Physical Absorption of CO_2 and Propene Into Toluene/Water Emulsions

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The physical absorption of CO_2 and propene into toluene/water emulsions is studied in a stirred cell and laminar film absorber. Experimentally observed mass-transfer rates are compared to an absorption model, based on Higbie's penetration theory describing physical gas absorption into an emulsion. For all absorption experiments in a stirred cell absorber (toluene fractions and stirring rates), experimentally observed mass-transfer rates are considerably higher than the rates predicted by the absorption model. Moreover, the absorption rate decreases with increasing stirring rate, whereas no influence of the stirring rate is predicted by the absorption model. In contradiction to the absorption experiments in a stirred cell absorber, the observed mass-transfer rates in the laminar film absorber agree with the model simulations. Probable existence of a very thin toluene layer is observed on top of the emulsion for the stirred cell experiments, likely due to minor phase separation. Since in the laminar film absorber gas-liquid interface and the gravity force are parallel, this phenomenon does not probably occur significantly for absorption experiments in this absorber. The observed mass-transfer phenomena can be explained, at least qualitatively, from the occurrence of a thin toluene layer.

Introduction

The absorption of a gas into a liquid is a frequently encountered operation in process industry. Gas absorption can be enhanced considerably either homogeneously by a chemical reaction or heterogeneously by a second phase present in the liquid. An example of homogeneous enhancement is the absorption of the acid gases H_2S, COS, and CO_2 into basic alkanolamine solutions. Heterogeneous enhancement can be achieved by the presence in the liquid of a finely dispersed second phase with a higher specific capacity for the gas to be absorbed than the continuous phase. This second phase can be either a solid phase or a liquid phase which is immiscible with the continuous liquid phase. The former system is usually referred to as a slurry whereas the latter system is called an emulsion. Examples of gas absorption into a slurry are the absorption of H_2 into a metalhydride/silicone oil slurry (Holstvoogd et al., 1986) and the absorption of various gases into activated carbon/water slurries (Alper et al., 1980; Schumpe et al., 1987; Tinge et al., 1987, 1990).

Recently gas absorption into emulsions has received considerable attention in literature. Bruining et al. (1986) presented some experiments for the absorption of oxygen into aqueous sodium sulphite solutions in the presence of a dispersed organic phase. The limited experimental data of Bruining et al. (1986) were, however, systematically higher than their theoretically derived maximum enhancement factor. Mehra and Sharma (1986) and Mehra et al. (1988) studied experimentally the absorption enhancement of propene and butene into chlorobenzene/aqueous sulfuric acid emulsions. These absorption experiments could be described reasonably well by the mass-transfer model developed by Mehra (1988).

For a full and correct understanding of the mass-transfer phenomena which underly gas absorption into emulsions, physical absorption experiments are obviously indispensable. However, true physical absorption experiments into emulsions seem not to be available in open literature. In the present work, therefore, experiments have been carried out for the physical

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absorption of CO_2 and propene into toluene/water emulsions. These systems were investigated in a stirred cell absorber with a flat, horizontal gas-liquid interface and in a laminar film absorber. The experimental data were compared with predictions by an unsteady-state numerical flux model, which describes physical gas absorption into an emulsion.

Literature

Recently, enhancement of mass-transfer rates by means of an immiscible second liquid phase has received a lot of attention. Most publications deal with mass-transfer enhancement in gas-liquid systems, though mass-transfer enhancement in liquid-liquid and solid-liquid systems has been described also (Bunton et al., 1976; Janakiraman and Sharma, 1982, 1985a). A possibly important application of mass-transfer enhancement by means of emulsions in gas-liquid systems seems to be the oxygenation of the liquid phase in aerobic fermentation or biological wastewater treatment (Rols et al., 1990).

Early work on gas absorption enhancement by means of an emulsified second phase has been carried out by Yoshida et al. (1970) and Linek and Benes (1976). In both works the stability of the emulsions applied was probably not sufficient to obtain reliable experimental data for gas absorption into emulsions. Moreover, no data on droplet diameters are reported. Therefore, both works should be regarded as merely exploratory.

Bruining et al. (1986) investigated the absorption of oxygen into aqueous sodium sulphite solutions in the presence of a dispersed organic phase in a stirred cell absorber. The sodium sulphite concentration was chosen such that the bulk concentration of oxygen equalled zero and that no mass-transfer enhancement due to chemical reaction occurred. They developed a simple penetration theory absorption model which allowed to calculate a maximum possible enhancement factor:

$$E_{\max} = \sqrt{(1+\epsilon_{\rm dis}(M-1))} \tag{1}$$

with:

$$M = \frac{(m)_{\text{dispersed phase}}}{(m)_{\text{continuous phase}}} \tag{2}$$

The enhancement factor was defined as the ratio of the fluxes in the presence of droplets and in the absence of droplets. In the derivation of Eq. 1 it was assumed that the interfacial concentration of oxygen was entirely determined by the continuous phase. The maximum enhancement factor is attained when the oxygen concentrations in continuous and dispersed phase are in equilibrium with each other. However, the experimentally determined enhancement factor for most experiments presented by Bruining et al. (1986) was actually higher than predicted from Eq. 1.

