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Mass transfer coefficients of styrene into water/silicone oil mixtures: New interpretation using the "equivalent absorption capacity" concept

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HIGHLIGHTS

- Styrene absorption into water/silicone oil mixtures was investigated.
- Mixtures were considered pseudo-homogeneous phases.
- Oil addition hindered the mass transfer rate compared to the air/water system.
- An apparent decrease in K_La values due to silicone oil addition was observed.
- It is questionable to study the change in K_La in terms of silicone oil addition.

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ABSTRACT

The physical absorption of styrene into water/silicone oil systems at a constant flow rate for mixtures of different compositions (silicone oil volume fraction ϕ = 0%, 1%, 2%, 3%, 4%, 5%, 6%, 8%, and 10%) was investigated in laboratory-scale bubble reactors using a dynamic absorption method. Experimental results previously analyzed assuming no contact between gas and silicone oil [10] were reconsidered by applying the "equivalent absorption capacity" concept characterized by the value of the styrene partition coefficient between air and the mixture (H_{mix}). The results indicate that silicone oil addition slightly hinders the styrene mass transfer rate compared to the air/water system. Moreover, a dramatic decrease in K_La values due to silicone oil addition is observed. In comparison with similar measurements available in the literature, it is noted that this decrease in K_La value could be related to the change in the partition coefficient ratio $m_R = H_{water}/H_{oil}$. Two explanations concerning the relationship between the change in a hydrodynamic parameter (K_La) and that in a thermodynamic parameter (m_R) are proposed. Finally, it appears questionable to study the change in K_La in terms of silicone oil addition.

1. Introduction

Styrene, a xenobiotic volatile organic compound (VOC), is widely used in industrialized countries (production of resins and polymers such as polystyrene) and represents a severe environmental hazard which requires treatment. Biological treatment technologies, which have been recognized for many years as a cost-effective method for purifying air contaminated with low concentrations of odorous compounds [1,2], are limited by the low solubility of styrene in water and its toxicity towards biomass. Nonetheless, a Non-Aqueous Phase (NAP) such as silicone oil (a water-immiscible, biocompatible and non-biodegradable organic solvent) can be added to culture systems in order to overcome these physical constraints. In such multiphase gas/liquid/liquid systems (usually called Two Phase Partitioning Bioreactors: TPPBs [3]), mass transfer mechanisms between phases are still disputed but significant advances have been recently made. For example, Dumont et al. [4] have experimentally characterized and modeled the change in the partition coefficient of a substance (i.e. toluene; dimethylsulfide – DMS; dimethyldisulfide – DMDS) between air and water/silicone oil mixtures with the silicone oil volume fraction (ϕ). It was observed that silicone oil addition leads to a dramatic decrease in the partition coefficient and it was established that water/silicone oil mixtures can reasonably be considered a pseudo-homogeneous liquid from a mass transfer point of view. According to these authors, the absorption capacity of a biphasic water/silicone oil mixture can be classed as the absorption capacity of a pseudo-homogeneous phase whose physical properties (molecular weight and density) can be calculated from the physical properties of water and silicone oil ("equivalent absorption capacity" concept). This change in the partition coefficient was

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Nomenclature

A	interfacial area (m^{-1})
C	concentration (mol/m^3)
D	diffusion coefficient (m^2/s)
H	partition coefficient (–)
H'	partition coefficient ($Pa.m^3\ mol^{-1}$)
K_L	mass transfer coefficient ($m\ s^{-1}$)
K_La	volumetric mass transfer coefficient (s^{-1})
m_R	partition coefficient ratio (–)
R	universal gas constant ($J.mol^{-1}\ K^{-1}$)
T	temperature (K)
V_G	volume of the gas phase (m^3)
V_L	volume of the emulsion (m^3)

Greek Letters

δ	film thickness (m)
ϕ	dispersed liquid volume fraction (–)
τ	time constant (s)

