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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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## **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  $\phi = 0\%$ , 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 ( $H_{\text{mix}}$ ). 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  $K_{L}a$  values due to silicone oil addition is observed. In comparison with similar measurements available in the literature, it is noted that this decrease in  $K_{L}a$  value could be related to the change in the partition coefficient ratio  $m_R = H_{\text{water}}/H_{\text{oil}}$ . Two explanations concerning the relationship between the change in a hydrodynamic parameter ( $K_{L}a$ ) and that in a thermodynamic parameter ( $m_R$ ) are proposed. Finally, it appears questionable to study the change in  $K_{L}a$  in terms of silicone oil addition.

**Keywords:** Absorption; Mass transfer; Multiphase reactors; Bioreactors; Hydrophobic VOC; Silicone oil

## 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 ( $\phi$ ). 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 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  $K_{L,a}$  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  $K_{L,a}$  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  $\phi = 10, 15$  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 ( $K_{L,a}$ ) 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<sup>®</sup> fluid 47V5 (dimethylpolysiloxane:  $(\text{CH}_3)_3\text{SiO}[\text{SiO}(\text{CH}_3)_2]_n\text{Si}(\text{CH}_3)_3$ ) 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  $K_{L,a}$  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  $\phi$  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:

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

The validity of Eq. (3) was checked experimentally for 3 VOCs (toluene, dimethylsulfide and dimethyldisulfide) in water/silicone oil mixtures [12]. It must be pointed out that the change in  $H_{mix}$  versus  $\phi$  deviates from linearity according to the ratio  $m_R = H_{water}/H_{oil}$ .

The styrene partition coefficient between air and water (Henry's law constant) given by the literature is  $H_{water} = 0.1130$  ( $H'_{water} = H_{water}RT = 280 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$  [13]). Considering the styrene partition coefficient between air and the silicone oil used in this study, no data are available in the literature. In order to determine this partition coefficient, two methods were used. First, the partition coefficient was measured experimentally according to the procedure described in Darracq *et al.* [4]. Secondly, the model proposed by Hernandez *et al.* [5] was applied to the experimental styrene absorption data reported in [8]. In the first case,  $H_{oil} = 0.00044$  ( $H'_{oil} = 1.1 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ ) and the ratio  $m_R = H_{water}/H_{oil} = 257$ . In the second case (see Fig. 8 in [8]),  $H_{oil} = 0.00029$  ( $H'_{oil} = 0.7 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ ) and the ratio  $m_R = H_{water}/H_{oil} = 390$ . Both these results confirm that styrene is much more soluble in silicone oil than in water. Although the difference between the results seems considerable (34%), this influence on the change in the partition coefficient of styrene between gas and liquid mixtures is moderate, as

highlighted in Fig. 1. This is mainly due to the large difference between  $H_{\text{water}}$  and  $H_{\text{oil}}$  (whatever the value of  $H_{\text{oil}}$ ), which leads to a large value for the ratio  $m_R$ .

Fig. 1

#### 4. $K_L a$ calculations

In the paper published in 2006 [10],  $K_L a$  were determined assuming that no contact between the gas and the organic liquid phase could occur. Thus, the main parameter for the  $K_L a$  calculation was the Henry's law constant ( $H_{\text{water}}$ ). In the present paper, it is assumed that styrene absorption occurs between the gas phase and a liquid mixture acting as a pseudo-homogeneous phase. Assuming ideal mixing in the gas and liquid phases, the transient VOC absorption rate in the liquid phase is given by:

$$-V_G \frac{dC_G}{dt} = K_L a V_L (C_L^* - C_{L(t)}) \quad (4)$$

As the operation is batchwise with respect to the liquid and gas phases, the conservation of mass gives at any time:

$$V_G C_{G(t=0)} + V_L C_{L(t=0)} = V_G C_{G(t)} + V_L C_{L(t)} \quad (5)$$

As no styrene is present in the absorbing mixture at  $t = 0$ , Eq. (5) can be rearranged as:

$$C_{L(t)} = \frac{V_G}{V_L} (C_{G(t=0)} - C_{G(t)}) \quad (6)$$

At equilibrium, styrene is partitioned between the gas phase and the liquid mixture. Thus:

$$C_{G(t \rightarrow \infty)} = \frac{H_{\text{mix}} V_G}{V_L + H_{\text{mix}} V_G} C_{G(t=0)} \quad (7)$$

A combination of Eqs. (2, 4, 6 and 7) leads to (after integration between  $t = 0$  and  $t$ ):

$$\ln \left[ \frac{C_{G(t)} - C_{G(t \rightarrow \infty)}}{C_{G(t=0)} - C_{G(t \rightarrow \infty)}} \right] = -K_L a t \quad (8)$$



By plotting the left member of Eq. (8) versus time, a straight line is obtained whose slope gives the volumetric mass transfer coefficient  $K_L a$ .

