

Liquid-Phase Mass Transfer in High-Pressure Systems with a Supercritical and a Liquid Phase¹

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Liquid-phase diffusion coefficients and mass-transfer coefficients were measured in binary two-phase systems at high pressures. Both were determined from the rates of absorption of the gaseous component into the liquid. Diffusion coefficients were measured by observing unsteady-state diffusion into a semiinfinite liquid phase and fitting transient counterdiffusion mass-flow rates to the visually determined change of the position of the interface between the liquid and the supercritical phase. Mass-transfer coefficients in the liquid phase were determined from the absorption rate of the gaseous component into a falling liquid film of known flow and physical properties. Experiments were performed with the binary systems carbon dioxide-oleic acid, carbon dioxide-methyl myristate, and carbon dioxide-methyl palmitate. Liquid-phase diffusion coefficients rise significantly with concentration as viscosity decreases. Temperature also has a strong effect on diffusivities. Experimental mass-transfer coefficients in nearly saturated liquids agree well with calculations for falling films with known properties, whereas far from equilibrium, Marangoni convection greatly enhances mass-transfer rates. Close to the critical point of the binary system at a given temperature, a sharp decline of the mass-transfer coefficient is observed.

KEY WORDS: diffusion coefficient; falling film; high-pressure system; liquid phase; mass-transfer coefficient; supercritical phase.

1. INTRODUCTION

Thermodynamic equilibria form the basis for high-pressure processes. However, the actual size of a separation or reaction vessel is not determined just by phase equilibria. For the design of such an apparatus,

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mass-transfer kinetics must be known as well. Mass transfer has so far been systematically studied only in the supercritical phase [1-3]. In a large number of processes at elevated pressures, such as supercritical extraction of liquids, chemical reactions, or advanced oil recovery techniques, a liquid phase coexists with the supercritical or compressed gas phase. Due to high gas solubilities in the liquid, liquid-phase mass transfer also plays an important role in these applications. As the gas dissolves in the liquid, viscosity is significantly reduced, thus also greatly affecting diffusivity.

Mass-transfer rates depend on interfacial area, concentration gradients, and mass-transfer coefficients. In contrast, diffusion coefficients alone do not give any direct information on the amount of matter actually exchanged. They do, however, describe minimal mass transfer by diffusion alone in the absence of convection. Most correlations for predicting mass-transfer coefficients make use of diffusion coefficients. Finally, the diffusivity is a property that, at a given pressure and temperature, is specific of the chemical substances present and of their concentrations in the mixture. In contrast, mass-transfer coefficients also strongly depend on flow conditions and on the geometry of the apparatus.

The purpose of this paper is to present experimental techniques and results of measuring diffusion coefficients and mass-transfer coefficients in the liquid phase of binary high-pressure gas-liquid systems. Carbon dioxide is widely used as supercritical fluid in various industrial applications, since it is inexpensive, nontoxic, and nonflammable, and also was studied in this work. Techniques such as supercritical extraction may be utilized for fractionation or purification in the fat and oil industry; therefore, three lipids—oleic acid (*cis*-9-octadecenoic acid), methyl myristate (tetradecanoic acid methyl ester), and methyl palmitate (hexadecanoic acid methyl ester)—were chosen as liquid components.

2. EXPERIMENTS

The apparatus used for the experiments is described in detail in Refs. 4-6. Its central part was a thermostated high-pressure view cell.

Diffusion coefficients were determined by observing the rate of unsteady-state absorption of the supercritical fluid into the liquid, which formed a semiinfinite phase throughout the experiment. A glass capillary with an inner diameter of 0.720 mm, small enough to ensure that no natural convection took place, was used for the experiments. The capillary was partly filled with liquid, sealed at its lower end, and finally, inserted into the cell, which contained no further liquid. Carbon dioxide was then charged into the cell until the set pressure was reached. The interface between the liquid phase and the supercritical phase moved upward as the fluid was absorbed

in the liquid. This movement was visually observed with the help of a cathetometer. Diffusion coefficients were then calculated by fitting the mass-flow rates obtained from a counterdiffusion model (cf. Section 3) to the change of position of the interface as a function of time.

