catalyst surface for the key component α, mol/m^3

E_a = activation energy, J/mol
G = mass velocity in the reactor bed, kg/m^2·s
h = heat transfer coefficient, J/m^2·s·K
ΔH_R = heat of reaction, J/mol(23)
k_i,k_α = mass transfer coefficients for components i and α, m/s
m = catalyst weight in the reactor, kg
N_i = effluent rate for component i, mol/s
$N_{io},N_{\alpha o}$ = inlet rates for components i and α, mol/s
N_o = total inlet rate, mol/s
N_T = total effluent rate, mol/s
P_T = total pressure, N/m^2
R_g = gas constant, J/mol·K
r_o = observed reaction rate based on unit catalyst volume, mol/s·m^3
T_b = bulk phase temperature in the reactor, K
T_s = temperature at the catalyst surface, K
V_p = catalyst particle volume, m^3
X = conversion for the key component α, $(N_{\alpha o} - N_\alpha)/N_{\alpha o}$
X^∞ = conversion corresponding to zero external gradients
$y_{io},y_{\alpha o}$ = mole fraction at the inlet for components i and α
X = preexponential factor, s^{-1}

Greek Letters

α = key component, cyclohexane
$\beta_1 \ldots \beta_9$ = constants in Eq. 18
$\gamma_1 \ldots \gamma_{n+1}$ = constants in Eq. 23
κ = constant in Eq. 11
$\lambda_1 \ldots \lambda_6$ = constants in Eq. 17
ν_i,ν_α = stoichiometric coefficients for component i and α
$\Delta\nu$ = sum of the stoichiometric coefficients
ξ = parameter defined by Eq. 14
ρ_p = density of the catalyst particle, kg/m^3
$\sigma_1 \ldots \sigma_{n+1}$ = constants in Eq. 22
ϕ = reciprocal mass velocity $(1/G)$, m^2·s/kg
ψ = parameter defined by Eq. 24

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Evaporation of Water through Surfactant Layers

B. J. McCOY

Department of Chemical Engineering
University of California
Davis, CA 95616

A recent model using Fick's law to describe gas diffusion in a surfactant film and into the water, with local equilibrium solubility conditions at the interfaces, effectively described the observed phenomena for three rather different experiments (Ly et al., 1979). In the present paper we extend that model to mass transfer of H_2O through surface-active films. Blank (1979) has discussed the possibility of applying Fickian diffusion analysis to permeation through monolayers, but did not have at hand the necessary mathematical model required for a full evaluation. The present work is a step toward the development of such a mathematical model.

Figure 1 pictures a surfactant layer of thickness δ covering a semi-infinite volume of water. The concentration gradients sketched are for water evaporating into air, although the case of condensation and mass transfer *to* the liquid water is also described by the model. Letting subscripts a and s refer to quantities in the air and surfactant regions respectively, we write the diffusion equations for concentration of water $c(x,t)$ as a function of position x and time t,

$$\frac{\partial c_s}{\partial t} = D_s \frac{\partial^2 c_s}{\partial x^2} \quad 0 \le x \le \delta \tag{1}$$

$$\frac{\partial c_a}{\partial t} = D_a \frac{\partial^2 c_a}{\partial x^2} \quad \delta \le x \le \infty \tag{2}$$

The initial condition specifies that for $t \le 0$ the water vapor in the air is in equilibrium with the surfactant film (but not with the underlying bulk water),

$$c_a(x,t = 0) = c_i \tag{3}$$

$$c_s(x,t = 0) = c_i/K \tag{4}$$

The distribution coefficient K, which is related to the Henry's law constant, is discussed more completely below.

When the surfactant film is formed on the liquid water for $t > 0$ we assume local equilibrium is instantaneously established at the interface to give the boundary condition

$$c_s(x = 0,t) = c^* \tag{5}$$

where c^* is the solubility of H_2O in the film. Equilibrium is assumed to hold locally at the air/surfactant interface,

$$c_a(x = \delta,t) = K\, c_s\, (x = \delta,t), \tag{6}$$

and the flux is continuous there,

$$-D_s \left.\frac{\partial c_s}{\partial x}\right|_{x=\delta} = -D_a \left.\frac{\partial c_a}{\partial x}\right|_{x=\delta} \tag{7}$$

Far enough into the air, the concentration remains unchanged,

$$c_a(x \rightarrow \infty,t) = c_i \tag{8}$$

For a three-phase equilibrium between air, water, and the non-volatile surfactant, the concentration of water vapor in the air

