To the Editor:

Hseih and Rajamani, in their article titled "Mathematical Model of the Hydrocyclone Based on Physics of Fluid Flow" (May 1991, p. 735), have undertaken the formidable task of mathematically modeling classification of solid particles in a hydrocyclone. They used viscosity as modified by the presence of particles in modeling fluid flow and particle movement. This discussion of their contribution is restricted to matters concerning viscosity.

Use of viscosity adjusted to account for the local concentration of particles is appropriate in considering bulk flow through a hydrocyclone. In this regard, the experimental results represent flow conditions with viscosity either uniformly equal to that of the mother liquid (considered herein as water) or uniformly equal to a higher viscosity (in this case, that of a water-glycerol mixture). In operating hydrocyclones, bulk flow would be established by viscosity that varied positionally from that of water to that of the most concentrated suspension. Hence, the validating data do not represent conditions in operating hydrocyclones.

Use of viscosity modified in accordance with the local concentration of particles ordinarily seems inappropriate in modeling the movement of particles relative to the liquid. The drag force opposing radial movement of particles is caused by flow of interstitial liquid. In separations involving migration of a few large particles through a slurry of fine, nonseparating particles, the authors' assumption would approach reality, but only if the volume of the large particles contributed negligibly to the total local volumetric concentration of particles used in calculating modified fluid viscosity. When slurry gradation and hydrocyclone operation allow effective separation, however, the viscosity of the liquid causing drag forces on particles approaches that of water. In many applications, the fluid moving over particle surfaces would more closely resemble water than the bulk suspension. Whereas the authors concluded that increase in slurry viscosity due to particles dramatically increases the cut size and decreases the sharpness of separation, those effects would be absent when the fluid flowing relative to particles was essentially water.

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Reply:

Our article is concerned with the size classifying hydrocyclone, particularly about hydrocyclones processing very dilute (less than 10% by weight of solids) feed flow. We did this intentionally to avoid the difficulties that would arise with concentrated solid feeds in our first modeling work. Laser-Doppler measured velocities are shown both for water and water-glycerol mixture feeds. We did this just to be sure that our Navier-Stokes numerical solution predicted measured velocities for different viscosity fluids.

We agree with Richard Dick's comment that, in real hydrocyclones, viscosity varies spatially. Due to centrifugal force, particle separation occurs instantaneously, and hence there is spatial variation of concentration. Accordingly, the suspension viscosity varies with location. Current-day laser-Doppler instruments are used primarily for transparent fluid flows, and hence it is impossible to do these measurements in particle-laden suspensions.

For dealing with concentrated feed flows, one would need a model for distributing the solid concentration spatially consistent with the force balance on particles. This can be achieved using the particle tracking algorithm described in the article. Particle concentration is distributed in proportion to the residence time of a particle of a given size at a particular mesh point. Then, the Navier-Stokes equation set must be solved iteratively until the two models converge. Indeed, our future work would take this course.

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To the Editor:

I would like to comment on the article titled "Supercritical CO2 Extraction of Organic Contaminants from Aqueous Streams" by Ghonasgi et al. (June 1991, p. 944).

The authors utilized the Carnahan-Starling-DeSantis-Redlich-Kwong (CSDRK) EOS with the molecular volume b dependent on temperature. Criteria of the temperature-dependent term on b from van der Waals-type equations of state were well documented by Salim and Trebble (1991), and the following discussion is an extension of the criteria to Carnahan-Starling-type equations of state. Considering only the repulsive term of the equation, we can summarize some essential formula as follows:

$$\left(\frac{\partial P}{\partial T}\right)_V = P \left(1 + \frac{2RT}{V}\right) b^\ast \Gamma_1$$

$$C_v - C_v^* = -4RT \left(1 - \frac{b^*}{b}\right) \Gamma_2$$

$$-2RT^2 \left(1 - \frac{b^*}{b}\right)^2 \left(\frac{b}{b^*}\right)^3 \Gamma_2$$

$$-2RT^2 \left(1 - \frac{b^*}{b}\right)^2 \left(\frac{b}{b^*}\right)^2 \Gamma_1$$

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To the Editor:

In the R&D note titled "Determination of Arrhenius Constants by Linear and Nonlinear Fitting," Chen and Aris (April 1992, p. 626) discussed procedures for fitting the nonlinear Arrhenius function to experimental data. They correctly warn that linearization of nonlinear functions for the purpose of mathematical convenience has pitfalls associated with it. In the study of chemical kinetics, nonlinear relationships abound and so the warning is most appropriate. The authors conclude that the use of nonlinear least-squares estimation will produce more accurate estimates of parameters in the Arrhenius equation. This conclusion is, however, true only under certain circumstances.

Normal least squares produces optimal estimates of parameters when the error variance of each measurement is constant, a logarithmic transformation of the function produces the correct weighting for normal least-squares analysis. When fitting a function to observations in which the relative error of the measurements is nearly constant, a logarithmic transformation of the function produces the correct weighting for normal least-squares analysis.

