LETTERS TO THE EDITOR

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 CO_2 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:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T} + \left(\frac{2RT\xi}{V}\right)\left(\frac{b'}{b}\right)\Gamma_1 \quad (1)$$

$$C_\nu - C_\nu^* = -4RT\left(\frac{b'}{b}\right)\Gamma_2 - 2RT^2\left(\frac{b''}{b} - \left[\frac{b'}{b}\right]^2\right)\Gamma_2 - 2RT^2\xi\left(\frac{b'}{b}\right)^2\Gamma_1 \quad (2)$$

$$C_p - C_p^* = C_v - C_v^* + R\frac{\left(\frac{P}{RT}+\frac{Tb'}{2V^2}\Gamma_1\right)^2}{\frac{P}{VRT}+\left(\frac{b}{2V^3}\right)\Gamma_1} - R \qquad (3)$$

where

$$b' = \frac{db}{dT} \qquad (4)$$

$$b'' = \frac{d^2b}{dT^2} \qquad (5)$$

$$\xi = \frac{b}{4V} \qquad (6)$$

$$\Gamma_1 = \frac{2+2\xi-\xi^2}{(1-\xi)^4} \qquad (7)$$

$$\Gamma_2 = \frac{2\xi-\xi^2}{(1-\xi)^3} \qquad (8)$$

As $0<\xi<1$, Γ_1 and Γ_2 are obviously positive-definite. The first criterion of thermodynamic consistency is:

$$\left(\frac{\partial P}{\partial T}\right)_V > 0 \qquad (9)$$

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

$$C_p > 0 \qquad (10)$$

$$C_v > 0 \qquad (11)$$

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 b term in cubic polynomial of temperature used by the authors must be used very cautiously.

Literature cited

Salim, P. H., and M. A. Trebble, "A Modified Trebble-Bishnoi Equation of State: Thermodynamic Consistency Revisited," *Fluid Phase Equilib.*, **65**, 59 (1991).

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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 the same. If the variance of the measurements changes with the magnitude of the quantity being measured, then weighted least squares must be used to account correctly for the degree of certainty associated with each measurement. For example, nonuniform variance is usually observed when data are generated by gas chromatography—an analytical technique common in the study of chemical kinetics. Typically such measurements exhibit an error structure in which the *relative* error of the measurements is nearly constant. The parameter estimation problem is then correctly treated by weighting the observations explicitly in the parameter estimation routine or by transforming the fitted function into a variable space which produces the correct weighting for normal least-squares analysis.

When fitting a function to observations in which the relative error of the measurements is constant, a logarithmic transformation of the function produces the correct weighting for obtaining optimal parameter estimates. Thus, a log-linear fit of the Arrhenius expression to kinetic data is very often statistically advantageous compared to the nonlinear fit. From a historical perspective, the convergence of mathematical convenience and statistical correctness in the log-linear fit under such circumstances is fortuitous, but the point is that no one strategy is inherently "correct" for fitting nonlinear functions. The error structure of the measurements must be a central concern if the optimal parameter estimates are to be obtained.

The results presented by Chen and Aris in Table 1 of their note show that the nonlinear fit of the Arrhenius function produced a residual equal to 36% of the measurement for the data obtained at 30°C. In kinetic studies carried out in the gas phase, gas chromatography typically gives results with substantially greater precision than this. If the residuals presented in Table 1 of Chen and Aris are plotted as both absolute and relative errors, it becomes evident that the "relative residuals" are better behaved for the log-linear fit while the absolute residuals are better behaved for the nonlinear fit. Thus, it is incumbent on the scientist to appraise the appropriateness of optimizing the absolute or relative magnitude of model residuals. The "accuracy" of the parameter estimates depends on identifying correctly the error structure inherent in the experimental data.