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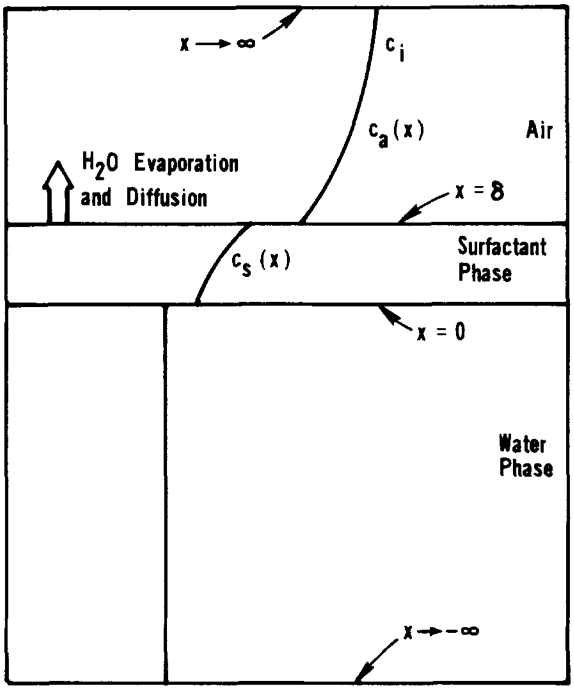

Figure 1. Evaporation of water by diffusion through a surfactant film and into air. The concentration profile shows water vapor in the air $c_a(x)$ and water dissolved in the surfactant phase $c_s(x)$.

is the vapor pressure p^* divided by RT, the gas constant times the absolute temperature. The distribution coefficient K can be expressed in terms of the solubility of water in the surfactant film:

$$K = p^*/c^* RT = 1/HRT \qquad (9)$$

where $H = c^*/p^*$ is Henry's law constant for the solubility of water in the surfactant film. If the solubility of H_2O in the surfactant film is known, then K can be calculated from Eq. 9. However, since the surfactant film, unlike bulk liquids, usually is a structure of highly oriented molecules, c^* is not readily estimated. Thus, it will be necessary to treat K as a parameter whose approximate upper limit only may be calculated a priori from equilibrium data.

Equations 1–8, defining the model for diffusion of H_2O through a surfactant film of thickness δ and into a semi-infinite volume of air, are identical to the equations for diffusion of a soluble gas through a surfactant film into water. To see this one has only to make the transformations of subscripts $s \rightarrow 1$ and $a \rightarrow 2$, as well as $c^* \rightarrow H_s P_o$ (in the notation of Ly et al., 1979). The solution by Laplace transformation (e.g., Carslaw and Jaeger, 1959, for a comparable heat transfer problem) gives the concentration of H_2O in air

$$c_a(x,t) = (2/b)\,(Kc^* - c_i) \sum_{n=0}^{\infty} (-1)^n\,(a/b)^n \times \operatorname{erfc}\left[\frac{(x-\delta)/\sqrt{D_a} + \delta(2n+1)/\sqrt{D_s}}{2\sqrt{t}}\right] + c_i \qquad (10)$$

where

$$a = 1 - K\sqrt{D_a/D_s}$$
$$b = 1 + K\sqrt{D_a/D_s}$$

The flux of evaporating water at the air/surfactant interface is given by

$$J(x=\delta) = -D_a\,(\partial c_a/\partial x)_{x=\delta} = \frac{2D_a}{b\sqrt{\pi D_a t}}(Kc^* - c_i)\sum_{n=0}^{\infty}(-1)^n (a/b)^n \exp -\left(\frac{\delta(2n+1)}{2\sqrt{D_s t}}\right)^2 \qquad (11)$$

The amount of evaporation from the interface in time t for $\delta^2/D_s t \ll 1$ is

$$Q_s = \int_0^t J(x=\delta)dt = \frac{4}{b}\sqrt{\frac{D_a t}{\pi}}\,(Kc^* - c_i) \qquad (12)$$

since for small $\alpha_n = \delta^2(n+1)^2/D_s$ we have

$$\int_0^t t^{-1/2} e^{-\alpha_n/t}\,dt \simeq 2t^{1/2} \qquad (13)$$

The series can be truncated since typically $a/b \sim 10^{-1}$. Therefore, according to Eq. 12, the amount of water evaporated increases as $\sqrt{t}$ and is independent of the film thickness δ when $\delta^2/D_s t \ll 1$, i.e., for thin films and long times. The evaporation rate given by Eq. 12 is simpler than the expression for absorption of gases through surfactant films because the fluxes are necessarily evaluated at different positions in the two systems.

