LETTERS TO THE EDITOR

To the Editor:

APPLICATION OF h-TRANSFORMATION TO MULTICOMPONENT ADSORPTION IN FIXED BEDS

Your journal recently published a paper by Tien, Hsieh, and Turian [*AIChE J.* 22, 498 (1976)], which analyzes the application of the *h*-transformation to multicomponent Langmuir adsorption in fixed beds, a method worked out by us some time ago (Helfferich and Klein, 1970). In their paper, the authors present a detailed numerical example, and we appreciate their thus focussing attention on our method. However, we cannot agree with some of their conclusions, and feel that a few clarifying remarks will be helpful in this context.

The method is designed for multicomponent systems with interdependent sorption equilibria that make standard chromatographic theory inapplicable. The *h*-transformation transforms the concentrations c_i and q_i in the mobile and stationary phases into new variables h_i. All quantities of interest are then readily calculated from algebraic expressions involving the h_i and equilibrium data. The transformation is applicable to stoichiometric ion exchange with constant separation factors, and the issue debated here is the extension to nonstoichiometric sorption following a generalized, multicomponent Langmuir isotherm. The essence of the extension is the proof that an *n*-component, nonstoichiometric Langmuir system is mathematically equivalent to an $(n + 1)$-component stoichiometric ion exchange system. The proof adds a ficticious, $(n + 1)$th species to the Langmuir system in such a way that it makes up for the deviations from stoichiometric exchange, and then proceeds to establish equivalence and derive the conversion equations needed to calculate the fixed-bed behavior of the Langmuir system from the previously established solutions for the ion exchange system. The conversion involves a normalization factor R (symbol ξ used in the paper by Tien et al.), defined as the ratio of the total concentrations in the stationary and mobile phases in the equivalent stoichiometric system (including the fictitious species; see Eq. 5-30 in our book):

$$R = \sum_{i=1}^{n+1} q_i \Bigg/ \sum_{i=1}^{n+1} c_i \tag{1}$$

Stoichiometry of exchange assures that the total concentrations in both phases, Σq_i and Σc_i, remain constant, but leaves the choice of R for the Langmuir system open because the concentrations of the fictitious species need not match any specified values. We have thus stated that the choice of R is arbitrary (although some choices entail negative concentrations of the fictitious species and may therefore be objectionable on esthetical grounds, even if entirely acceptable mathematically). Tien et al. conclude that the choice is not arbitrary, and proceed to suggest a procedure for finding "correct" values of R. Tien et al. find that different choices of R, while not affecting the calculations of concentrations in the bed, give different values for the bounds of the zones within which the concentrations exist. They express bounds in terms of Vermeulen's throughput parameter T, and find T to be inversely proportional to R, an observation with which we entirely agree. However, what is overlooked here is that the choice of R automatically generates the units of measure for T. Different choices of R thus give rise to different numerical values of T for a given bound, although they do not affect the position calculated for the bound in terms of the physical variables, distance and time.

The mathematical relations are as follows. Our approach uses adjusted, normalized velocities v instead of throughput parameters T. The two are related by $1/v = T$ (see Eq. 4-42 in our book). The conversion from adjusted, normalized velocities v to actual physical velocities u (say, in cm/s) is

$$u = \frac{u_o}{1 + (1/v)\Sigma q_i/\Sigma c_i} \tag{2}$$

where u_o is the velocity of mobile phase flow (see Eq. 2-20 in our book). With Eq. (1) above and substitution $1/v = T$, Eq. (2) reduces to

$$u = \frac{u_o}{1 + TR} \tag{3}$$

As Tien et al. have noted, our method yields values of T that are inversely proportional to R. This is as it should be: Eq. (3) above demonstrates that only the product TR, which is invariant to the choice of R, enters into the calculation of a bound in terms of physical variables.

Seen in this light, the procedure suggested by Tien et al. to find "correct" values of R becomes superfluous, as any value of R will do. Their procedure involves a comparison with a solution derived earlier by Glueckauf (1946), in order to select R so that the numerical values of the bounds in both approaches become equal. What this amounts to is merely a calculation of the normalization factor inherent in Glueckauf's slightly different approach.

We may perhaps be faulted for not having reiterated the conversion from adjusted, normalized to true velocities in the extension of our approach to Langmuir systems, and not having given a sample calculation, and we are grateful to Tien et al. for bringing this point to attention. However, we believe to have refuted the claim that our procedure gives multiple solutions, and to have shown the extension suggested by Tien et al. to be superfluous. Needless to add, we share their hope that this profitable discussion will help to draw attention to the use of the *h*-transformation as a powerful method.

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LITERATURE CITED

Glueckauf, E., "Contribution to the Theory of Chromatography", Proc. Roy. Soc. (London), A 186, 35 (1946).