A considerable amount of work on gas absorption into emulsions has been carried out by Mehra (Mehra and Sharma, 1985, 1986, 1988; Mehra, 1988, Mehra et al., 1988). Mehra (1988) presented a penetration theory flux model which describes gas absorption into a liquid in the presence of an emulsified phase and accompanied by a first-order reaction both in the continuous and in the dispersed phase. It was assumed that the interfacial gas concentration was entirely determined by the continuous phase. Model simulations were compared to experimental data obtained in a stirred cell absorber for the absorption of propene, 1-butene, and isobutene into chlorobenzene/aqueous sulfuric acid solutions. In these systems a first-order reaction occurs in the continuous phase (Sankholkar and Sharma, 1973). Agreement between experiment and calculation was shown to be acceptable, although the comparison between model simulation and experiment was seriously hampered by the absence of reliable physical solubility data for propene, 1-butene, and isobutene in aqueous sulfuric acid. Moreover, it should be pointed out that the model description presented by Mehra (1988) was not validated by physical absorption experiments but only by absorption experiments in reactive emulsion systems. Chaudhuri and Sharma (1989) reported some experimental data for the enhanced absorption of COS into emulsions of toluene in aqueous alkaline solutions. Their experimentally determined absorption rates were in acceptable agreement with the absorption rates predicted by the model of Mehra (1988).

Modeling

Several authors have proposed an unsteady-state pseudo-homogeneous model to describe gas absorption into a liquid in the presence of a second immiscible phase with finite capacity (Holstvoogd et al., 1986; Mehra, 1988, 1990). The use of a steady-state pseudo-homogeneous model has been proposed in literature (Janakiraman and Sharma, 1985b). It should be realized, however, that a steady-state model is not able to describe the time-dependent saturation of droplets or particles with finite capacity. Recently, heterogeneous models have been developed to describe gas absorption into slurries (Holstvoogd et al., 1988; Karve and Juvekar, 1990).

In the present work physical absorption of a gas into an emulsion is described by means of a pseudo-homogeneous model based on Higbie's penetration theory. This leads to the following partial differential equations for continuous and dispersed phase respectively:

$$(1-\epsilon_{\rm dis})\frac{\partial(A)_{\rm con}(x,t)}{\partial t} = D_{\rm eff}\frac{\partial^2(A)_{\rm con}(x,t)}{\partial x^2} - k_{L,{\rm con}}a_{\rm dis}\left\{(A)_{\rm con}(x,t) - \frac{(A)_{\rm dis}(x,t)}{M}\right\} \tag{3}$$

$$\epsilon_{\rm dis}\frac{\partial(A)_{\rm dis}(x,t)}{\partial t} = k_{L,{\rm con}}a_{\rm dis}\left\{(A)_{\rm con}(x,t) - \frac{(A)_{\rm dis}(x,t)}{M}\right\} \tag{4}$$

Initial and boundary conditions are given by:

$$t=0 \quad x>0: \quad (A)_{\rm con}(x, t=0) = (A)_{\rm con,bulk} \tag{5}$$

$$t>0 \quad x=0: \quad -D_{\rm eff}\left\{\frac{\partial(A)_{\rm con}(x,t)}{\partial x}\right\}_{x=0} = k_g\left\{(A)_g - \frac{(A)_{\rm con}(x=0,t)}{m_{A,{\rm con}}}\right\} \tag{6}$$

$$t>0 \quad x=\infty: \quad (A)_{\rm con}(x=\infty, t) = (A)_{\rm con,bulk} \tag{7}$$

$$t=0 \quad x>0: \quad (A)_{dis}(x, t=0) = (A)_{dis,bulk} \tag{8}$$

The mass-transfer model represented by Eqs. 3 to 8 assumes that no direct contact takes place between gas phase and dispersed phase and that, as a result, the interfacial concentration is entirely determined by the gas solubility in the continuous phase. This assumption seems justified for systems in which the dispersed phase is an insoluble solid. In the case of emulsions, however, it should be regarded more carefully as even very little phase separation may affect the interfacial concentration considerably.

For the calculation of the bulk concentrations in continuous and dispersed-phase equilibrium conditions are assumed. The effective diffusivity D_{eff} is calculated according to the approach of Jefferson et al. (1958) for the effective thermal conductivity in dispersions (see also Crank, 1975; Wubs et al., 1991). The resistance to mass transfer from continuous to dispersed phase is assumed to be entirely determined by the mass-transfer resistance in the continuous phase. Considering the higher gas solubility in the dispersed phase and the curvature of the interface between continuous and dispersed phase, this assumption seems very reasonable. The mass-transfer coefficient $k_{L,con}$ is calculated from Eq. 9, which supposes negligible interaction among the droplets.

$$k_{L,con} = \frac{2D_{A,con}}{d_p} \tag{9}$$

The set of Eqs. 3 to 8 was solved using the discretization technique of Baker and Olifant. Details concerning the numerical solution method can be found elsewhere (Cornelisse et al., 1980; Holstvoogd et al., 1986).

Solving Eqs. 3 to 8 yields time- and place-dependent concentration profiles, from which the average mass-transfer flux over the contact time can be calculated. In gas absorption accompanied by chemical reaction the effect of the chemical reaction on the mass-transfer flux is often represented by an enhancement factor. This enhancement factor is defined as the ratio of the mass-transfer flux with reaction and the physical mass-transfer flux at the same hydrodynamic conditions and the same driving force. For physical gas absorption into emulsions a similar enhancement factor can be introduced to describe the effect of the emulsified droplets on the mass-transfer rates:

$$E = \frac{(J)_{\epsilon_{dis}}}{(J)_{\epsilon_{dis}=0}} \tag{10}$$

The mass-transfer flux in the absence of droplets is calculated from Eqs. 3, 5, 6, and 7 with ϵ_{dis} and a_{dis} set to zero.

In Figure 1 some simulation results are presented for a system with a high solubility ratio ($M=100$). This figure illustrates clearly the influence of emulsified phase fraction and droplet size on the calculated enhancement factors as a function of the contact time. At very short contact times the emulsified droplets do not yet take part in the mass-transfer process due to the mass-transfer resistance to these droplets, whereas the liquid volume represented by emulsified phase is taken into account in the calculation of $J_{\epsilon dis=0}$. Consequently, an enhancement factor somewhat smaller than 1 is calculated at very short contact times. At sufficiently large contact times a maximum enhancement factor is calculated which coincides with the maximum enhancement factor given by Eq. 1 (Bruining et al., 1986). At intermediate contact times the absorption flux is increased by the presence of the emulsified droplets but the concentration of A in the emulsified phase does not reach equilibrium with the concentration of A in the continuous phase.