It is easily shown that the amount of evaporation from a pure water surface is given by

$$Q_w = 2\sqrt{D_a t/\pi}\,(p^*/RT - c_i) \qquad (14)$$

Therefore from Eqs. 12 and 14, and since from Eq. 9, $K c^* = p^*/RT$,

$$Q_w/Q_s \simeq \frac{1}{2}(1 + K\sqrt{D_a/D_s}), \qquad (15)$$

which is independent of c_i, c^*, and p^*, as well as δ and t, as long as

$$\delta^2/D_s t \ll 1.$$

To show the order of magnitude of the parameters in Eq. 15, consider a simple experiment described by Sherwood et al. (1975). "Fill two identical litre beakers with distilled water. Add a tiny pinch of hexadecanol (cetyl alcohol) to one and set the two aside for a week or more. By the time evaporation has reduced the level of the pure water by 4 in. (0.1 m), the level in the beaker with the hexadecanol will have dropped only about an in. (0.025 m)."

Although the data for amount of surfactant (thickness of surfactant film) and evaporation time are rough estimates, this does not adversely affect application of the model since Eq. 15 is independent of δ and t. Effectively, the approximate treatment of these two parameters supports the validity of Eq. 15. Let us determine the value of K that will give $Q_w/Q_s = 4$. The diffusivity of H_2O in air, D_a, is $0.3 = 10^{-4}$ m²/s. We assume that the diffusivity of H_2O in the surfactant film, D_s, is the same order of magnitude as polar gases through the films of the earlier study (Ly et al., 1979), thus we set $D_s \simeq 10^{-12}$ m²/s. Solving for K in Eq. 15 gives $K \sim 10^{-3}$. An approximate upper limit to K can be estimated from the solubility of water in organic liquids. For example, $c^* = 0.0151$ g H_2O/100 g saturated solution of n-heptane at 25°C (Linke, 1958) and Eq. 9 predicts $K \sim 0.2$. However, polar molecules are apparently much more soluble in oriented thin films so that $K \sim 10^{-3}$ is consistent with this upper limit. In the earlier study (Ly et al., 1979) we likewise calculated values of K for surfactant film diffusion problems, which showed a high storage capacity of the thin film for polar molecules.

For most situations a film covering the surface of water will reduce the evaporation rate, and $Q_w/Q_s > 1$. However, there has been some discussion of the possibility that certain surface active films may enhance evaporation. From Eq. 15 one finds that enhancement, $Q_w/Q_s < 1$, implies

$$K\sqrt{D_a/D_s} < 1 \qquad (16)$$

Since we expect that $D_s \ll D_a$, the inequality (Eq. 16) can hold for $K \lll 1$, i.e., for very large values of c^* (Eq. 9). This is consistent with the work of Deryagin et al. (1960, 1961), who predicted enhanced evaporation for small values of $\delta/c^* D_s$. Using the values of D_a and D_s in the previous paragraph, we find from Eq. 16 that $K < 3 \times 10^{-4}$ is the condition for enhanced evaporation. The physical explanation for enhanced evaporation is that the surfactant has a high affinity for H_2O, i.e., that c^* is large. In other words, the surfactive film draws H_2O from the bulk and allows it to evaporate

