readily apparent to attendees at the International Drying Symposia. Some areas where there has been considerable recent activity but are not represented much in the book, are:

1. mathematical modeling of spray-air dynamics and of the resultant quantitative drying characteristics,
2. measurement and analysis of transport processes involved in the falling-rate period of drying, in the loss or retention of volatile flavor and aroma substances, and in thermal degradation,
3. description and interpretation of the factors governing changes in particle size and shape during spray drying, starting with the studies of Verhey in the early 1970's.

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LETTERS TO THE EDITOR

To the Editor:

Tanmoy Chakravarty, C. W. White, III, and W. D. Seider in their R&D Note in the *AIChE Journal* [31(2), 316(1985)] comment on the three liquid phases of the system ethylene glycol (1)/lauryl alcohol (2)/nitromethane (3) that was studied by Francis (1956) as well as by Gautam & Seider (1979). In this R&D Note Chakravarty et al. state: "In 1979 Gautam and Seider used the Rand method and a new algorithm for phase splitting to compute the compositions at equilibrium for a mixture of 40 mol % of ethylene glycol, 30% lauryl alcohol and 30% nitromethane at 295 K and 1.013 bar (1 atm). The extended Van Laar equation was used with the interaction coefficients for the binary pairs determined by Null (1970) who fit the experimental data of Francis (1956) with three liquid phases at equilibrium."

According to Chakravarty et al. (1985), Null (1970) used extended Van Laar equation to represent the experimental data of Francis (1956) for the ethylene glycol/lauryl alcohol/nitromethane system at 295 K and 1.013 bar (1 atm) and obtained the interaction coefficients in Table 2. See Table 1 in this letter which gives three liquid phases with compositions (plotted in Figure 1) that show poor agreement with the experimental data of Francis, especially for the phase concentrated in lauryl alcohol. Null's Figure 6.17 shows a mistakenly good comparison, but unfortunately, the calculated compositions are mole percents and were not converted to weight percents when plotted with the experimental data.

Chakravarty et al. have corrected this mistake, but another mistake seems to remain. The calculation procedure used in their R&D Note is similar to Null's in the sense they start with a liquid mixture which is split into three liquid phases. This feed mixture was 40 mol % of (1), 30% (2) and 30% (3) in Null's work as well as in Gautam and Seider (1979) and in their R&D Note. We plotted this as point F on Figure 1. Observe that this feed is not within the triangle defined by the three experimental liquid phases, although it is within the triangles calculated from the parameters of Null and from Chakravarty et al. It is impossible for this feed to be split into the three experimental liquid phases, unless a negative value for the amount of one of the phases at equilibrium was obtained allowing the material balances to be solved.

Analyzing the parameters used by the different authors for this system, it should be stated that according to Null, "The constants for the binary Van Laar equations were obtained from the mutual solubilities, as indicated on the plots given by Francis." Obviously Null predicts the

Table 1. Van Laar binary parameters and calculated compositions of the three liquid phases at equilibrium of the system ethylene glycol (1)/lauryl alcohol (2)/nitromethane (3).

	Null (1970) (From mutual solubility data)		Chakravarty et al. (1985) (From three liquid phases and mutual solubility data)		Ruiz and Marcilla (From mutual solubility data)		Ruiz and Marcilla (From three liquid phases data)	
a_{12}	1.496		−0.8904		1.218		−1.212	
a_{13}	4.588		3.501		3.211		3.126	
a_{21}	3.16		7.51		4.819		14.264	
a_{23}	4.68		2.655		4.684		2.135	
a_{31}	1.593		1.594		1.829		1.593	
a_{32}	2.878		2.457		2.715		2.852	
	mol % (3)	mol % (2)	mol % (3)	mol % (2)	mol % (3)	mol % (2)	mol % (3)	mol % (2)*
	98.13	0.86	92.88	2.66	93.17	0.77	89.54	1.35
	27.26	3.45	32.42	0.79	27.67	0.76	34.74	2.07
	9.56	72.00	23.55	37.19	11.00	65.49	24.50	30.51

*This calculated composition coincide with the Francis experimental data.

