Calorimetric Studies of CO_2 Absorption into Toluene/Water Emulsions*

H. KIERZKOWSKA-PAWLAK and R. ZARZYCKI

Faculty of Process and Environmental Engineering, Technical University of Łódź,
PL-90-924 Łódź, Poland

Absorption of CO_2 into toluene/water emulsions was investigated at 293 K using a reaction calorimeter. The experimental results on Henry's constants for CO_2 indicated that the gas solubility in toluene/water emulsions could be calculated from the solubilities in the pure liquids. The molar heats of absorption were found to decrease with increasing toluene fraction in the emulsion. The observed mass transfer rates were considerably higher than the absorption rates predicted by the absorption model. Moreover, the enhancement factor, which was defined as the ratio of the mass transfer rate in the presence of the microphase to that in its absence, was found to decrease with an increase in stirring rate. The present results confirmed the earlier assumption of the probable existence of a very thin toluene layer on the top of the emulsion. However, contrary to the previous studies of this system, the observed enhancement factors were not time-dependent. The above disagreement can be explained by differences in estimating the volumetric liquid side mass transfer coefficient for CO_2 absorption into emulsion.

Absorption of a gas into a liquid is a frequently encountered operation in process industry. Gas absorption can be enhanced homogeneously by a chemical reaction in the liquid phase. Heterogeneous enhancement can be achieved by the presence in the liquid of a finely dispersed second phase with a specific capacity for the absorbed gas higher than the continuous phase. This second phase can be either a solid phase or a liquid, which is immiscible with the continuous phase.

An important application of the mass transfer enhancement by means of emulsions in gas-liquid systems is the oxygenation of the liquid phase in aerobic fermentation or biological wastewater treatment [1]. At present, some hydrocarbons are removed efficiently in the process of flue gas treatment by absorption in the oil/water emulsions.

In the available literature, there are few attempts of mathematical modelling of physical gas absorption into emulsions [1, 2]. The main assumptions incorporated in the existing models are the pseudohomogeneity and the thermodynamic stability of the emulsion. Moreover, it was assumed that the interfacial gas concentration, c_A^*, was entirely determined by gas solubility in the continuous phase. According to both the cited papers, the absorption rates measured experimentally were higher than those calculated from these models.

In the present work, the absorption of CO_2 into toluene/water emulsions was investigated in the reaction calorimeter under isothermal and isobaric conditions. The use of a reaction calorimeter for absorption studies is a novelty. The earlier experiments concerning the rate of CO_2 absorption into toluene/water system were carried out in a typical laboratory apparatus, containing the laminar jet and the stirred cell [1, 2]. Contrary to previous investigations, the present experimental technique additionally enabled a determination of gas solubility and molar heat of absorption.

