were so, the reliability of this interesting and thought-provoking approach would be unfortunately in doubt.

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Reply:

To respond to Prof. Fahidy's comments on the statistical reproducibility of the Hurst exponent, H, in our article, "Stochastic Analysis of a Three-Phase Fluidized Bed: Fractal Approach" (Fan et al., 1990c), we quote directly from Ott (1984):

"The quantity

$$\frac{\bar{y} - \mu_0}{\frac{s}{\sqrt{n}}}$$

is called t-statistic, and its distribution is called the Student's t distribution or, simply, Student's t.

The quantity

$$\frac{\bar{y} - \mu_0}{\frac{s}{\sqrt{n}}}$$

will possess a t distribution only when the sample is selected from a normal population, . . ."

Only two statistics, the mean and standard deviation, but not the test of the population mean have been reported in our article because of the lack of information on the underlying distribution of H. To the best of our knowledge, this distribution is still unknown; our subsequent studies including simulation of the fractional Brownian motion (FBM) have indicated that H typically is not normally distributed. Nevertheless, it is appropriate to resort to a t test to verify the reliability of estimated H as done by Prof. Fahidy, since a slight deviation from normality would not affect the t test significantly; however, the procedure followed by him appears to be incorrect.

For Professor Fahidy's intended test,

if the measurements of our Figures 8b and 8c under the two different sets of operating conditions are statistically indistinguishable, the appropriate hypothesis should be

$$H_0:\quad \mu_1=\mu_2$$

$$H_a:\quad \mu_1\neq\mu_2$$

where μ_1 and μ_2 are the population means of H under the two different sets of operating conditions. Unfortunately, Table 3 in our article presents only the values of estimated H under one set of operating conditions, i.e., U_ℓ = 0.076 m/s, U_g = 0.0129 m/s, and probe no. 2 (Figure 8c); this makes it impossible to perform the above hypothesis test. Instead, a test can be performed to validate our claim that H = 0.93 for this set of operating conditions and the resultant data (Table 3). The corresponding set of hypotheses for a two-tailed test is mathematically represented as:

$$H_0:\quad \mu=0.93$$

$$H_a:\quad \mu\neq 0.93$$

Using the data from Table 3, the test statistic is computed as:

$$|t| = \left|\frac{0.925-0.930}{0.0428/\sqrt{10}}\right|$$

$$= |-0.3694| = 0.3694$$

With α = 0.05 and df = 9, the critical t value is 2.262. Consequently, we fail to reject the null hypothesis, H_0. This result exhibits the reproducibility or consistency of the estimation H under a given set of operating conditions. Similar results have been obtained under other sets of operating conditions, although they are not presented in our article.

Applications of the FBM theory in general and rescaled-range (R/S) analysis in particular to complex, multiphase flow systems, such as three-phase fluidized beds, are still in their infancy. Yet, we continue to obtain surprisingly meaningful or even useful results. For example, the FBM modeling and R/S analysis of pressure fluctuations in liquid-solid fluidized beds have yielded values of major frequencies that are in close accord with those resulting from the conventional spectral analysis (Fan et al., 1990a). Moreover, the flow regime or pattern transition implied by a sharp variation in the magnitude of H is in agreement with our visual observations; essentially, it also agrees quantitatively with that implied by similar variations in the magnitudes of the parameters recovered from the spectral analysis (Fan et al., 1990b). Even more surprising is the fact that the sharp variation in the magnitude of H is in parallel with variations in the magnitudes of different parameters measured totally independently in other liquid-solid fluidized beds (Kang et al., 1985, 1990).

Admittedly, much remains to be done with respect to the application of FBM-based analysis and modeling. Usually, the distribution of H is unknown or, at least, extremely difficult to determine. Regardless, it is our belief that analyzing and understanding the behavior of extremely complex systems, e.g., multiphase flow systems, require a full repertoire of approaches, some of which are more suitable, sensitive or practically useful than others in revealing different facets of the systems' behavior. The FBM-based approach, while not all-encompassing, definitely belongs to this repertoire of approaches meritorious under certain circumstances.

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To the Editor:

C. Erkey and A. Akgerman in a valuable article (**36**, p. 1715, November 1990) applied well-established tracer techniques to determine adsorption equilibrium constants and mass transfer coefficients at supercritical conditions. The final sentence of their article reads: "The technique can also be expanded to obtain the whole adsorption isotherm." It seems useful to point out that in general the moment method employed in the article is applicable only for first-order mass balances, for example, when the isotherm is linear. However, the complete isotherm then is not relevant since the equilibrium constant does not vary with concentration. When the isotherm is nonlinear, the moment method described by their Eqs. 1-4 is not applicable. In such cases, the usual method of obtaining the complete isotherm is by the numerical solution of the nonlinear mass conservation equations followed by a multivariable optimization procedure. This approach is time-consuming and often hazardous. Ramachandran and Smith (1978) have shown that there is another restricted method, based on deriving different, approximate moment equations. This method, which has been developed for slurry reactors, retains the simplicity of the procedure applicable when the isotherm is linear.

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Reply:

In the last sentence of our article, "The technique can also be expanded to obtain the whole adsorption isotherm," we intended to imply that dynamic tracer experiments can be conducted to obtain the whole isotherm (Erkey and Akgerman, 1990). It is true that Eqs. 1 to 4 are not applicable for the nonlinear isotherms.

We thank Professor Smith for pointing out that our concluding statement can easily be misinterpreted. It is possible to use the dynamic response technique to obtain nonlinear adsorption isomers by measuring the retention time of a pulse of different solute concentrations in the carrier fluid. Also, step responses of different concentrations can be used and the isotherms extracted from the breakthrough curves (Ruthven and Kumar, 1980; Ching et al., 1990). The technique is analogous to the method developed by Ramachandran and Smith (1978) that involves determination of the first moments at different gas concentrations in slurry reactors.

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