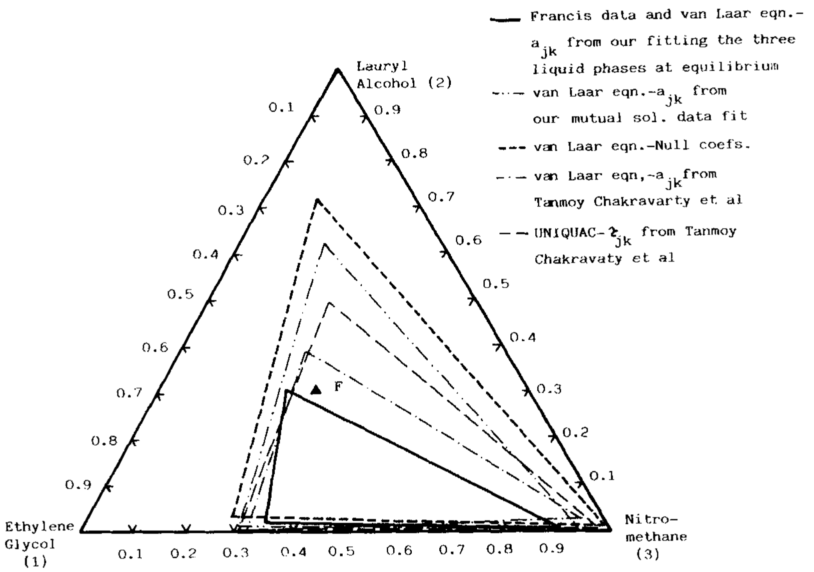

Figure 1. Figure 2 from Chakravarty et al. (1985), including the feed F, and the compositions calculated in this letter.

composition of the three liquid phases at equilibrium using the feed mixture already indicated. We say prediction, because the calculated compositions for the three liquid phases at equilibrium in the ternary system were not used to calculate the parameters. The predicted compositions for the three liquid phases are rather different from the experimental data in Table 1. On the other hand, Null's parameters seem to be obtained by interpolation from Table 6.1 of Null's book, but not from fitting the experimental data of Francis. We fit these mutual solubility data and obtained the parameters shown in Table 1, which are significantly different from those reported by Null. It can be seen in Figure 1 that prediction with these parameters is better than that obtained with Null's parameters.

Chakravarty et al. state: "In an attempt to obtain better agreement, we fit the data while biasing the concentrations of the phase concentrated in lauryl alcohol and holding $c_{jk} = 0$ and $E_j = 0$, but without significant improvement. Then, we added the mutual solubility data for the binary pairs and obtained much better agreement, Figure 2. However, a negative interaction coefficient is introduced, Table 2." It seems that in the first calculation stage they used only the data for the three liquid phases at equilibrium to calculate the parameters, but without success. Secondly, they biased the concentration of the phase concentrated in lauryl alcohol, with no improvement, and finally added the mutual solubility data for the binary pairs and obtained much better agreement. However, their calculated compositions are quite different from the experimental compositions. We believe that it is possible to be successful in the first calculation stage.

Indeed, we obtained the Van Laar interaction parameters for the binary pairs by fitting the three liquid phases at equilibrium and solving the system of six equations with six unknowns, the a_{12}, a_{13}, a_{21}, a_{23}, a_{31}, and a_{32} binary interaction coefficients:

$$\begin{aligned}
\gamma_1^I x_1^I - \gamma_1^{II} x_1^{II} &= 0 \\
\gamma_1^I x_1^I - \gamma_1^{III} x_1^{III} &= 0 \\
\gamma_2^I x_2^I - \gamma_2^{II} x_2^{II} &= 0 \\
\gamma_2^I x_2^I - \gamma_2^{III} x_2^{III} &= 0 \\
\gamma_3^I x_3^I - \gamma_3^{II} x_3^{II} &= 0 \\
\gamma_3^I x_3^I - \gamma_3^{III} x_3^{III} &= 0 \qquad (1)
\end{aligned}$$

where γ_i^P is the activity coefficient of the component i in the phase P and x_i^P the mole fraction of the component i in the phase P. Obviously, the three material balances ($\Sigma x_i^P = 1, P = I, II, III; i = 1, 2, 3$) have been combined with (1). The system (Eq. 1) was solved for the parameters by a simplex method.