EXPERIMENTAL

The reaction calorimeter CPA (Chemical Process Analyser, ChemiSens, Lund, Sweden) used in this work is a mechanically agitated stainless steel/glass reactor with an effective volume of 250 cm^3. A Peltier element mounted inside the bottom of the reactor serves as an efficient heating and cooling device and keeps temperature at a nearly constant level. Ports in the lid allow charging and sampling from both the gas and liquid phases. The system continuously measures the heat production rate, the reactor temperature, pH, the stirring rate, power, and the system pressure. All operating conditions as a function of time are recorded using the special data acquisition system based on
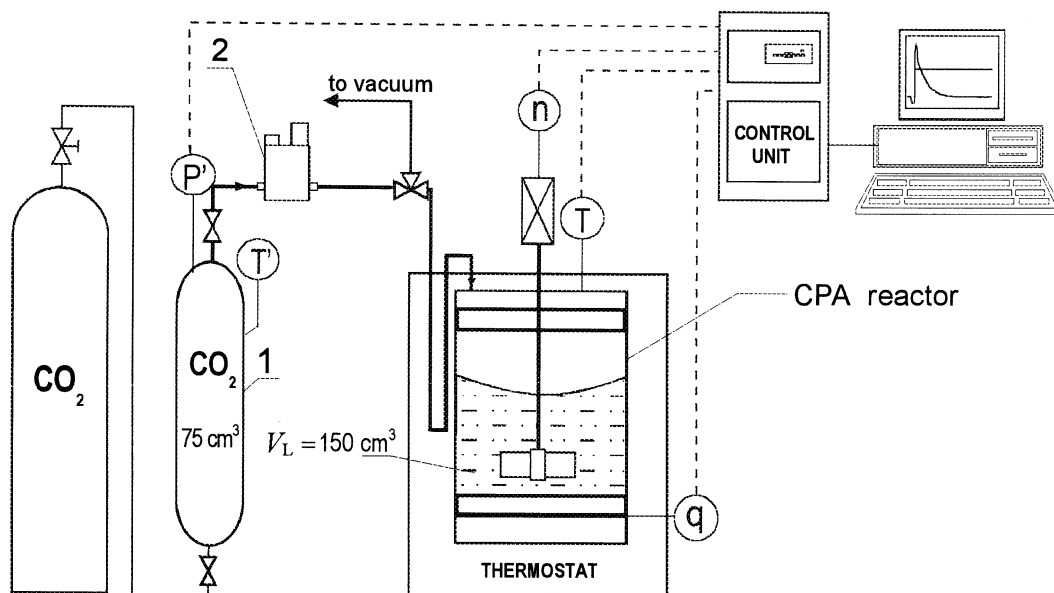

Fig. 1. Experimental set-up. 1 – Intermediate tank, 2 – downstream pressure regulator, n – stirring speed transducer, T – temperature sensor in the reactor, T' – temperature sensor in the intermediate tank, P' – pressure transducer, q – heat flow transducer.

the Wonderware InTouch (Wonderware Corporation, USA) environment. The scheme of the experimental set-up modified for the aim of absorption studies is shown in Fig. 1.

Calorimetric studies on the mass transfer in CO_2/toluene/water system involved measurements of the gas phase pressure (p'_A) in the intermediate tank and heat generation rate (q) with respect to time during semibatch isothermal absorption of the gas. Before starting the experiment, the emulsion in the amount of 150 cm^3 was first degassed and heated to 293 K. After equilibrium was established, pure carbon dioxide was charged to the reactor by a special feed line through the downstream pressure regulator, which enabled constant pressure p^*_A of 0.3 MPa to be kept in the reactor. After a few seconds when the pressure reached the set value, the process was initiated by switching on the stirrer at the desired mixing rate. The subsequent decrease of the gas pressure in the intermediate tank and additionally the rate of heat production was recorded until the equilibrium state. The measurements were carried out at a constant temperature of 293 K. The toluene fraction in the emulsion was in the range from 1 to 20 vol. %. The emulsifier applied was cetyltrimethylammonium bromide. The stirring rate varied from 400 to 600 min^{-1}. Fig. 2 illustrates that switching of the stirrer initiated the absorption process, which was manifested by the heat generation and the pressure decrease in the intermediate tank. The total pressure drop in the intermediate tank was necessary for calculating the gas solubility, while the time dependence of p'_A enabled the absorption rate N_A to be determined.

RESULTS AND DISCUSSION

CO_2 Solubility in Toluene/Water Emulsions

The gas solubility was expressed by Henry's constant (He $= p^*_A/c_A$). In the calculation of the amount of absorbed gas the Beatty—Bridgeman state equation was used. Due to the low solubility of CO_2 in the systems studied, constant liquid phase volume was assumed.

