tions and ideal gas enthalpy values, while the liquid enthalpies were found by a combination of Equation (10) results and ideal gas state enthalpies.

DISCUSSION

From the results in Table 1 we can see that the values of $(\Delta H)_{P,T}$ found in this work were not in agreement with values obtained via another method by others. This, plus their unsmoothness makes the present values suspect.

Because of the relatively greater importance of the third right-hand member of Equation (10), compared to the first and second right-hand members, it seems obvious that the biggest weakness in the isobaric Gibbs-Duhem method for calculating liquid enthalpy of mixtures is in the handling of the temperature-composition data and obtaining derivatives. It also appears that the equation of state used is of lesser importance.

An alternate would have been to calculate $\ln f_i$ via an equation of state and the temperature-composition data, curve fitting these as a function of temperature and then differentiating. This alternative was not followed because of a desire to do as much of the calculation job as possible by already available equations, such as the equation of state, and to minimize the empiricism of curve fitting.

Another alternative would have been to use graphical differentiation with calculated $\ln f_i$ vs. T plots. This was ruled out as being impractical for design applications.

CONCLUSIONS

Theoretically, the isobaric Gibb-Duhem equation can be used to predict the enthalpy of saturated liquid mixtures from experimental temperature-composition data and an equation of state, using an expression presented herein. This method for computing saturated liquid enthalpies for mixtures is very sensitive to the input data, the equation of state, and the technique used in smoothing and differentiating the composition-temperature data, especially the latter.

From a practical viewpoint, this method cannot be recommended until a better method is found to evaluate the derivative $(dy_i/dT)_P$ for components of the mixture. Graphical methods are not acceptable.

NOTATION

x_i = mole fraction of i in liquid
y_i = mole fraction of i in vapor
z_i = mole fraction of i in system, liquid or vapor
f_i = the fugacity of component i in the mixture
$\overline{V}_i$ = partial molal volume of component i in mixture at T and P of the system
V = $\Sigma z_i \overline{V}_i$ = molal volume of mixture at T and P of the system
$\overline{H}_i$ = partial molal enthalpy of component i in mixture at T and P of the system
H = $\Sigma z_i \overline{H}_i$ = molal enthalpy of the mixture at system T and P conditions
H^o = $\Sigma z_i H_i^o$ = molal enthalpy of the mixture at the system temperature and the ideal gas condition of zero pressure
$(\Delta H)_{P,T}$ = $(H^V - H^L)_{P,T}$ = enthalpy difference for coexisting equilibrium vapor and liquid at P and T of system
H^V = enthalpy of saturated vapor mixture at dew point
H^L = enthalpy of saturated liquid mixture at bubble point
$H^o{}_{dp}$ = $\Sigma y_i H_i^o$ = ideal gas state enthalpy of dew point mixture
$H^o{}_{bp}$ = $\Sigma x_i H_i^o$ = ideal gas state enthalpy of bubble point mixture

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Correlation of Interphase Mass Transfer Coefficients for Transport of Gases through Insoluble Monolayers

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In a recent paper, Sada and Himmelblau (2) studied the transport of gases through insoluble monolayers and interphase mass transfer coefficients were reported for several gas-monolayer systems. However, the authors concluded that the mass transfer coefficients did not appear to be amenable to simple correlation as a function of the surface coverage of the monolayers. The purpose of this communication is to show that a correlation of the data is, indeed, possible and can be achieved through the use of a physical model.