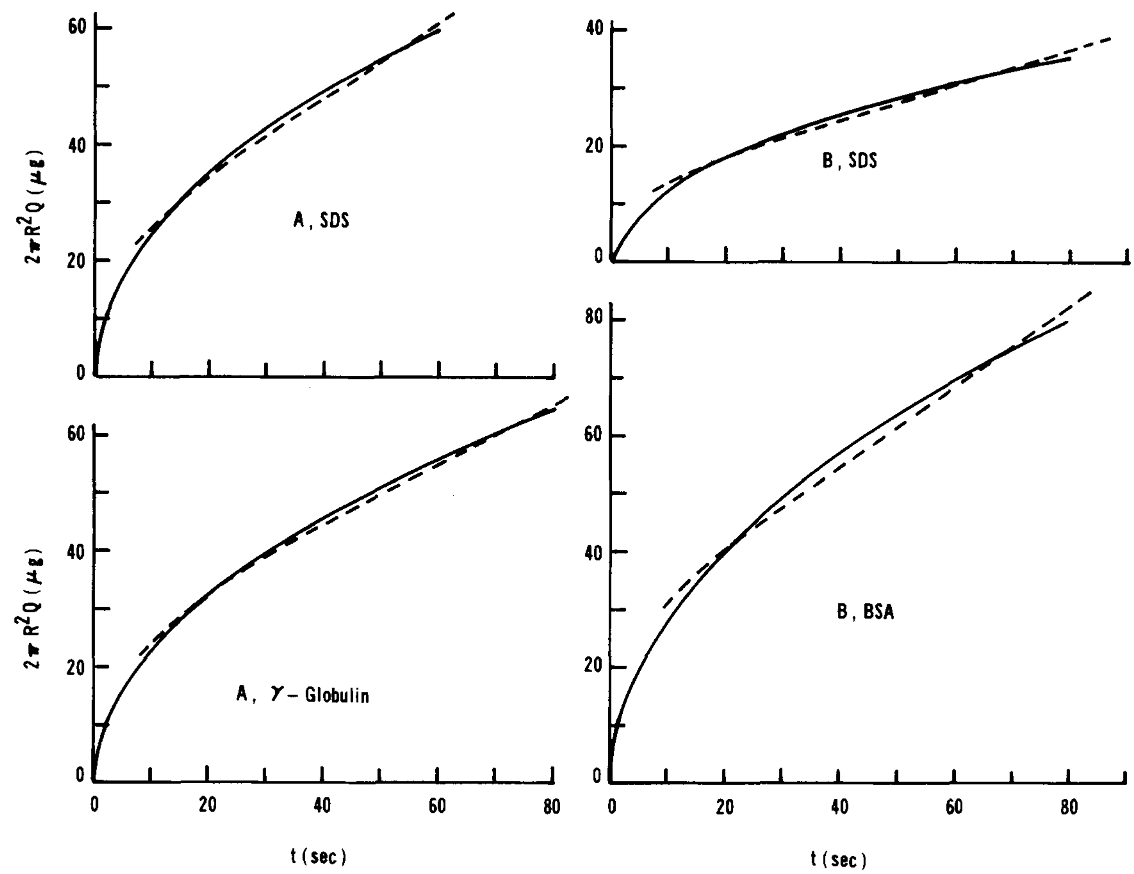

Figure 2. Evaporation of water through different surface-active films for rings A and B; dashed line is data of Blank and Mussellwhite (1968), solid line is present theory.

at the air interface. However, Blank and Mussellwhite (1968) have suggested that several of the experimental observations of enhanced evaporation through surfactant films may be due to film drainage effects (increased area of mass transfer) or to nonequilibrium effects at very short times. Of course the present model does not apply to these cases.

Of potential interest is the case of super-saturated air, for which $p^*/RT < c_i$ and the sign of Q_s in Eq. 12 is reversed, i.e., condensation of water vapor occurs according to Eq. 12. The presence of a surfactant film reduces condensation unless the inequality (Eq. 16) holds, i.e., when the exposed surface of the surfactant has a high affinity for water vapor.

Most experiments of evaporation of water through surfactant films have the objective of measuring a permeability. According to Eq. 12 the evaporation into a semi-infinite volume of air increases as $\sqrt{t}$, rather than t. We will examine some time-dependent data to determine the accuracy of our model and of the steady state assumption.

Blank and Mussellwhite (1968) show data for evaporation of water as a function of time from rings which had been dipped into the film-forming solution and carefully weighed on a microbalance as evaporation occurred. Although air currents could be a complicating factor, we assume these are negligible. The surface-active agents were sodium dodecylsulfate (SDS), bovine serum albumin (BSA), and γ-globulin, Figure 2. We may analyze the data by writing Eq. 12 as

$$2\pi r^2 Q_s = E\sqrt{t} \qquad (17)$$

where

$$E = 2\pi r^2 4\sqrt{D_a/\pi}\,(p^*/RT - c_i)/(1 + K\sqrt{D_a/D_s}) \qquad (18)$$

and $2\pi r^2$ is the area of mass transfer.

We calculate E as the average of values based on pairs of data points:

$$E_i = \frac{Q_i - Q_{i+1}}{\sqrt{t_i} - \sqrt{t_{i+1}}}\,2\pi r^2 \qquad (19)$$

Since the evaporation rates near $t = 0$ are not shown in the plots of experimental data, we arranged the data to fit on the plot of Eq. 17, Figure 2; this curve-fitting procedure will determine K. For the range of data plotted, i.e., between 10 and 80 s, the present theory is well within the expected error, ±30%, of the experimental data. Blank and Mussellwhite (1968) attributed the curved nature of their data to film drainage effects, which they assumed to exist. Although such effects may be present in the data, our theory predicts that at least part, if not all, of the curvature is due to the unsteady $\sqrt{t}$ dependence of evaporation.