The results of solubility measurements are listed in Table 1. In general, the CO_2 solubility increases with increasing toluene fraction in the emulsion. The analysis of the data indicates that the gas solubility in toluene/water emulsions can be calculated from the solubilities in the pure liquids. The experimental results can be described by the following equation

$$\frac{1}{\text{He}_{\text{emulsion}}} = \frac{1 - x_{\text{tol}}}{\text{He}_{\text{water}}} + \frac{x_{\text{tol}}}{\text{He}_{\text{tol}}} \qquad (1)$$

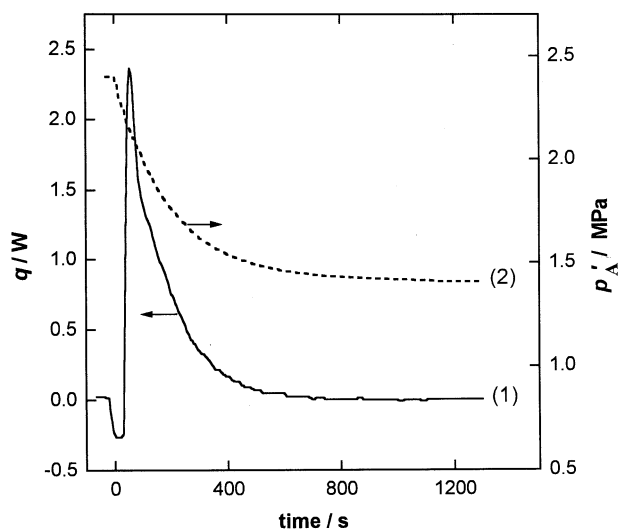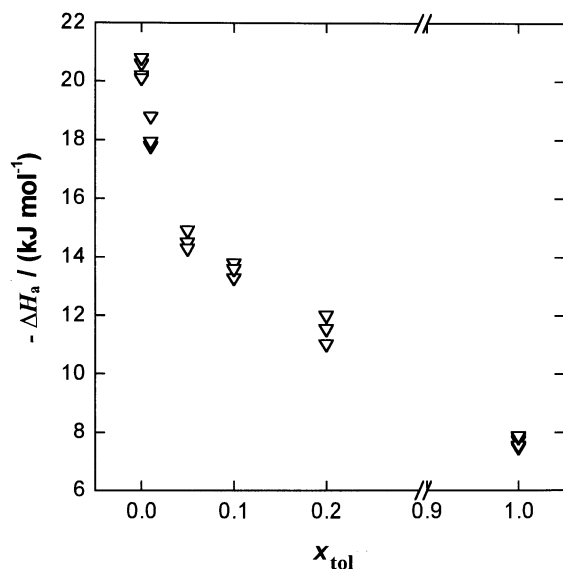### The Molar Heat of CO_2 Absorption into Toluene/Water Emulsions

The molar heat of absorption ΔH_a was determined from the following equation

$$-\Delta H_a = \frac{Q_a}{\Delta n_A} = \frac{\int_0^\infty q(t)\mathrm{d}t}{\Delta n_A} \qquad (2)$$

where Δn_A is the amount of substance of absorbed CO_2 and Q_a is the overall heat evolved during the

Table 1. Henry's Constants for CO$_2$ in Toluene/Water Emulsion at 0.3 MPa and 293 K

x_{tol}	0	0.01	0.05	0.1	0.2	1
He/(MPa m^3 kmol^{-1})	2.71	2.69	2.54	2.36	2.15	1.015

Fig. 2. Illustration of absorption experiment ($x_{tol} = 0.1$, $n = 500$ min^{-1}, $p_A^* = 0.3$ MPa). Heat generation rate q (1), pressure decrease p_A' (2).

Fig. 3. The molar heat of absorption *vs.* toluene fraction in the emulsion.

absorption, which was calculated by integrating the heat production rate curve. Fig. 3 shows that the molar heat of absorption decreased with an increase of toluene fraction in the emulsion.

Rate of CO$_2$ Absorption into Toluene/Water Emulsions

The mass balance equation based on the film theory, written for the component entering the liquid phase, has the following form

$$N_A = \frac{(dn_A)_L}{dt} = -\frac{(dn_A)_G}{dt} = (k_L a)V_L(c_A^* - c_A) \quad (3)$$

The film model predicts a linear dependence of gas absorption rate N_A and the driving force. N_A could be obtained from the present experimental data by differentiating the time curve of n_A based on the pressure decrease recorded as a function of time. The main problem in determining the $k_L a$ value from eqn (3) lies in the estimation of c_A^* for the emulsion. In the previous model calculations [1, 2], it was assumed that the interfacial concentration was entirely determined by the gas solubility in the continuous phase. In theory, 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.