Mass-transfer experiments were performed by measuring the rate of absorption of carbon dioxide into a falling liquid film of known flow and physical properties. The liquid phase was withdrawn from the bottom of the view cell, recirculated with the help of a gear pump, and reentered from above so that it flowed downwards along one of the side walls of the view cell, where it came into contact with the gas phase. The gas was saturated with the liquid component before entering the cell so that mass-transfer resistance occurred only in the liquid phase. CO_2 mole fractions in the film were determined by measuring the density of the liquid phase, which is a function of CO_2 concentration, and by taking samples. Mass-transfer coefficients were then calculated from the mass flow of absorbed CO_2 , the surface area and the density of the liquid film, and the logarithmic concentration gradient.

3. THEORY

The counterdiffusions of carbon dioxide into the liquid phase and of the liquid component into the supercritical phase were, in principle, calculated following a model proposed by Schlünder [7]. The analytical solution obtained there is valid only if densities and diffusivities in both phases remain constant. The model therefore was refined in this work. It is described in detail in Refs. 4 and 5. Mass balances and kinetics yield the following differential equation for the liquid phase:

$$\frac{\partial x_1}{\partial t} = \frac{\partial \delta_l}{\partial x_1} \left(\frac{\partial x_1}{\partial z} \right)^2 + \delta_l \frac{\partial^2 x_1}{\partial z^2} + \frac{1}{y_{1,\text{Ph}} - x_{1,\text{Ph}}} \times \left[\delta_{l,\text{Ph}} \left(\frac{\partial x_1}{\partial z} \right)_{\text{Ph}} + \frac{\rho_g}{\rho_{l,\text{Ph}}} \frac{\delta_g}{S} (y_{1,\infty} - y_{1,\text{Ph}}) \right] \frac{\partial x_1}{\partial z} \quad (1)$$

where x_1 and y_1 are the mass fractions of component 1, CO_2 , in the liquid and compressed gas phases, respectively, δ_l and δ_g are binary diffusivities and ρ_l and ρ_g densities in the liquid and gas phases, z is the coordinate perpendicular to the interface counted positively into the gas phase, t is time, and S is the extension of the volume in the capillary not occupied by the liquid phase. The subscripts Ph and ∞ refer to interfacial and to bulk properties. In the partial differential equation, densities and diffusivities at a given location z change as the CO_2 concentration varies with time.

Liquid-phase densities and their dependence on composition were determined in Ref. 6. The concentration dependence of the diffusion coefficient in the liquid phase was derived from that of the viscosity, shown to be exponentially dependent on the CO₂ mole fraction [4], by following a model of Hayduk and Cheng [8].

Measurements [4, 6] showed that gas-phase density remained virtually constant due to low solubilities of the liquid component in the supercritical phase. The diffusion coefficient there, derived from a correlation developed by Funazukuri *et al.* [9], was also considered constant.

Equation (1) was solved numerically to obtain the concentration profile in the liquid phase. With the help of the concentration gradient at the interface, mass flux \dot{m} was calculated from Eq. (2):

$$\dot{m}(t) = \frac{1}{y_{1,\text{ph}} - x_{1,\text{ph}}} \left[\rho_{l,\text{ph}} \delta_{l,\text{ph}} \left(\frac{\partial x_1}{\partial z} \right)_{\text{ph}} + \rho_g \frac{\delta_g}{S} (y_{1,\infty} - y_{1,\text{ph}}) \right] \quad (2)$$

A simple balance of the liquid phase yielded

$$\dot{m}(t) = \rho_l \frac{dz}{dt} \quad (3)$$

where ρ_l is the mean density of the liquid phase and dz/dt is the measured change of position of the interface.

In the falling-film experiments, the liquid-phase mass-transfer coefficient β_l was calculated from the mass flow of absorbed CO₂, \dot{M}_{abs} :

$$\dot{M}_{\text{abs}}(t) = \bar{b} l \rho_l \beta_l \ln \frac{1 - \bar{x}(t)}{1 - x_{\text{ph}}} \quad (4)$$

where \bar{b} is the mean breadth of the film, l is its length, and \bar{x} and x_{ph} are the mean and interfacial CO₂ mass fractions of the film. The liquid-phase properties depend on CO₂ concentration and thus on time.