On the other hand, when the binary interaction coefficients are fixed, the system of Eq. 1 can be solved for the six unknowns x_i^P. Obviously, if the binary interaction parameters are obtained by fitting the three liquid phases at equilibrium, the calculated mole fractions at equilibrium are indentical to the experimental ones, since the system of six equations (Eq. 1) with six unknowns is fully determined. Table 1 shows results from our correlation that are indentical to the experimental data. The parameters of Chakravarty et al. are very close to our parameters. Why were they not successful in their first stage calculation? We think at this calculation stage they obtained the same set of Van Laar parameters we obtained, but a negative amount of one of the phases at equilibrium appeared when using such parameters in order to recalculate the compositions of the three liquid phases into which mixture F was split. Remember that the feed used by them is outside the triangle defined by Francis's data and by the corresponding Van Laar parameters calculated from Eq. 1. Consequently, in their final calculation stage they slightly modified the parameters by introducing the mutual solubility data in order to obtain a triangle, defined by these new parameters, including the wrongly chosen F point in Figure 1. In our calculation procedure we do not use feed split into three liquid phases. When using such methods, care should be taken in choosing an appropriate feed within the experimental triangle.

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Reply:

The principal objective of our R&D Note was to explain the unusual iteration history of the Gibbs free energy observed by Gautam and Seider (1979) just prior to the publication of their manuscript. In seeking an explanation, most of the calculations were for mixture F (40 mol % ethylene glycol, 30% lauryl alcohol, and 30% nitromethane), one of 50 feed mixtures selected by Gautam and Seider (1979) to fall within the region of three liquid phases, as computed by the extended Van Laar equation with the binary interaction coefficients presented by Null (1970). Sometime later, Chakravarty et al. (1985) discovered (1) the thermodynamic inconsistency of the extended Van Laar equation and its relationship to the iteration history of the Gibbs free energy, (2) the mistakenly good comparison between the computed and experimental compositions in Figure 6.17 of Null (1970), and (3) the location of mixture F outside the experimentally determined region of three liquid phases.

In our R&D Note, Mixture F was retained because the bulk of calculations were for this mixture and because the impact of thermodynamic inconsistency on the minimization algorithm could be illustrated for this mixture, as well as any other mixture in the three-phase region given by the extended Van Laar equation with Null's interaction coefficients. To emphasize the importance of improving the agreement with the experimental data, we demonstrated that a significantly better fit could be obtained.

Unfortunately, this has contributed to the confusion of Ruiz and Marcilla and possibly to the confusion of others. This would have been avoided had we presented results for a feed mixture within the experimentally determined region of three liquid phases.

Ruiz and Marcilla present an exact fit of the data. For systems that can exhibit three liquid phases, their method (solution of Eq. 1) may be preferred to our unstated method of minimizing a weighted-sum-of-the-squares of the differences between calculated and experimental distribution coefficients. It is noteworthy that they, likewise, computed a negative a_{12} and show comparable values for the other interaction coefficients. Most important, however, is that their mistaken inference be corrected. Mixture F did not enter into the determination of our binary interaction coefficients. The calculated distribution coefficients were computed as the ratio of the liquid phase activity coefficients, evaluated at the experimental compositions of the three liquid phases at equilibrium and of the two liquid phases when mutual solubility data of the binary pairs was added.

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To the Editor:

In "Cluster Diffusion in Liquids" [*AIChE J.* **26**(1), 43 (1980)], Cussler has shown that in concentrated nonideal solutions an equation of the form

$$D_{AB} = D_o \times \left\{ \frac{1}{1 + \frac{K}{X_A X_B}\left[\left(\frac{\partial \ln X_A}{\partial \ln a_A}\right)_{T,P} - 1\right]} \right\}^{1/2} \qquad (1)$$

is quite successful in predicting the composition variation of binary liquid diffusion coefficients. However, a wrong value of 0.5 was found for *K* by Cussler on comparison of Eq. 1 with experimental data of five nonideal binary liquid systems. A close examination of his Figure 6 indicates that *K* is of the order 0.3. It is important to note this error since the value of *K* has been presented as a major conclusion of Cussler's work.