THE MODEL

We may consider the transport of gases through an insoluble monolayer as a case of gas molecules diffusing through the void areas created by the compacting of monolayer molecules. If we neglect the interactions among the molecules, then the number of gas molecules diffusing through the film per unit time per unit area, or the interphase mass transfer coefficient (k_F), under steady state conditions, must be some functions of the void area and the radius of the gas molecule. Figure 1 is a plot of k_F vs. A on a semilogarithmic scale for the 1-hexadecanol monolayer system. Straight lines are obtained for each gas. Other gas-monolayer systems yield similar results. From the above observation, an equation of the following form is proposed to correlate the interphase mass transfer coefficients:

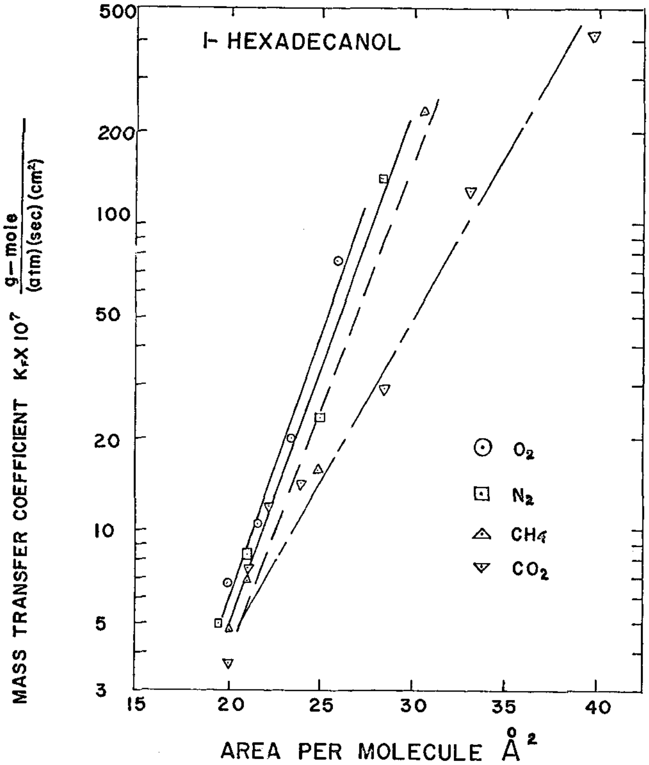

Fig. 1. Mass transfer coefficients as a function of the surface coverage.

Table 1. Correlations for Interphase Mass Transfer Coefficients: Values of Partial Regression Coefficients for Equation (1)

Monolayer System	$a \times e^{\pm t \ln S_a}$	$b \pm tS_b$	$c \pm tS_c$	Confidence limits for Estimated k_F
1-hexadecanol*	$1.20 \times 10^{-7} \times e^{\pm 4.07}$	-3.80 ± 2.98	0.33 ± 0.05	$k_F \times e^{\pm 0.71}$
1-octadecanol*	$1.11 \times 10^{-5} \times e^{\pm 2.39}$	-6.54 ± 1.62	0.23 ± 0.03	$k_F \times e^{\pm 0.41}$
1-eicosanoic acid†	$6.83 \times 10^{-8} \times e^{\pm 8.07}$	-5.51 ± 5.11	0.37 ± 0.25	$k_F \times e^{\pm 0.92}$
1-decosanol*	$2.37 \times 10^{-6} \times e^{\pm 4.18}$	-4.85 ± 3.08	0.23 ± 0.05	$k_F \times e^{\pm 0.62}$
1-decosanoic acid*	$8.90 \times 10^{-10} \times e^{\pm 4.17}$	-2.67 ± 2.45	0.35 ± 0.08	$k_F \times e^{\pm 0.42}$

* Confidence limits given at the 5% level of significance.
† Confidence limits given at the 10% level of significance.

$$k_F = a r^b e^{cA} \tag{1}$$

In Equation (1), the area coverage per molecule of the film (A) is used instead of the void area; this is justifiable since these two quantities are directly proportional to each other especially when the interphase mass transfer coefficients are determined at high surface pressures of the monolayers where the monolayer molecules are highly compacted (*2*). Data for the radii of gas molecules are available in many standard handbooks (*1*).