The mass-transfer coefficients thus obtained were compared to those calculated from models of mass transfer in film absorption as developed by Müller [10] or listed in Ref. 11.

4. RESULTS

Binary diffusion coefficients of carbon dioxide in oleic acid, methyl myristate, and methyl palmitate exhibit a moderate dependence on concentration, as shown in Fig. 1 for the system carbon dioxide—methyl myristate at a pressure of 80 bar. The diffusion coefficient at infinite dilution, i.e., $x_{\text{CO}_2} = 0$, as is the case far from the interface, is independent of pressure at

a given temperature. It is characterized by the pure-liquid viscosity, which in turn remains virtually constant in the range of pressures studied. In the saturated system, there again is hardly any dependence on pressure except near the critical point of the mixture. At these pressures, the CO_2 solubility in the liquid is only insignificantly improved as the pressure rises, so that the viscosity decreases only slightly. Temperature has an indirect effect on diffusivities, as it leads to lower viscosities. However, the mole fraction of CO_2 in the saturated liquid phase becomes significantly smaller with rising temperature, as may be clearly seen in Fig. 1.

Representative results of the falling-film experiments are shown in Figs. 2 and 3. Comparison of measured and predicted [10, 11] mass-transfer coefficients as a function of CO_2 mole fraction plotted in Fig. 2 shows that the experimental values are about two to four times higher than the calculated ones. As the liquid becomes saturated with CO_2 , however, the experimentally determined mass-transfer coefficients approach those predicted by the models. This behavior was observed at all temperatures and for all the systems studied in this work. Except near the critical pressure of the mixture at a given temperature, mass-transfer coefficients at all pressures are larger than those calculated from the models.

Why? The system properties required for the correlations proposed by the models—diffusivity, density, and viscosity—have been determined with a high accuracy [4, 6]. Improved mass-transfer rates must therefore be caused by a mechanism the models do not take into account. Laminar

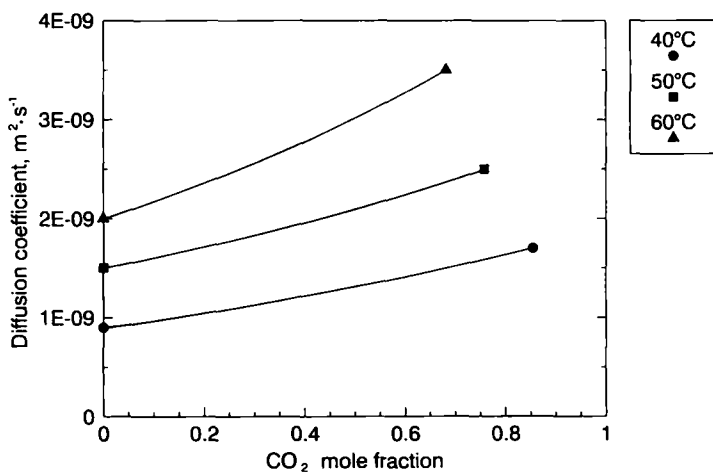


Fig. 1. Binary diffusivities in the liquid phase of the system carbon dioxide-methyl myristate at 80 bar.

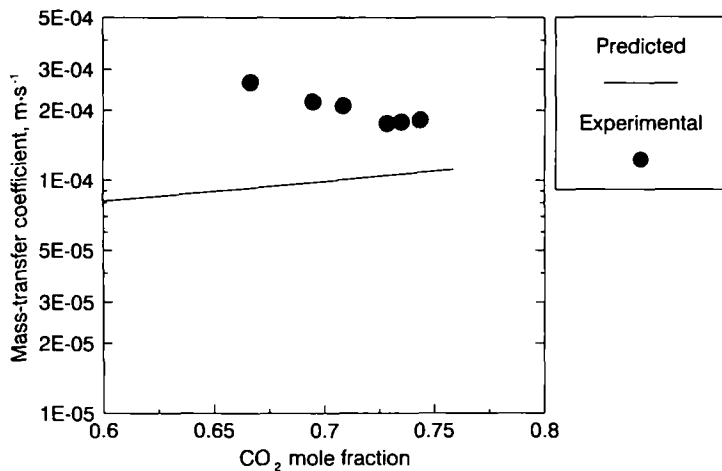


Fig. 2. Liquid-phase mass-transfer coefficient in a falling film as a function of CO_2 mole fraction in the system CO_2 -methyl myristate at 50°C and 80 bar.