The values of E calculated from Eq. 17 may be used to estimate K for the experiments with Eq. 18. We let $D_a = 0.3$ cm²/s, $D_s = 10^{-8}$ cm²/s, $2\pi r^2 = 1.6 \times 10^{-4}$ m², and at 22°C, $p^* = 20$ mm Hg (2.7 kPa), which gives a driving force of $p^*/RT - c_i = 9.9 \times 10^{-6}$ g/cm³ at 50% relative humidity and 1.5×10^{-5} g/cm³ at 25% relative humidity. Although the humidity for the experiments was not measured, we report values of K for these two values of relative humidity in Table 1. The values of K all are within an order of magnitude of 10^{-3}, which, as mentioned earlier, is consistent with

TABLE 1. VALUES OF K CALCULATED FROM DATA OF BLANK AND MUSSELLWHITE (1968) WITH EQ. 18 FOR 25% AND 50% RELATIVE HUMIDITY

Surfactant	Ring	$E \times 10^3$ (kg/s$^{1/2}$)	@ 50% r.h. $K \times 10^4$	@ 25% r.h. $K \times 10^4$
SDS	A	7.80	2.9	5.1
γ-Globulin	A	7.22	3.2	5.6
SDS	B	4.02	7.3	12.0
BSA	B	9.05	2.2	4.1

the estimated upper limit of K. Due to uncertainty in estimating D_s, as well as to mathematical approximations that have been made, no more than semi-quantitative accuracy can be claimed for K. A more detailed study, not justified at present because of uncertainty regarding estimation of parameters, would require keeping more terms in the expansion, Eq. 11.

NOTATION

a $= 1 - K\sqrt{D_a/D_s}$
b $= 1 + K\sqrt{D_a/D_s}$
c = concentration of water
c^* = solubility of H_2O in the film
D = diffusion coefficient
δ = film thickness
H = Henry's law constant for solubility of water in the film
J = flux of evaporating water
K = distribution coefficient for water in air and in film
p^* = vapor pressure of water
Q_s = total evaporation from the film
Q_w = total evaporation from a pure water surface
R = gas constant
r = radius of ring
T = temperature
t = time
x = position coordinate

Subscripts

a = air region
i = initial condition
s = surfactant film region

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Reaction Rate Oscillations during Fischer-Tropsch Synthesis on Fe-Precipitated Nu-1 Zeolite-Type Catalysts

T. T. TSOTSIS

Department of Chemical Engineering
University of Southern California
Los Angeles, CA 90007
and

V. U. S. RAO
and
L. M. POLINSKI

Pittsburgh Energy Technology Center
Pittsburgh, PA 15236

The phenomenon of reaction rate oscillations in catalytic systems has been the subject of intensive investigations in the last thirteen years. In 1968, Hugo (1968) observed for the first time thermochemical oscillations during the exothermic decomposition of N_2O on a CuO catalyst. Since then reaction rate oscillations have been observed in several other catalytic systems, such as H_2 oxidation over Pt foils and wires (Luss et al., 1980; Schmitz et al., 1979) and Pt and Pd supported catalysts (Boudart et al., 1976), CO oxidation over supported and unsupported Pt catalysts (Carberry et al., 1978; Schmitz and Shientuch, 1977), C_2H_4 oxidation over Pt films (Vayenas et al., 1980) and NH_3 oxidation over Pt wires (Schmidt et al., 1980). Several comprehensive review papers have now appeared (Schmitz and Sheintuch, 1977; Slinko and Slinko, 1978). The majority of the above studies were performed at or near atmospheric pressures and in most cases in a single pellet reactor.

Quite recently in our laboratory, reaction rate oscillations have been observed during Fischer-Tropsch synthesis reaction over 13% Fe-precipitated zeolite type catalysts at medium pressures (2.2×10^3 Kpa) in a multipellet Berty CSTR reactor. Some of our observations are summarized in the present publication.*

The discovery of medium pore zeolites ZSM-5 by Mobil workers (Asgauer and Landolt, 1972) and Nu-1 type zeolite by ICI workers (Whittam and Spencer, 1978) have provided new routes in the indirect liquefaction of coal and its conversion to chemicals. Zeolites have from the point of view of catalysis, the very important property of solid acidity (Jacobs, 1977).

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