CORRELATIONS AND DISCUSSION

The interface mass transfer coefficients for each monolayer system are correlated by Equation (1) using a linear regression technique. The results are summarized in Table 1. The confidence limits on the partial regression coefficients as well as the estimated values of k_F for the specified levels of significance are also given. The F test is used to check the statistical significance of Equation (1). The results indicate that the regression is significant at the 1% level of significance for most of the monolayer systems except the 1-eicosanoic acid system which is significant at the 5% level. Therefore, we may conclude that the interphase mass transfer coefficient does indeed depend on the molecular radii of the gases and the area coverage per molecule of the monolayer.

Regression analysis is also performed on the data by excluding the carbon dioxide-monolayer systems; which results in a slightly improved correlation. Although the difference is not statistically significant, it is evident by comparing Figures 2 and 3. These figures summarize all the systems and are plots of k_F observed vs. k_F calculated, excluding and including the data for the carbon dioxide-monolayer systems, respectively. They demonstrate the scatter involved in each case. The discrepancies are believed to be the result of the rather strong interactions between carbon dioxide and water. The interactions are due to the relatively high solubility of carbon dioxide in water (ranging from 35 to 225 times greater as compared with the other gases). On the other hand, the gases nitrogen, oxygen, and methane are quite similar in nature in terms of their interactions with water. This is evident from their relatively close solubilities in water (*1*).

The data for area coverage above 32Å.²/molecule are excluded, since the reliability of these data is open to question. The experimental technique employed by Sada and Himmelblau (*2*, *3*) measures the local coefficient rather than the average ones. The authors indicate that the monolayer film starts to collapse and fold at an area coverage between 20 and 25Å.²/molecule. Obviously, at the beginning of collapse and folding of the monolayers, due to forces acting among molecules in the film, the distribution of void areas is still relatively uniform. Therefore,

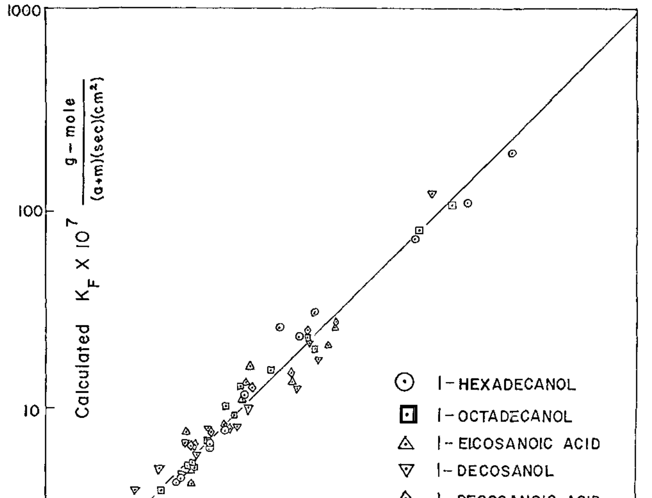

Fig. 2. Comparison of the observed and calculated mass transfer coefficient. (Data for carbon dioxide-monolayer systems excluded).