Contrary to previous investigations [1, 2], the absorption process in this work was carried out in semi-batch conditions under the constant pressure in the reactor. Hence, under such conditions the unknown interfacial gas concentration c_A^* was constant during the experiment and eqn (3) could be rearranged to the form

$$\ln N_A = -(k_L a)t + \ln N_{A0} \quad (4)$$

Eqn (4) indicates that the dependence of logarithm of N_A *vs.* time is a straight line with a slope representing the value of volumetric liquid side mass transfer coefficient. An example of $k_L a$ determination is shown in Fig. 4. The results of $k_L a$ for water and toluene/water emulsions in the employed range of stirring rate are presented in Fig. 5.

It is worth noticing that the measured heat production rate q gives additional information about the rate of the process. For the physical absorption the following equation holds

$$N_A = -\frac{q}{\Delta H_a} \quad (5)$$

Substituting eqn (5) into eqn (4) we obtain
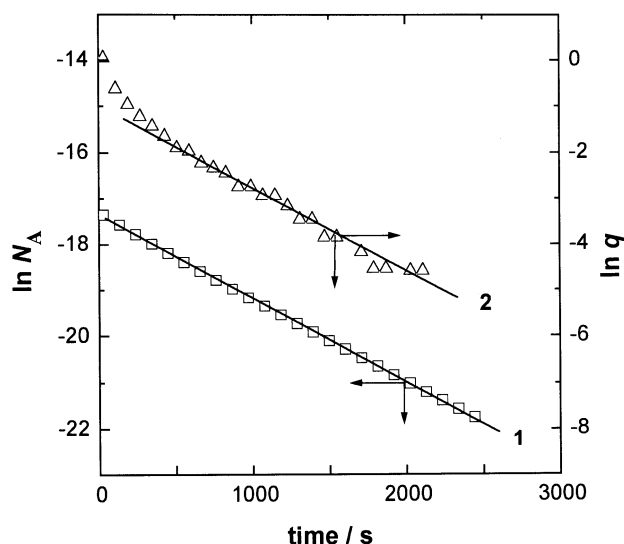
$$\ln q = -(k_L a)t + C_1 \quad (6)$$

Fig. 4. Illustration of $k_L a$ determination from eqns (4) and (6). Data based on the pressure decrease ($\square$) and heat generation rate ($\triangle$). 1. Linearization of eqn (4), $k_L a = 1.82 \times 10^{-3}$ s^{-1}; 2. linearization of eqn (6), $k_L a = 1.94 \times 10^{-3}$ s^{-1}.
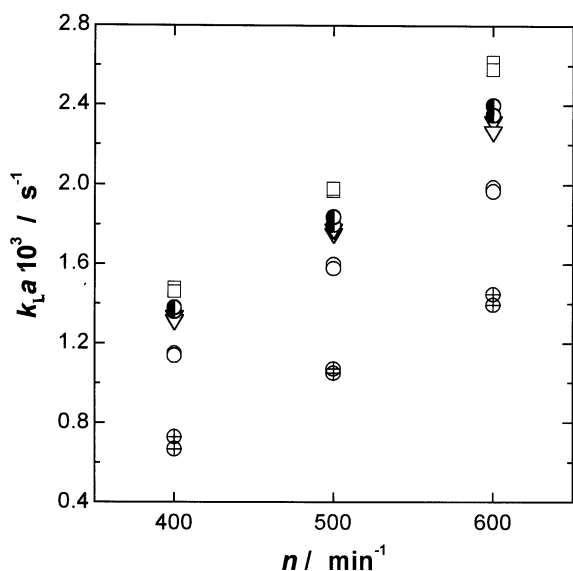

Fig. 5. $k_L a$ vs. stirring rate for different composition of emulsion. x_{tol}: 0 ($\oplus$), 0.01 ($\bigcirc$), 0.05 ($\triangledown$), 0.1 ($\bullet$), 0.2 ($\square$).

where $C_1 = \ln \dfrac{q_0}{|\Delta H_a|} + \ln |\Delta H_a|$ and q_0 is the heat generation rate for $t = 0$.