As 0 < \xi < 1, \Gamma_1 and \Gamma_2 are obviously positive-definite. The first criterion of thermodynamic consistency is:

\[
\left( \frac{\partial P}{\partial T} \right)_V > 0
\]  

and will surely be fulfilled if \( b' \geq 0 \). The second and third criteria:

\[
C_p > 0
\]

must be fulfilled either if \( b'' \) is strongly negative for positive \( b' \) or if \( b'' \) is zero when \( b' \) is zero.

Removal of temperature dependence from the molecular volume must guarantee the above thermodynamic consistency, while the term in cubic polynomial of temperature used by the authors must be used very cautiously.

Literature cited


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To the Editor:

In the article titled "Kinetics of COS with Primary and Secondary Amines in Aqueous Solutions" (February 1992, p. 244), Littel et al. presented data for the reaction between COS and aqueous solutions of primary and secondary amines including diglycolamine (DGA). Analyzing their experimental data, they have found that the observed pseudo-first-order reaction rate constant \( k_{\text{obs}} \) is a nonlinear function of amine leading to a fractional order between 1 and 2. To explain this behavior they proposed the fol-
lowing zwitterion mechanisms in an analogous manner to the reaction of carbon dioxide:

$$\text{COS} + R_2\text{NH} \rightarrow R_2\text{NH}^+\text{COS}^- \quad (1)$$

$$R_2\text{NH}^+\text{COS}^- + B \rightarrow R_2\text{N}^-\text{COS}^- + BH^+ \quad (2)$$

Similar results were reported by Alper (1989) at the AIChE meeting. He presented stopped flow data for the reaction between COS and aqueous primary/secondary amines, ethanol (trade name diglycolamine, aminoethyl-ether or 2-(2-aminoethoxy) ethanol) at 278, 288 and 298 K. Figures 3–5 of his presentation, in which values of $k_{app}$ had been plotted against amine concentration, showed clearly that the overall order in DGA was between 1 and 2. To explain the fractional orders, the author has already proposed the same zwitterion mechanism for COS too (that is, the reactions as given by Eqs. 1 and 2 where $B$ could be any base, such as water, OH$^-$ or amine itself).

Littel et al. (1992) cite somehow erroneous data of Singh and Bullin (1988) for DGA, but do not refer to the data of Alper (1989). Table 2 of Alper (1989) compares the previously published data at 1 kmol/m$^3$ DGA concentration, which are reproduced here in Table 1 by including also those of Littel et al. (1992). The latter is calculated using Eq. 9 of Littel et al. (1992), and Figure 1 compares the results of these calculations with the raw data of Alper (1989) for other DGA concentrations. The agreement is very reasonable.

In short, the idea of a two-step zwitterion mechanism for COS leading to fractional order in amine has already been confirmed by Alper (1989) before, and the data presented for DGA by Littel et al. (1992) agreed well with this prior literature.

### Literature cited


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**Table 1. Apparent Rate Constants at 1 kmol/m$^3$ DGA Concentration**

<table>
<thead>
<tr>
<th></th>
<th>$k_{app}$ (s$^{-1}$)</th>
<th>$T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alper (1989)</td>
<td>11</td>
<td>298K</td>
</tr>
<tr>
<td>Singh &amp; Bullin (1988)</td>
<td>2.3</td>
<td>300 K</td>
</tr>
<tr>
<td>Rahman (1984)</td>
<td>166</td>
<td>300 K</td>
</tr>
<tr>
<td>Littel et al. (1992)</td>
<td>15.3</td>
<td>298 K</td>
</tr>
</tbody>
</table>

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**Figures**

- Figure 1. Comparison between the data of Alper (1989) and Littel et al. (1992).
  (Lines refer to Eq. 9 of Littel et al., 1992.)

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**Reply:**

In his letter, Alper refers to work presented by him at the 1989 AIChE meeting, in which stopped flow data for the reaction between COS and aqueous DGA at 278, 288 and 298 K were discussed.

Regretfully, we have not been aware of his work presented at the AIChE meeting; however, it should be noted that work presented at such a meeting, which is not subsequently submitted and published in a journal, is not readily accessible and therefore is quite easily overlooked. We regret this omission all the more, because the Alper data and our data are in very satisfactory agreement and even complement each other very nicely to cover a temperature range from 278 K to 318 K.

In his paper, which has been now made available to us, he mentions a "two-step mechanism involving a zwitterion intermediate as one possible mechanism" to explain the kinetic experiments for COS with aqueous DGA (his conclusion). In his letter, he suggests to have been the first to propose a zwitterion mechanism for the reaction between COS and aqueous primary/secondary amines, whereas he incorrectly asserts that this claim has been put forward by us. A zwitterion intermediate for the cleavage of monothiocarbamates (the reverse of the reaction of COS with amine) has already been described by Ewing et al. in 1980. Actually reaction 2 in this paper presents a zwitterion reaction mechanism. The work of Millican et al. confirms and extends the work of Ewing et al. which was published in 1983. Both references have been cited in our article and are, to the best of our knowledge, the first description of a zwitterion reaction mechanism for the reaction between COS and aqueous primary/secondary amines. In our article, we provide additional strong evidence that this reaction mechanism is indeed valid with special emphasis on amines and reaction conditions of industrial interest.

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