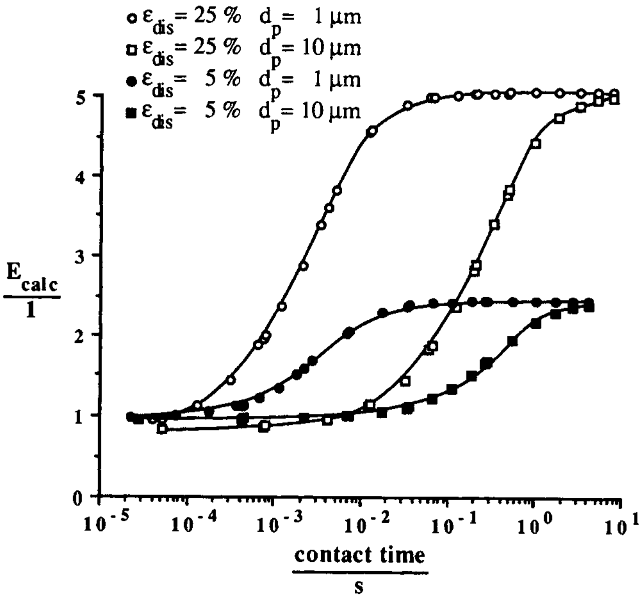

Figure 1. Calculated enhancement factors for physical gas absorption into emulsions.

$D_{A,con} = D_{A,dis} = 2\times10^{-9}\,\text{m}^2\cdot\text{s}^{-1}$, $m_{A,con} = 0.15$, $m_{A,dis} = 15$, $M = 100$.

The numerical mass-transfer model represented by Eqs. 3 to 8 requires a substantial amount of input data. Diffusivity and solubility data for carbon dioxide and propene in water and toluene were obtained from literature and are presented in Table 1. Gas absorption experiments for CO_2 and propene into water in the stirred cell absorber yielded a relationship between k_L and the stirrer speed. This relationship was used to estimate contact times for the absorption experiments into emulsions, assuming a *Re*, *Sc*, *Sh* relationship similar to that developed by Versteeg et al. (1987) for gas absorption into aqueous solutions in a stirred cell absorber. Densities, viscosities, and droplet sizes were measured in the present work.

Experimental

The emulsions used in the present work consisted of toluene in water stabilized by a nonionic emulsifier. The emulsifier

Table 1. Solubility and Diffusivity Data ($T=298$ K)

System	m	D (10^9 m$^2\cdot$s^{-1})	Reference
CO_2/H_2O	0.82	1.92	Versteeg and van Swaaij (1988)
CO_2/toluene	2.35	4.02	Littel et al. (1992)
propene/H_2O	0.15	1.24	Littel et al. (1992)
propene/toluene	15.5	2.30	Littel et al. (1992)

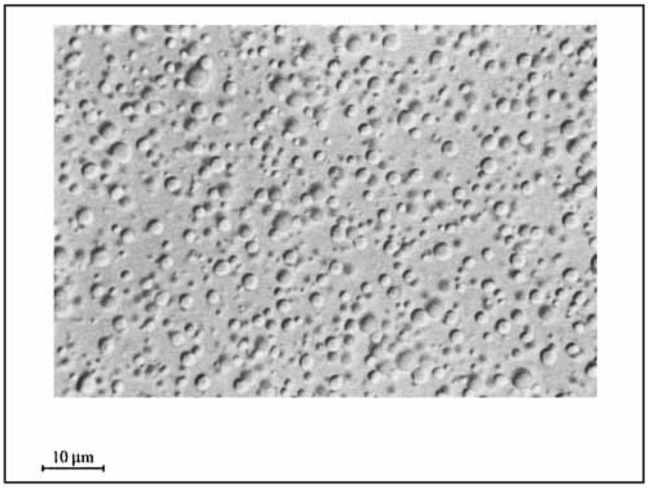

Figure 2. Representative microscopic image of toluene/water emulsion.

3 vol. % tol, dp = 3 μm.

applied was a polyethoxyalkylfenol (commercially available as Igepal CO-720). The concentration of emulsifier with respect to toluene was about 10% by volume. Toluene and Igepal CO-720 were obtained from Merck and Aldrich, respectively. The toluene droplet size in the emulsions was measured by means of an optical microscope with differential interference contrast (Olympus BH-2). For all toluene fractions applied, mean droplet sizes were smaller than 3 μm and droplet size distributions were rather narrow. Figure 2 shows a representative microscopic image of the toluene/water emulsions applied in the present work. It should be noted that the apparent toluene fraction which follows from Figure 2 is much higher than the actual toluene fraction due to the depth of field of the microscope with respect to the droplet size.

Emulsion densities were measured by means of a PAAR DMA58 densitometer. In initial experiments a linear relationship was determined between emulsion density and toluene fraction. This relationship was subsequently used to estimate accurately the toluene fraction in the emulsions used for mass-transfer experiments. Emulsion viscosities were measured with Ubbelohde viscosimeters. From measurements in Ubbelohde viscosimeters with different capillary diameters it was concluded that the emulsions applied in the present work showed Newtonian behavior for all toluene fractions used. This observation is in agreement with literature (Yan et al., 1991).