The general availability of sophisticated parameter estimation software makes it inappropriate to linearize mathematical models simply for the sake of convenience in parameter estimation. In general, however, parameter estimation should be performed in recognition of the error structure inherent in the experimental data. In a great many instances (kinetic data based on gas chromatography, for example), the use of normal least squares on the linearized Arrhenius function is the appropriate treatment for obtaining optimal parameter estimates.

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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_{app}) is a nonlinear function of amine leading to a fractional order between 1 and 2. To explain this behavior they proposed the fol-

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

	k_{app} (s^{-1})	T
Alper (1989)	11	298K
Singh & Bullin (1988)	2.3	300 K
Rahman (1984)	166	300 K
Littel et al. (1992)	15.3	298 K

lowing zwitterion mechanisms in an analogous manner to the reaction of carbon dioxide:

$$COS + R_2NH \Leftrightarrow R_2NH^+COS^- \quad (1)$$

$$R_2NH^+COS^- + B \Leftrightarrow R_2NCOS^- + BH^+ \quad (2)$$

Similar results were reported by Alper (1989) at the AIChE meeting. He presented stopped flow data for the reaction between COS and aqueous β, β'-hydroxy-aminoethyl-ether or 2-(2-aminoethoxy) ethanol (trade name diglycolamine, DGA) 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) agree well with this prior literature.

Literature cited

Alper, E., "Reaction Kinetics of Carbonyl Sulphide with Aqueous Diglycolamine by the Stopped Flow Technique," Paper No. 56F, *Gas Processing Fundamentals I*, AIChE Meeting, Houston (Apr. 2-6, 1989).

Rahman, M. A., "Study of Reactions of CO_2 and Sulfur Containing Compounds with Ethanolamines," PhD Thesis, Oklahoma State Univ. (1984).

Singh, M., and J. A. Bullin, "Determination of Rate Constants for the Reaction Between Diglycolamine and Carbonyl Sulfide," *Gas Sep. & Purif.*, **2**, 131 (1988).

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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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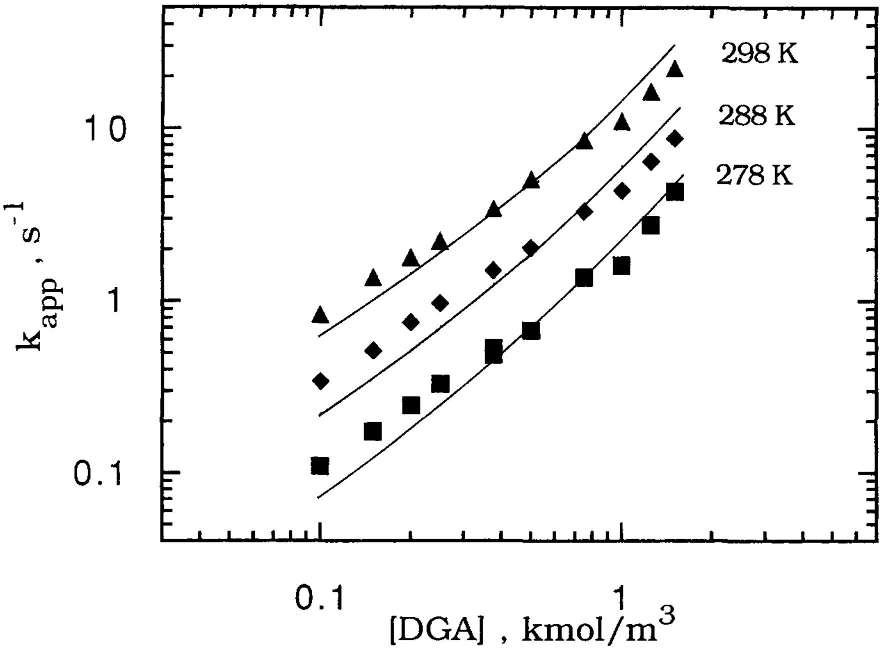

Figure 1. Comparison between the data of Alper (1989) and Littel et al. (1992).
(Lines refer to Eq. 9 of Littel et al., 1992.)