Eqn (6) indicates that in the case of isobaric and isothermal absorption of the gas the heat flow measurement enables $k_L a$ determination. Graphical illustration of the method based on the heat generation rate is also shown in Fig. 4. This method gave very similar values of $k_L a$ as those obtained from the pressure decrease. The above agreement demonstrates how

the heat flow data serve as an independent measure of the absorption rate. It should be stressed here that the method of $k_L a$ determination from the heat flow data presented in this study is original and has not been used before.

In physical gas absorption into emulsions the effect of the emulsified phase is often represented by the enhancement factor. This factor is defined as a ratio of the mass transfer rate in the presence of the microphase to that in its absence at the same hydrodynamic conditions and the same driving force [1]

$$E_{\exp} = \frac{(N_A)_{\text{emulsion}}}{(N_A)_{\text{water}}} = \frac{k_L a_{\text{emulsion}}}{k_L a_{\text{water}}} \qquad (7)$$

Under the assumption that the emulsion is stable and hence can be treated as a pseudohomogeneous system, the maximum possible enhancement factor E_{theor} can be calculated from the following equation [2]

$$E_{\text{theor}} = \sqrt{\left(1 + x_{\text{tol}}\left(\frac{\text{He}_{\text{water}}}{\text{He}_{\text{tol}}} - 1\right)\right)} \qquad (8)$$

The $\text{He}_{\text{water}}/\text{He}_{\text{tol}}$ ratio which occurs in eqn (8) is equal to 2.67 at $T = 293$ K and was determined from the present experimental data (Table 1). For the volume fractions of toluene 0.01, 0.05, 0.1, 0.2, the theoretical enhancement factors E_{theor} were equal to 1.01, 1.04, 1.08, 1.15, respectively. According to eqn (8) these values do not depend on the stirring rate.

The experimental values of enhancement factors were calculated from eqn (7) and are presented in Fig. 6. For all the experiments, the observed mass transfer rates were considerably higher than the absorption rates predicted by the absorption model (eqn (8)). Moreover, the enhancement factors were found
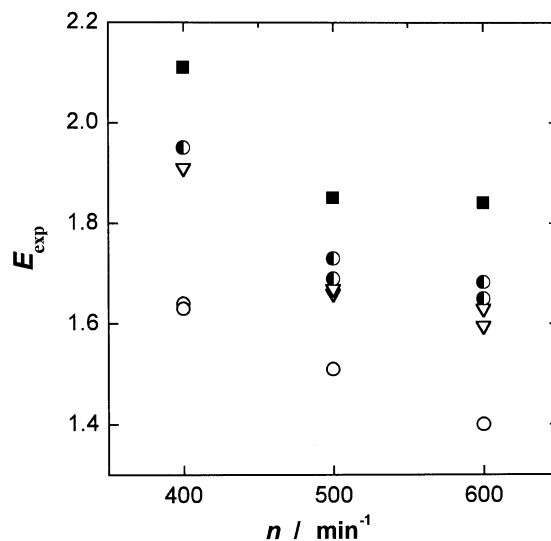

Fig. 6. $E_{\exp}$ for toluene/water emulsions vs. stirring rate. x_{tol}: 0.01 ($\bigcirc$), 0.05 ($\triangledown$), 0.1 ($\bullet$), 0.2 ($\blacksquare$).

to decrease with increasing stirring rate, whereas the absorption model predicted no influence of the stirring rate. These results are similar to those obtained by *Littel* and *van Swaaij* [1]. The authors explained the observed phenomena by a thermodynamic instability of the emulsion. They indicated that, under insufficient intensity of mixing, the system was no longer pseudohomogeneous. As a result of minor phase separation, toluene floats on the emulsion due to the gravity forces. Toluene forms a very thin layer, which covers the gas liquid interface. Thickness of this film increases with increasing toluene fraction in the emulsion and with decreasing stirring rate.