Solubility measurements were carried out in an experimental setup which consisted of a 1,000-mL stirred cell absorber with a high-intensity stirrer and a 230-mL gas storage vessel, both equipped with a pressure transducer. The gas storage vessel was used to determine exactly the amount of gas fed to the stirred cell absorber. The stirred cell absorber was operated batchwise with respect to gas and liquid phase. For propene absorption it was necessary to take into account nonideality of the gas in order to arrive at reliable solubility data (correction by means of the Redlich-Kwong equation of state).

Mass transfer was studied in a 1,250-mL stirred cell absorber with a flat, horizontal gas-liquid interface (geometric surface area 78×10^{-4} m^2). The stirred cell absorber was operated batchwise with respect to gas and liquid phase. The gas and liquid phase were stirred independently of each other by a turbine type stirrer. The decrease of the gas pressure, indicated by a pressure transducer, was recorded as a function of time. The initial pressure in each experiment was about 0.09–0.10 MPa. The absorption process was followed during the initial 40–50 min during which period the relative pressure decrease allowed an accurate calculation of the absorption flux. The relation between the relative pressure decrease and the absorption flux is given by Eq. 11 for a gas which follows the ideal gas law:

$$V_g \frac{d\left(\frac{P_A}{RT}\right)}{dt} = -J_A S \qquad (11)$$

The same stirred cell absorber was used in all absorption experiments. Further details concerning experimental procedure can be found elsewhere (Blauwhoff et al., 1984). Characterization of the stirred cell absorber was carried out by physical absorption of CO_2 and propene into water. This yielded the following relationships for the mass-transfer coefficients as a function of the stirrer speed:

$$k_{L,CO_2} = 1.87\times10^{-5}\, N^{0.85} \qquad (12)$$

$$k_{L,\text{propene}} = 1.48\times10^{-3} N^{0.85} \qquad (13)$$

Some gas absorption experiments into emulsions were carried out in a laminar film absorber. The laminar film flowed on the outer surface of a smoothed stainless steel tube with a diameter of 18×10^{-3}m. Film lengths up to 0.1 m and varying liquid velocities were applied. Experimental setup and procedure were essentially identical to those described by Nijsing et al. (1959).

For all mass-transfer experiments gas-phase resistance could be neglected as only pure gases were applied. All experiments were carried out at a constant temperature of 298 K.

Results

Physical data

Separate solubility measurements were carried out for carbon dioxide and propene in emulsions to check whether the gas solubility in emulsions can be calculated from the solubilities in the pure liquids. The experimental results could be described accurately by Eq. 14:

$$(m_A)_{\text{emulsion}} = (1-\epsilon_{\text{dis}})(m_A)_{H_2O} + \epsilon_{\text{dis}}(m_A)_{\text{toluene}} \qquad (14)$$

The presence of an emulsifier in the emulsion seems not to affect the gas solubility to a significant extent. All mass-transfer experiments carried out in the stirred cell absorber were allowed to reach equilibrium, in order to obtain additional information on the gas solubility. These experiments confirmed Eq. 14.

A relationship with the same form as Eq. 14 was found to describe the density of toluene/water emulsions. The emulsion viscosity as a function of the toluene fraction could be described by Eq. 15:

Table 2. Data CO_2 Absorption into Toluene/Water Emulsions ($T = 298$ K)

N (s^{-1})	Toluene (Vol. %)	k_L (10^5 m·s^{-1})	E_{model}	E_{exp} Min.	E_{exp} Max.
0.80	4.02	1.49	1.04	1.92	2.38
0.80	13.0	1.43	1.12	2.39	3.64
1.05	1.23	1.91	1.01	1.36	1.96
1.05	5.43	1.83	1.05	1.81	2.09
1.05	10.5	1.80	1.09	1.96	2.62
1.05	15.2	1.78	1.13	2.23	2.78
1.05	20.6	1.68	1.18	2.41	3.58
1.60	2.67	2.73	1.03	1.40	1.55
1.60	12.8	2.58	1.11	2.56	2.62
1.88	1.07	3.17	1.01	1.21	1.67
1.88	5.31	3.04	1.05	1.78	1.94
1.88	9.75	3.01	1.09	1.92	2.09
1.88	14.5	2.94	1.13	1.33	2.53
1.88	20.0	2.82	1.17	1.66	2.81
1.88	29.3	2.69	1.25	1.56	3.79
1.88	38.5	2.59	1.32	1.39	4.08

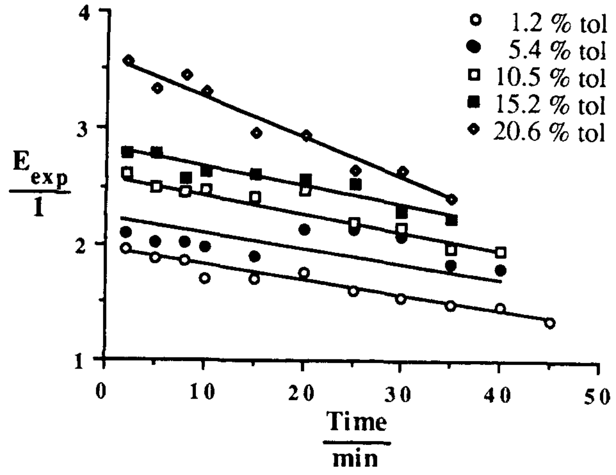

Figure 4. Influence of toluene concentration on the E_{exp} for CO_2.

$N = 1.05\ s^{-1}$.

$$\frac{\eta_{emulsion}}{\eta_{water}} = \exp\left\{\frac{3.0\epsilon_{dis}}{1 + 1.39\epsilon_{dis}}\right\} \tag{15}$$

Stirred cell absorption experiments for CO_2 into emulsions

Physical absorption experiments for CO_2 into toluene/water emulsions were carried out at various toluene fractions and stirring rates. The CO_2 solubility ratio M between water and toluene is 2.85 and, consequently, it was expected that the mass-transfer rate would only be slightly enhanced by the presence of toluene droplets.