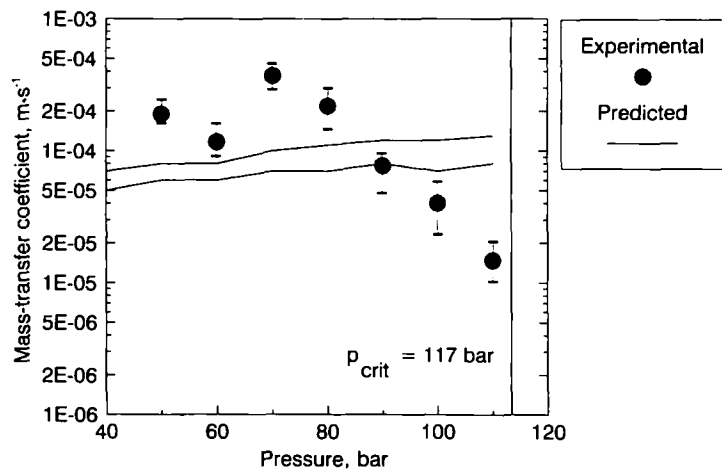


Fig. 3. Mass-transfer coefficients in falling liquid films of the system CO_2 -methyl myristate as a function of pressure at 50°C (mean values for the entire range of mole fractions studied at each pressure). The critical pressure of this system at 50°C is $p_{\text{crit}} = 117$ bar.

flow in the film is superposed by local convection, which is caused by Marangoni instabilities in the interface. The absorption of CO_2 in the liquid is exothermal and results in a temperature gradient within the interface. Because the three-phase system formed by the supercritical phase, the liquid phase, and the solid wall of the view cell is fully wetting [12], the film is thinner at its edge. Thus, absorption heat is conducted more rapidly to the wall there than in the center of the film, so that the temperature in the center of the film surface is higher than the set system temperature.

Interfacial tension in saturated CO_2 —lipid systems was shown to decrease with temperature [12]. The temperature difference between the center and the edge of the film surface thus results in a gradient of the interfacial tension directed from the film edge to the surface center. This gradient may be large enough to trigger local circulation within the film, which then superposes the actual film flow and is directed from the center of the film surface to its edge. An estimation shows that the velocities occurring in this circulation are high enough to result in mass-transfer coefficients which indeed are larger than those calculated for isothermal film flow.

As the mean CO_2 concentration in the film nears saturation, the absorption mass flow decreases, less absorption heat is released, and the local temperature increase becomes smaller. Thus, the gradient of the interfacial tension is reduced, and the mass-transfer coefficient approaches the value calculated for pure laminar flow without lateral convection.

As pressure is raised toward the critical point of the mixture, mass-transfer coefficients display the behavior plotted in Fig. 3. Values calculated from the models lie within the hatched area.

At pressures far from the critical pressure of the mixture at the given temperature, experimental values are higher than predicted. At higher pressures, the additional capacity of the liquid for absorbing CO_2 is smaller than at low pressures. Absorption thus essentially is isothermal, there is no significant lateral convection, and the measured mass-transfer coefficients correspond to those predicted by models.

Finally, close to the critical point of the binary system at a given temperature, a sharp decline of the mass-transfer coefficient is observed. This effect is a result of the widening of the interfacial region, which then represents an additional resistance as the solvation process of the molecules becomes limiting. Matter then is transported in the form of clusters rather than as molecules, causing the Fickian diffusion coefficient to approach zero [13, 14].

This work shows that correlations describing liquid-phase mass-transfer coefficients at high pressures give conservative estimations. Actual coefficients are higher except near the critical point of the mixture.

Mass transfer thus is generally better than predicted. The user of these correlations for the design of processes involving a supercritical fluid and a liquid finds himself on the safe side.

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