Helfferich, F., and G. Klein, "Multicomponent Chromatography", Marcel Dekker, *New York, 1970.*

Tien, Chi, J. S. C. Hsieh, and R. M. Turian, "Application of *h*-Transformation for the Solution of Multicomponent Adsorption in Fixed Bed, *AIChE J.*, **22**, 498 (1976).

Reply:

In our paper on the use of the h-transformation for the solution of multicomponent adsorption in fixed beds [*AIChE J.*, **22**, 498 (1976)], the throughput parameter, T, is defined as

$$T = \frac{(V - \epsilon v) \sum_{i=1}^{n} c_{i_{in}}}{v\rho \sum_{i=1}^{n} (q_{i_{in}})} \text{ [†]}$$

which is consistent with the definitions used for single solute systems. It is based on this definition that we concluded that ξ, the transformation parameter, cannot be chosen arbitrarily and developed procedures for determining the transition bounds. While these procedures may be viewed as less elegant from strict mathematical considerations and even as superfluous as contended by Helfferich and Klein, it has the practical advantage of being simple to follow and easy to apply. This is substantiated by the response we have received since the publication of the paper.

Another advantage of our method is that the procedures developed can be easily adapted to cases where the adsorbents are initially of various degrees of saturation; a point which was not discussed by Helfferich and Klein in their original work (1970) as well as in their more recent communication.

The formulation of the h-transformation method represents a significant advance in the development of fixed bed multicomponent adsorption theory. Unfortunately this method, up to now, has only found limited application by practical engineers largely because of its mathematical abstraction. In order to gain a wider acceptance, it is essential to recast the method on a basis which is conceptually easy to follow, which is the principal objective of our paper.

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Tien, Chi, Hsieh, J. C. S. and Turian, R. M., "Application of h-Transformation for the solution of Multicomponent Adsorption in Fixed Bed," *AIChE J.*, **22**, 498 (1976).

Helfferich, F., and Klein, G., "Multicomponent Chromatography—Theory of Interference," Marcel Dekker, New York (1970).

To the Editor:

With reference to the "An Empirical Method for Evaluating Critical Molar Volumes" by Alessandro Vetere, [*AIChE J.*, **22**, 950 (1976)], we have tried to put the correlation to use in our organisation and have the following comments to offer:

1) There appears to be an error in Equation (6). The % errors for acids and ketones are found to be 3.4 and 4.1 respectively.[*] These reduce to 2.2 and 2.8 if Equation (6) is read as

$$V_c = 33 + (\underset{i}{\Sigma} \Delta v_i M_i)^{1.029}$$

A similar conclusion can be drawn with other classes of compounds.

2) A comparison of error estimates for acids, ketones and ethers has been made[*] using the correlation and the Lydersen method, recommended by Reid and Sherwood[†]. It can be noticed that the latter method gives deviations which are lower than values obtained by the correlation. A similar trend is noticed for other classes of polar substances.

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To the Editor:

With reference to the letter by D. N. Rihani, he is right: the correct form of Equation (6) is

$$V_c = 33 + \left(\sum_i \Delta v_i M_i \right)^{1.028}$$

(Please note that the exponential value 1.028 is more correct than 1.029.)

Regarding the other points raised, I have the following remarks.

I agree with the calculations for acids and ketones, but the case of ethers deserves some explanation. First, the experimental value $V_c = 190$ for methyl ether reported by Kudchadker, et al. appears erroneous. Accordingly, I have assumed as more correct the value $V_c = 178$ reported by Reid and Sherwood (p. 577). Secondly, the correct group contribution for oxygen in furan, tetrahydrofuran and dioxane is $\Delta v_i = 0.790$, as indicated in Table 1 of my paper [functional group: —O—(ring)]. Last, I must apologize for a second error in Table 1: the group contribution for —O— in epoxidic compounds is 0.710 instead of −0.252 (I can't understand from where comes this strange value!).

In order to avoid any misinterpretation in the attached table[‡] I report in extenso the V_c calculation for the 10 ethers considered in my paper. The % error agrees quite well with the value reported in my paper.

Unfortunately, I have not revised the draft of my brief R&D note with the desired care. I apologize for this and I wish to thank you for your cooperation in amending my paper.

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[†] Nomenclatures the same as those in the original paper (Tien, et. al. 1976).

[*] The tables of calculation has been deposited as Document No. 03012 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 440 Park Ave. South, New York, N. Y. 10016 and may be obtained for $3.00 for microfiche or $5.00 for photocopies.

[†] Reid, R. C., and T. K. Sherwood, "Properties of Gases and Liquids, "McGraw-Hill, New York, 2 ed. (1966).

[‡] The table appears as document No. 03011 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 440 Park Ave. South, New York, N. Y. 10016 and may be obtained for $3.00 for microfiche or $5.00 for photocopies.