A survey of the experimental results is presented in Table 2 and in Figures 3 to 6. For all CO_2 absorption experiments into toluene/water emulsions (for all toluene fractions and all stirring rates applied), the observed mass-transfer rates were considerably higher than the absorption rates predicted by the absorption model. The enhancement factors calculated by the absorption model were maximum enhancement factors (Eq. 1) as equilibrium between continuous and dispersed phase was reached easily within the contact time. The disagreement between experiment and model prediction is illustrated in Figure 3 which shows the mass-transfer rate as a function of time for a 1.2% toluene/water emulsion. Model simulations predicted a very small effect on the mass-transfer rate for this system because of the low toluene concentration in combination with the low solubility ratio. However, experimentally a considerable increase of the mass-transfer rate is observed.

The influence of the toluene fraction on the enhancement factor (and therefore on the mass-transfer rate) is illustrated in Figure 4 and this figure clearly shows that the mass-transfer rate increases with increasing toluene fraction. The relative increase of the mass-transfer rate, however, is considerably larger than predicted by the absorption model. This leads to the behavior that, under the same initial conditions, an emulsion with a high toluene fraction reaches quicker equilibrium than an emulsion with a low toluene fraction (see also Figure 5). Considering the higher capacity of the emulsion with a higher toluene fraction, this behavior is rather peculiar for purely physical absorption.

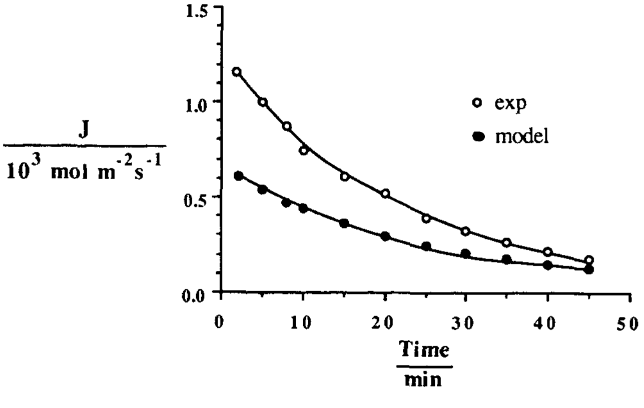

Figure 3. Experimentally observed CO_2 absorption rate in comparison to the predicted absorption rate by the absorption model.

1.23 vol % toluene, $N = 1.05\ s^{-1}$.

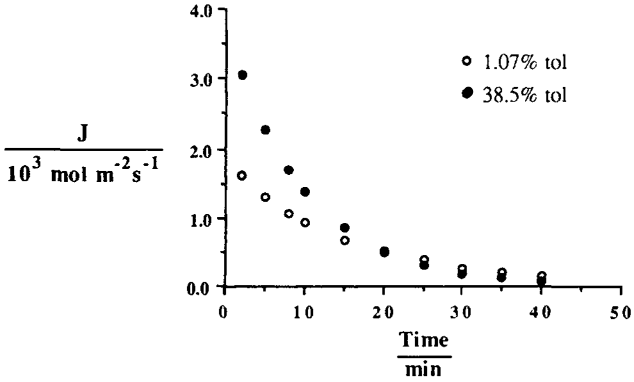

Figure 5. Experimentally observed CO_2 absorption rates.

$N = 1.88\ s^{-1}$.

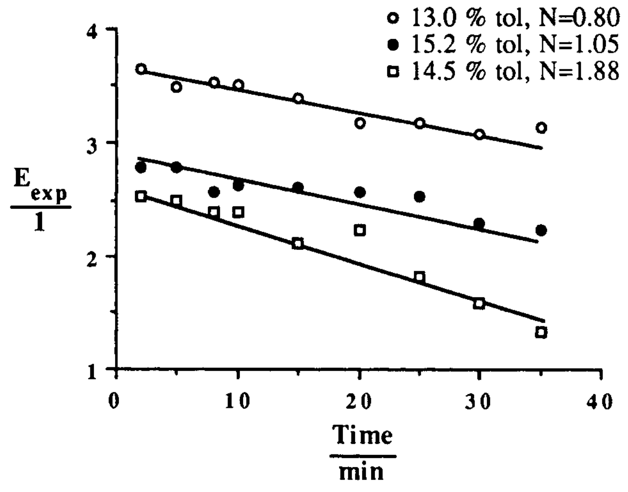

Figure 6. Influence of the stirring rate on the E_{exp} for CO_2.

Table 3. Data Propene Absorption into Toluene/Water Emulsions ($T = 298$ K)

N (s^{-1})	Toluene (Vol. %)	k_L (10^5 m·s^{-1})	E_{model}	E_{exp} Min.	E_{exp} Max.
0.75	14.4	1.18	3.96	9.30	11.8
1.05	1.64	1.52	1.64	2.12	2.77
1.05	5.71	1.51	2.62	4.46	4.72
1.05	11.0	1.54	3.50	6.71	9.53
1.05	15.4	1.58	4.10	8.21	12.7
1.05	21.5	1.59	4.80	10.1	13.9
1.40	14.3	2.00	3.96	6.85	10.5
1.65	13.7	2.30	3.88	7.44	8.00
1.88	0.99	2.51	1.42	3.50	3.69
1.88	5.73	2.47	2.62	3.72	4.80
1.88	10.3	2.52	3.39	6.26	8.68
1.88	15.0	2.58	4.05	6.27	8.88
1.88	19.9	2.60	4.62	4.64	9.42
1.88	29.2	2.80	5.56	6.99	14.4
1.89	14.4	2.58	3.96	5.79	8.40
2.00	34.5	3.18	6.03	13.9	18.6

Figure 6 shows that the stirring rate has a substantial effect on the observed enhancement factors: the enhancement factors were found to decrease with increasing stirring rate. The absorption model predicts no influence of the stirring rate on the mass-transfer rate, as long as equilibrium between continuous and dispersed phase is reached within the contact time.