Superscripts

$*$	equilibrium concentration of solute between liquid phase and gas phase

Subscripts

G	relative to the gas phase
L	relative to the liquid phase
mix	relative to the water/oil mixture
oil	relative to the silicone oil phase
water	relative to the water phase

confirmed by using the modeling framework proposed by Hernandez et al. [5]. From the "equivalent absorption capacity" concept, the influence of the silicone oil volume fraction on the physical absorption of any hydrophobic VOC in water/silicone oil mixtures was quantified [6,7]. Moreover, by studying styrene absorption, Dumont and Andrès [8] have highlighted that the change in K_La versus the silicone oil volume fraction depends on the mass transfer model used for its determination. According to these authors, who used the "equivalent absorption capacity" concept, a dramatic decrease in the K_La with increasing silicone oil volume fraction could be observed in relation to the decrease in the value of the partition coefficient. Recently, this result was also confirmed experimentally for hydrophobic VOCs such as DMS, DMDS and toluene [9]. Moreover, for toluene, the experimental results suggested that the mass transfer pathway is in the order gas → water → oil for the operating conditions (i.e. silicone oil volume fraction ϕ = 10%, 15% and 20%). It must be stressed that this experimental observation represents a valuable advance in understanding the mechanisms of mass transfer between a gas phase and two non-miscible liquid phases.

In 2006, because the influence of the addition of an organic solvent to water on the mass transfer mechanisms of VOCs was not well understood, the volumetric mass transfer coefficients (K_La) of styrene in water/silicone oil mixtures were studied using a dynamic method. The results were subsequently published [10]. It was then assumed that the gas phase contacts preferentially the water phase (i.e. gas → water → oil) and thus the partition coefficient of styrene between air and water (i.e. the Henry's law constant) was used for calculations, whatever the silicone oil volume fraction. In the light of the advances made since 2006, the aim of the present paper is to reconsider the results published previously by applying the "equivalent absorption capacity" concept to the experimental data i.e. to use the actual value of the partition coefficient which characterizes the mass transfer of styrene between the gas phase and the liquid mixtures. The results obtained from this new analysis are compared with those published in Dumont et al. [10] for styrene and also with results reported in the literature for VOC absorption in multiphase systems.

2. Materials and methods

Given that this part is described extensively in [10], it is summarized here and only the main points are presented (readers can refer to the original paper for more information). The physical absorption of styrene into mixtures of water and silicone oil, Rhodorsil® fluid 47V5 (dimethylpolysiloxane: $(CH_3)_3SiO[SiO(CH_3)_2]_nSi(CH_3)_3$) with a viscosity of 5 mPa s, was investigated in laboratory-scale bubble reactors using a dynamic absorption method (T = 298 °C). In this procedure, a known gas volume polluted with styrene was continuously passed through the liquid mixture, via a circulating loop. The operation was carried out batchwise with respect to the liquid and gas phases and the decrease in styrene concentration in the gas phase was recorded against time. Compositions of water/silicone oil mixtures were 0%, 1%, 2%, 3%, 4%, 5%, 6%, 8% and 10% (v/v). The mixture volumes ranged from 0.3 L to 1.5 L according to the mixture composition in order to have the same styrene driving force for each experiment between the beginning and the end of the absorption. In this way, the same decrease in the styrene concentration in the gas phase was monitored during experiments (carried out at least in triplicate). Changes in emulsion volume were taken into account in order to calculate K_La as will be shown later.

3. Partition coefficient of styrene between air and water/silicone oil mixtures

The general term "partition coefficient" is used to characterize the partition of styrene between air and the absorbing liquid (mixture). When water is the absorbing liquid, the term "Henry's law constant" can be used.

When the liquid phase is a mixture of water/organic solvent, the concentration in the liquid phase at equilibrium C_L^* with the gas phase C_G is given by the following relation [11]:

$$C_L^* = (1-\phi)\left(\frac{C_G}{H_{water}}\right) + \phi\left(\frac{C_G}{H_{oil}}\right) \quad (1)$$

where $(1-\phi)$ and ϕ are the volumetric fractions of water and silicone oil (v/v), respectively. H_{water} and H_{oil} represent the partition coefficients for the VOC in water and in silicone oil, respectively. Eq. (1) can be rewritten as:

$$C_L^* = \frac{C_G}{H_{mix}} \quad (2)$$

with:

$$\frac{1}{H_{mix}} = \frac{1-\phi}{H_{water}} + \frac{\phi}{H_{oil}} \quad (3)$$