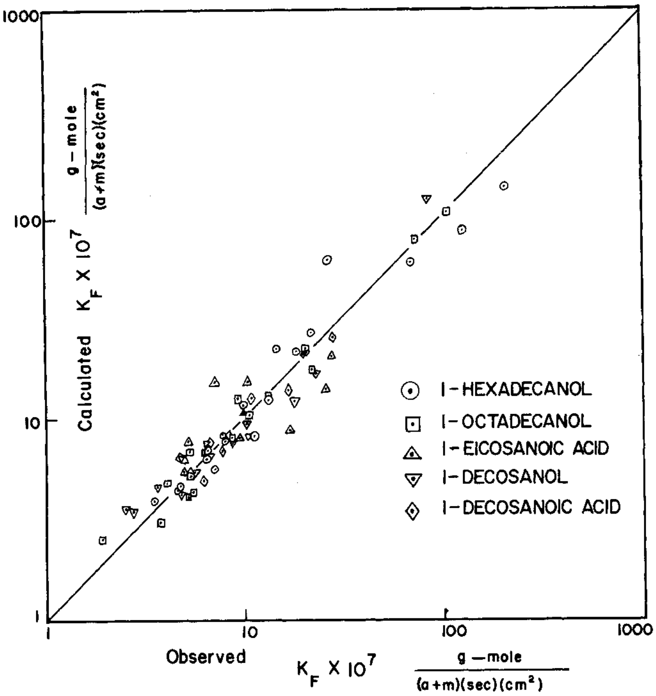

Fig. 3. Comparison of the observed and calculated mass transfer coefficient. (Data for carbon dioxide-monolayer systems included).

the local coefficient will be very close to that of the average value based on the entire surface area. When the area coverage per molecule is increased further, the distribution of void areas in the film becomes irregular. Eventually, the film breaks away and forms islands which cover part of the water surface. Under this condition, the local coefficient can be quite different from the average value because of its dependence on the sampling location. The choice of the ranges of applicability for Equation (1) is somewhat arbitrary and is based on the experimental data. It will be of value if the above observations are verified experimentally.

CONCLUSIONS

A correlation has been proposed for the transport of gases through insoluble monolayers in the form of Equation (1). This equation is applicable to an area coverage below 32Å.²/molecule of the monolayer and when interactions among molecules of water, gas, and monolayer may be neglected. Therefore, it is suggested that the correlation should be applied only to slightly soluble gases and at high surface pressure of the film where the monolayer molecules are highly compacted. If information is available on the molecular size of the monolayer, then the actual void area in the film can be calculated. By also taking into consideration the interactions among molecules, we may very well be able to correlate all the systems by a single equation. However, this can be done only after the structure of the monolayer molecules and their interactions with water and gas are fully understood.

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NOTATION

a, b, c = empirical constants, defined by Equation (1)
A = area per molecule, Å.²/molecule
k_F = interphase mass transfer coefficient in monolayer, g.-mole/(atm.)(sq.cm.)(sec.)
r = radius of gas molecule, Å.
S_a, S_b, S_c = standard error of partial regression coefficients
t = Student's t

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Optimal Control Profile Specification for Boundary Value Systems

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Very little interest has been shown in the problem of specifying the optimal control profile for a second-order system with boundary conditions. Important systems involve space distribution with backmixing or recycle. The flow reactor with axial dispersion has been studied only with respect to specification of optimal isothermal conditions (*1*) and the temperature profile which maximizes the product yield for a single reversible reaction (*5*). Here, a general second-order system is analyzed for optimal control profile specification and applied in a study of the axial dispersion reactor with a series of first-order reactions.

The problem under consideration concerns the specification of a control profile vector $\mathbf{u}(z)$, such that the performance index J is maximimized where

$$J(\mathbf{u}) = \int_0^1 L(\mathbf{y}, \mathbf{u}, z)\, dz \tag{1}$$

subject to the set of nonlinear second order differential state equations and boundary conditions for $j = 1$ to J as follows:

$$\ddot{y}_j - c_j\dot{y}_j + c_j r_j(\mathbf{y}, \mathbf{u}) = 0 \tag{2}$$

$$-c_j^{-1}\dot{y}_j(0) + y_j(0) = y_j^o \tag{3}$$

$$\dot{y}_j(1) = 0 \tag{4}$$

The variables $y_j(z)$ may be such variables as pressure, temperature, or composition which determine the state of the process at any position z. The rate terms r_j are determined by the state of the system at any position z. The objective function J is indicated as a function only of the control vector $\mathbf{u}$ since specification of $\mathbf{u}$ determines the state vector $\mathbf{y}$ by Equations (2) to (4).

The second-order differential Equations (2) may be reduced to $I = 2J$ first-order differential equations by specifying new state variables, x_i, such that

$$x_{2j-1} = y_j \quad \text{and} \quad x_{2j} = \dot{y}_j \tag{5}$$

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