For all absorption experiments the observed enhancement factors were time-dependent, as can be concluded from Figures 4 and 6 and from Table 2 in which the observed minimum and maximum enhancement factors are given. This may indicate an influence of the driving force on the enhancement factors (that is, the absorption flux appears to be not entirely proportional to the driving force).

Stirred cell absorption experiments for propene into emulsions

Propene absorption experiments into toluene/water emulsions were carried out at various toluene fractions and stirring rates. The solubility ratio M for propene between water and toluene is 103 and a significant effect of the presence of toluene droplets on the mass-transfer rate was expected.

A survey of the experimental results is presented in Table 3 together with the enhancement factors calculated by the absorption model. These calculated enhancement factors were maximum enhancement factors (Eq. 1) as equilibrium between emulsified and continuous phase was just reached within the contact time. The observed enhancement factors were substantially higher than the enhancement factors predicted by the absorption model.

The absorption rate was found to increase with increasing toluene concentration but the relative increase of the absorption rate due to the increased toluene concentration was larger than predicted by the absorption model. The same effect was observed for the absorption of CO_2 into emulsions although the effect was less pronounced for the propene absorption experiments.

The data in Table 3 show that the observed enhancement factors decrease with increasing stirring rate. This effect of the stirring rate on the mass-transfer rate is remarkable and cannot be explained by the absorption model as long as equilibrium between emulsified and continuous phase is reached within the contact time.

In all absorption experiments for propene into emulsions a time dependence of the experimentally determined enhancement factor was observed (see Table 3). This may indicate that the mass-transfer rate was not entirely proportional to the driving force. The same phenomenon was also observed for CO_2 absorption into toluene/water emulsions.

Laminar film absorption experiments

In order to elucidate the phenomena observed in the stirred cell experiments, absorption experiments have been carried out in a laminar film absorber. The absorption of CO_2 was studied into a 6.8% and 18.8% toluene in water emulsion and the absorption of propene was investigated into a 3.4% and 18.7% toluene in water emulsion. The experimentally observed absorption rates were compared to the absorption rates calculated with the absorption model. The results of these comparisons are summarized in Figures 7 and 8 for CO_2 and propene, respectively. Some typical values for experimentally observed and calculated enhancement factors are presented in Table 4.

The model simulations showed that for CO_2 equilibrium between the concentrations in continuous phase and emulsified phase was still easily reached within the contact time, whereas for propene this equilibrium was not entirely reached for the experiments at the lower contact times. From the agreement for propene between experiment and model calculation it can be concluded that the mass transfer between continuous and emulsified phase seems to be acceptably described by Eq. 9, which assumes negligible interaction among the droplets.

Figures 7 and 8 show that model calculation and experiment coincide within experimental accuracy, which was estimated to be about 10%. This conclusion from the laminar film experiments is in striking contrast with the observations from the absorption experiments in a stirred cell absorber. It should

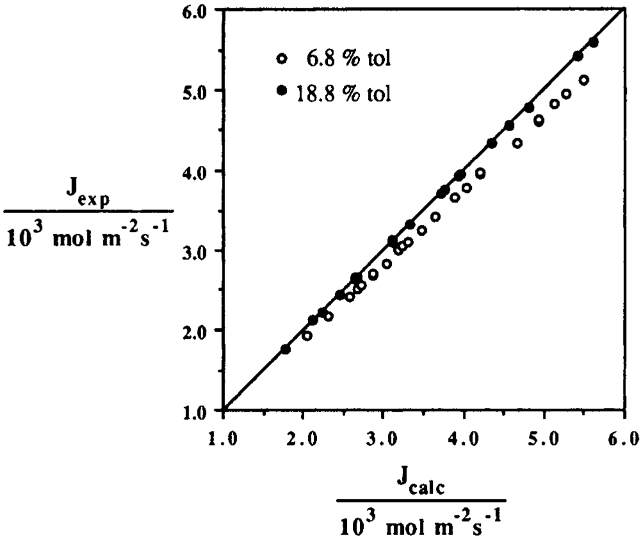

Figure 7. Parity plot for laminar film absorption experiments for CO_2.

be noted that special attention was paid to the contact times applied in the laminar film experiments: the higher contact times for the laminar film experiments were comparable to the lower contact times for the stirred cell experiments. Therefore, the differences between the laminar film and stirred cell experiments cannot be explained from differences in specific contact times.

Discussion

In the stirred cell experiments for both CO_2 and propene the observed mass-transfer rate was substantially higher than the mass-transfer rate predicted by the absorption model. This discrepancy urges to investigate the assumptions underlying the absorption model more closely.

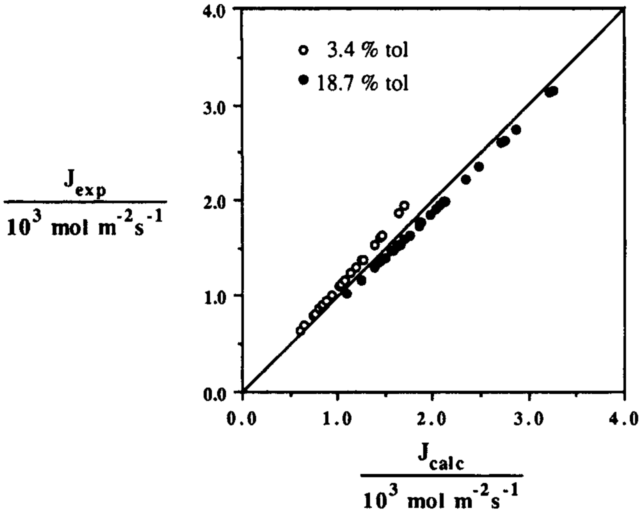

Figure 8. Parity plot for laminar film absorption experiments for propene.