Considering the absorption of a pure gas into emulsion on the basis of film theory, the mass transfer resistance is located in the liquid film next to the gas-liquid interface. In the case of the emulsions studied in this work, the gas-liquid interface is covered by the toluene layer. The existence of this layer, which has a higher absorption capacity than the continuous phase (water), causes that the observed absorption rate is much higher than that calculated from the absorption models [1, 2]. Obviously, an increase in stirring rate would result in a thinner toluene layer, and this will result in a decrease of the observed enhancement factor. It should be noted that a significant enhancement of the absorption ($E_{exp} = 1.6$) occurs for a 1 % toluene/water emulsion. Model calculations (eqn (8)) predict a very small effect of the dispersed phase on the mass transfer for this system because of the low toluene concentration. However, considerably higher toluene fraction, $x_{tol} = 0.2$, results in only 30 % increase of the mass rate compared to a 1 % toluene/water emulsion. This result can be explained by the basic assumption underlying the film model that the toluene concentration in the bulk of the liquid phase does not influence the absorption rate. A higher toluene fraction would probably be accompanied by more significant phase separation and this would result in a thicker toluene layer and a higher absorption rate.

It should be noted that, in contradiction to the previous study of this system [1], the observed enhancement factors were not time-dependent. This disagreement can be explained by differences in estimating the volumetric liquid side mass transfer coefficient. In the previous paper, the rate of absorption into emulsion was curiously not entirely proportional to the driving force so the value of $k_L a$ also varied during the experiment. In the present work, the problem in correct estimating the driving force was omitted by calculating $k_L a$ from the slope of the absorption rate logarithm *vs.* time.

CONCLUSION

The CPA reaction calorimeter was used for measurements of the rate of CO₂ absorption into toluene/water emulsions. The experimental technique applied demonstrates an advantage of continuous monitoring of several quantities, which are involved in the absorption process. A single calorimetric run gives several pieces of information on gas solubility, heat of absorption, and also the process rate. Based on the heat flow data, a new method for determining the liquid side mass transfer coefficient was proposed.

The experimental results on Henry's constants for CO₂ indicated that the gas solubility in toluene/water emulsions could be calculated from the solubilities in the pure liquids. The molar heats of absorption were found to decrease with increasing toluene fraction in the emulsion. These values varied from -20.5 kJ mol⁻¹ for pure water to -7.7 kJ mol⁻¹ for toluene.

For all experiments of CO₂ absorption into toluene/water emulsion, the observed mass transfer rates were considerably higher than the absorption rates predicted by the absorption model. Moreover, the enhancement factor, which was defined as the ratio of the mass transfer rate in the presence of the microphase to that in its absence, was found to decrease with increasing stirring rate, whereas no influence of the stirring rate is predicted by the absorption model. The present results confirmed the earlier assumptions of the probable existence of a very thin toluene layer on the top of the emulsion [1]. However, in contradiction to the previous study of this system [1], the observed enhancement factors were not time-dependent. This disagreement can be explained by different methods of estimating the volumetric liquid side mass transfer coefficient.

None of the existing mathematical models takes into consideration the thermodynamic instability of the emulsion. From the disagreement of experimental findings and theoretical calculations it can be concluded that the theory does not involve all the essential processes occurring in the absorption.

SYMBOLS

E	enhancement factor	
ΔH_a	enthalpy of absorption	kJ mol⁻¹
He	Henry's constant	MPa m³ kmol⁻¹
$k_L a$	volumetric liquid side mass transfer coefficient	s⁻¹
n	stirring rate	min⁻¹
n_A	amount of substance of CO₂	kmol
N_A	absorption rate of CO₂	kmol s⁻¹
p_A	partial pressure of CO₂	MPa
q	heat flow rate	W
x_{tol}	volume fraction of toluene in the emulsion	

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2. Bruining, W. J., Joosten, G. E. H., Beeneckers, A. A. C. M., and Hofman, H., *Chem. Eng. Sci. 41*, 1873 (1986).