If Eq. 1 is valid, the slope of a plot of

$$\log\left[(D_o/D_{AB})^2 - 1\right] \quad \text{versus}$$

$$\log\left\{\frac{1}{X_A X_B}\left[\left(\frac{\partial \ln X_A}{\partial \ln a_A}\right)_{T,P} - 1\right]\right\}$$

should be one and the intercept should be equal to *K*. In an attempt to verify Eq. 1, Figure 1 is prepared using the original sources of data of the five systems considered by Cussler and data for two additional nonideal systems (acetone-water and ethanol-water). Diffusion data for acetone-water has been published by Tyn and Calus (1975) and data for phase equilibria reported by Prausnitz et al. (1980). Similarly, diffusion and phase

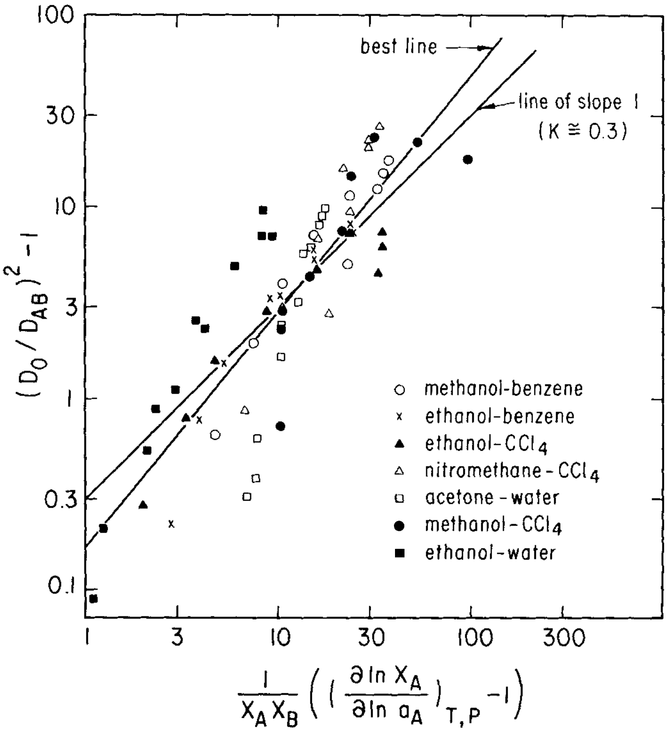

Figure 1. Variation of the diffusion coefficient with composition in some nonideal solutions (all diffusion data at 298 K).

equilibrium data for ethanol-water is available in Hammond and Stokes (1953). In the preparaton of Figure 1, in order to cover the whole composition range, the mole fraction of component A is varied from zero to one with an increment of 0.1. In the case of ethanol-water and acetone-water two additional data points, one smaller than a mole fraction of 0.1 and one larger than a mole fraction of 0.9, are included.

An examination of Figure 1 indicates that the scatter of the data is much larger than that shown in Figure 6 of Cussler's work. Furthermore, a line of slope one forced to the data points yields a value of $K = 0.3$ and is not the best line. The best line as calculated by the regression analysis has a slope $m \simeq 1.23$ and $K \simeq 0.17$. Even then, the scatter of the data from the best line is significant. This finding suggests that an equation of the form

$$\frac{D_{AB}}{D_o} = \left\{ \frac{1}{1 + K\left[\frac{1}{X_A X_B}\left(\frac{\partial \ln X_A}{\partial \ln a_A}\right)_{T,P} - 1\right]^m} \right\}^{1/2} \qquad (2)$$

may be more appropriate.

The data of the systems considered in this work, when taken separately, yield widely different values for m and K. Therefore it seems that use of Eq. 1 or Eq. 2 with universal constants is quite questionable.

Notation

a = activity
D_o = reference value of the diffusion coefficient, $(D^o_{AB})^{X_B}(D^o_{BA})^{X_A}$
D_{AB} = mutual diffusion coefficient
D^o_{AB} = mutual diffusion coefficient for infinitely dilute A
D^o_{BA} = mutual diffusion coefficient for infinitely dilute B
K = constant in Eq. 1 and Eq. 2
m = exponent in Eq. 2
P = pressure
T = temperature
X = mole fraction

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