Table 4. Typical Enhancement Factor Values in the Laminar Film Absorption Experiments

	Toluene (Vol. %)	k_L (10^5 m·s^{-1})	E_{model}	E_{exp}
CO_2 Absorption	6.7	14.8	1.06	1.00
		9.32	1.06	1.00
		5.91	1.06	1.00
CO_2 Absorption	18.8	14.1	1.16	1.16
		9.80	1.16	1.16
		4.60	1.16	1.16
Propene Absorption	3.4	11.6	1.99	2.22
		7.95	2.05	2.23
		4.63	2.08	2.23
Propene Absorption	18.7	10.1	4.34	4.14
		7.36	4.40	4.14
		3.96	4.44	4.14

In the model calculations it is assumed that the toluene fraction in the mass-transfer zone is identical to the toluene fraction in the bulk of the liquid. For gas absorption into slurries of activated carbon in water, a similar assumption was shown to be probably incorrect and it was argued by means of model simulations that the actual carbon concentration in the mass-transfer zone was probably much higher than the carbon concentration in the bulk of the liquid (Holstvoogd et al., 1988). A similar phenomenon may explain the high absorption rates observed for gas absorption into emulsions in a stirred cell absorber. Therefore, model simulations have been carried out for the absorption of CO_2 into a 1.2% toluene emulsion ($N = 1.05 \cdot s^{-1}$) in which the toluene fraction in the mass-transfer zone was varied. The simulation results, at zero bulk concentration of CO_2, are presented in Figure 9. The experimentally observed maximum enhancement factor at zero bulk concentration for CO_2 absorption into a 1.2% toluene emulsion was 1.96. From a comparison of this experimental result with the model simulations presented in Figure 9, it can be concluded that an explanation of the observed phenomena

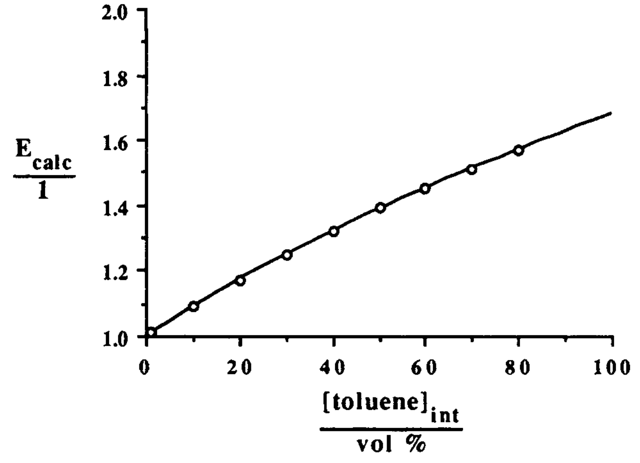

Figure 9. Calculated effect of an increased toluene fraction in the mass-transfer zone.

CO_2 absorption into 1.2% toluene, $(A)_g = 40$ mol·m^{-3}, $(A)_L = 0$, $k_L = 1.9 \times 10^{-5}$ m·s^{-1}.

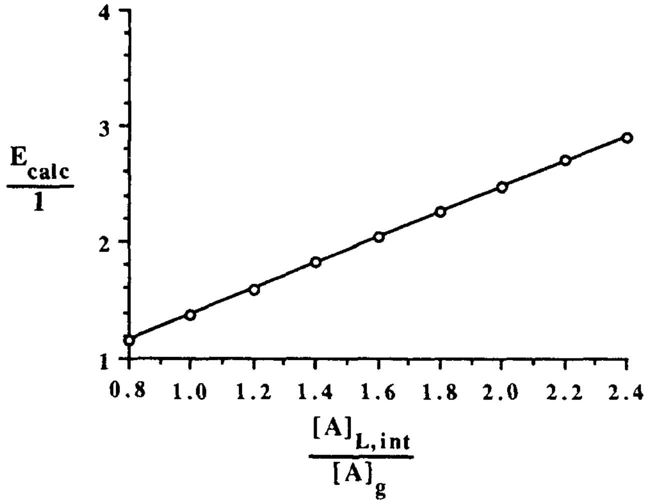

Figure 10. Calculated effect of an increased interfacial concentration: $m*(A)_g$.

CO_2 absorption into 20% toluene, $(A)_g = 40\ mol \cdot m^{-3}$, $(A)_L = 0$, $k_L = 1.7 \times 10^{-5}\ m \cdot s^{-1}$.

from a higher toluene fraction is not valid. Therefore, this explanation must be rejected.

A second important assumption underlying the absorption model is that no direct contact exists between gas phase and emulsified phase. So in the model calculations it is assumed that the interfacial concentration is entirely determined by the gas solubility in the continuous phase. Theoretically, the actual gas solubility which determines the interfacial concentration may vary between the gas solubility in the continuous phase and that in the emulsified phase. Therefore, model simulations were carried out for CO_2 absorption into a 20% toluene emulsion ($N = 1.05 \cdot s^{-1}$) in which the interfacial concentration was varied between these two extreme situations. The simulation results at zero bulk concentrations are reported in Figure 10. Comparison of the results in Figure 10 to the maximum experimental enhancement factors (E_{exp} at zero bulk concentration) in Table 2 for 20% toluene emulsions shows that the explanation of the observed phenomena from an increased interfacial concentration is invalid.

In summary, the observed discrepancies between experimentally observed and calculated mass-transfer rate cannot be explained from either an underestimation of the actual toluene fraction in the mass-transfer zone or an underestimation of the interfacial concentration. However, a combination of both effects is able to explain, at least qualitatively, the observed phenomena. The simplest physical image which follows from a combination of both effects is the existence of a very thin toluene layer on top of the emulsion (see Figure 11), which covers the gas-liquid interface at least partially. This thin toluene layer may be the result of minor phase separation because thermodynamically stable emulsions are very hard to obtain and the separated toluene will float on the emulsion due to gravity forces. Another reason for a thin toluene layer between gas and emulsion may follow from interfacial energy considerations, and the situation pictured in Figure 11 may have the lowest interfacial energy. The former explanation appears to be confirmed by the absorption experiments in a laminar film absorber, in which gas-liquid interface and gravity force are parallel. For the laminar film absorber, experimentally observed and calculated mass-transfer rates agreed within experimental accuracy. From the experimental absorption data a thickness of the toluene layer of about 20-80 μm can be estimated which amounts to about 30-60% of the total corresponding film thickness.

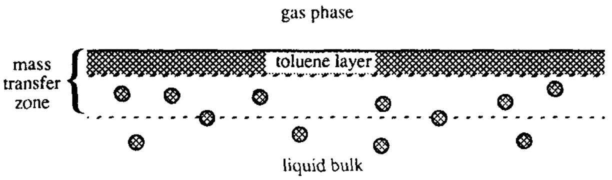

Figure 11. Gas-liquid interface in stirred cell experiments.

The assumption of a thin toluene layer on top of the emulsion can explain several phenomena observed in the stirred cell experiments. The experimental enhancement factors were found to decrease with increasing stirring rate. Obviously, an increasing stirring rate would result in a thinner toluene layer, and this will result in a decrease of the observed enhancement factor. The experimental enhancement factors were found to increase more than proportionally with the toluene fraction. A higher toluene fraction would probably be accompanied by more phase separation and this would result in a thicker toluene layer and higher mass-transfer rates. The observed enhancement factors appeared to decrease with decreasing driving force. This phenomenon might be related to the phenomena reported by Littel et al. (1991) for gas absorption into nonaqueous solutions in a stirred cell absorber. As yet the assumption of a thin toluene layer appears to explain most of the observed phenomena for gas absorption into toluene/water emulsions. However, it should be realized that only indirect evidence could be obtained for the existence of a thin toluene layer. Physical absorption experiments in emulsions with a dispersed phase heavier than water, as applied by Mehra et al. (1988) for reactive emulsions, may elucidate and complement the observations in the present work.

Conclusions

The physical absorption of CO_2 and propene into toluene/water emulsions has been studied in a stirred cell absorber and in a laminar film absorber. The experimentally observed mass-transfer rates have been compared to an absorption model, based on Higbie's penetration theory, which describes physical gas absorption into an emulsion. The absorption model assumes that no direct contact exists between gas and emulsified phase.

For all absorption experiments in a stirred cell absorber (for all toluene fractions and all stirring rates), the experimentally observed mass-transfer rates were considerably higher than the mass-transfer rates predicted by the absorption model. Moreover, the absorption rate enhancement was found to decrease with increasing stirring rate whereas no influence of the stirring rate was predicted by the adsorption model. In contradiction to the absorption experiments in a stirred cell absorber, the observed mass-transfer rates in the laminar film absorber did agree, within experimental accuracy, with the model simulations.

Closer analysis of the observed phenomena indicated the probable existence of a thin toluene layer on top of the emulsion for the stirred cell experiments. This thin toluene layer is possibly the result of minor phase separation. Since in the laminar film absorber gas-liquid interface and the gravity force are parallel, this phenomenon did probably not occur to a significant extent for the absorption experiments in this absorber. The observed mass-transfer phenomena can be explained, at least qualitatively, from the occurrence of a thin toluene layer. It should be noted, however, that only indirect evidence for the existence of such a layer could be obtained in the present work.

The present work shows that validation of an absorption model by means of extensive physical absorption experiments is necessary for a full and correct understanding of the mass-transfer phenomena involved.

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Notation

a_{dis} = specific droplet surface area ($a_{\mathrm{dis}} = 6\epsilon_{\mathrm{dis}}/d_p$), $\mathrm{m^{-1}}$
C = concentration, $\mathrm{mol \cdot m^{-3}}$
d_p = droplet diameter, m
D = diffusivity, $\mathrm{m^2 \cdot s^{-1}}$
D_{eff} = effective diffusivity, $\mathrm{m^2 \cdot s^{-1}}$
E = enhancement factor
J = mole flux, $\mathrm{mol \cdot m^{-2} \cdot s^{-1}}$
k_g = gas-phase mass-transfer coefficient, $\mathrm{m \cdot s^{-1}}$
k_L = liquid-phase mass-transfer coefficient, $\mathrm{m \cdot s^{-1}}$
$k_L a$ = volumetric liquid-phase mass-transfer coefficient, $\mathrm{s^{-1}}$
$k_{L,\mathrm{con}}$ = droplet mass-transfer coefficient (Eq. 10), $\mathrm{m \cdot s^{-1}}$
m = dimensionless physical gas solubility
M = solubility ratio (Eq. 2)
R = ideal gas constant, 8.314 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
S = gas-liquid interfacial area, $\mathrm{m^2}$
t = time variable, s
T = temperature, K
x = space variable, m

Greek letters

ϵ = volume fraction dispersed phase
η = viscosity, Pa·s
ρ = density, $\mathrm{kg \cdot m^{-3}}$

Subscripts

A = component A
bulk = bulk conditions
calc = calculated
con = continuous phase
dis = dispersed (or emulsified) phase
eff = effective
exp = experimental
int = gas-liquid interface
g = gas phase
L = liquid phase
max = maximum

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