As experiments were carried out batchwise with respect to both phases (gas and water/silicone oil mixture), Eq. (4) is a first-order linear ordinary differential equation whose analytical solution is derived from Eq. (8):

$$C_{G(t)} = C_{G(t \rightarrow \infty)} + (C_{G(t=0)} - C_{G(t \rightarrow \infty)}) \exp(-t/\tau) \quad (9)$$

where  $\tau$  is the time constant of the system corresponding to  $1/K_L a$ . The time constant represents the time needed for the system to reach 63.2% of the final (asymptotic) value, and it is usually assumed that equilibrium is reached at  $t = 3 \tau$  (i.e. 95% of  $C_{t=0}^G - C_{t \rightarrow \infty}^G$ ).

## 5. Results and discussion

Fig. 2 shows typical examples of  $K_L a$  determination using Eq. (8). Once determined, the corresponding time constants  $\tau = 1/K_L a$  were calculated in order to compare the experimental data with the model corresponding to Eq. (9) as illustrated in Fig. 3. It must be stressed that all the experimental data were satisfactorily modeled using  $H_{oil} = 0.00029$  ( $H'_{oil} = 0.7 \text{ Pa.m}^3 \cdot \text{mol}^{-1}$ ; i.e.  $m_{styrene} = H_{water}/H_{oil} = 390$ ). Using  $H_{oil} = 0.00044$ , it was not possible to fit Eq. (9) to the experimental data and consequently this value should not be used. The time constant  $\tau$  characterized absorption very well for all the water/silicone oil mixtures used whatever the oil volume fraction. In other words, there is no doubt about the  $K_L a$  values for  $\phi > 0$ . However, for  $\phi = 0\%$ , the experimental points and the model begin to diverge at  $t/\tau \approx 0.5$ . Consequently, this  $K_L a$  value should be viewed with some degree of reservation. Nonetheless, the styrene absorption experiment in water was repeated four times and the results were reproducible (standard deviation 5%). Moreover, it is important to note that the results obtained in this study must not be considered absolute values but relative ones with the main

objective being to determine the change due to silicone oil addition. Thus, the doubt surrounding the  $K_L a$  value for  $\phi = 0\%$  is not very significant.

Fig. 2

Fig. 3

In order to quantify the change in mass transfer due to silicone oil addition, it was necessary to account for the change in mixture volume between each experiment (this varied from 0.3 to 1.5 L for mixtures and 10 L for water and was necessary to obtain approximately the same variation in the styrene concentration for each experiment between the beginning and the end of the absorption). Writing Eq. (4) for air/water systems and for air/water/silicone oil systems and taking into account the change in mixture volume, the ratio of mass transfer rates is given by the following equation:

$$\frac{\left(\frac{dC_G}{dt}\right)_\phi}{\left(\frac{dC_G}{dt}\right)_{\phi=0}} = \frac{(V_L)_\phi (K_L a)_\phi (C_L^* - C_L)_\phi}{(V_L)_{\phi=0} (K_L a)_{\phi=0} (C_L^* - C_L)_{\phi=0}} \quad (10)$$

From Fig. 4, it can be observed that the mass transfer ratio  $(dC_G/dt)_\phi / (dC_G/dt)_{\phi=0}$  is less than one and it can be concluded that silicone oil addition slightly hinders styrene mass transfer relative to the air/water system considered a reference. Given that the water/silicone oil mixtures are assumed to react as a pseudo-homogeneous phase characterized by a given partition coefficient  $H_{\text{mix}}$ , it can logically be concluded that the driving force in the liquid phase  $(C_L^* - C_{L(t)})$  increases with the silicone oil volume fraction. Thus, the ratio  $(C_L^* - C_{L(t)})_\phi / (C_L^* - C_{L(t)})_{\phi=0}$  can be calculated and it can be shown that this driving force ratio

varies as the ratio ( $H_{\text{water}}/H_{\text{mix}}$ ) which is equal to  $(1 + \phi m_R)$ . As observed in Fig. 4, the driving force ratio increases linearly versus  $\phi$ . In another way, Fig. 4 gives the change in the  $K_{L,a}$  ratio versus  $\phi$  (which also takes into account the change in the volume of the liquid phase). It appears that silicone oil addition leads to a dramatic decrease in  $K_{L,a}$  that can be related to the change in the partition coefficient ( $H_{\text{mix}}$ ; see Fig. 1). Because no enhancement is observed (mass transfer rate ratio between 0.7 and 1) while the driving force in the liquid side increases dramatically, it could be suggested that the  $K_{L,a}$  determined in this study drops significantly to balance the large increase in the driving force due to oil addition. In other words, the  $K_{L,a}$  value experimentally determined is only an “apparent” value which should not be used to characterize the hydrodynamics of the system. Hence, this result indicates that the study of  $K_{L,a}$  change due to NAP addition is highly questionable. In fact, oil addition changes the partition coefficient value ( $H_{\text{mix}}$ ) of water/silicone oil mixtures and it is thus possible to question the usefulness of comparing  $K_{L,a}$  obtained for mixtures of different absorption capacities. For more than thirty years, numerous studies have tried to assess the enhancement of gas/liquid mass transfer due to the addition of a dispersed second liquid phase and many models have been built in order to quantify it [14-15]. However, Clarke and Correia [16], by demonstrating that the  $K_{L,a}$  behavioral trends reported in the literature could be classified into 3 types (*type 1*:  $K_{L,a}$  peak; *type 2*:  $K_{L,a}$  increase; *type 3*:  $K_{L,a}$  decrease or  $K_{L,a}$  constant), highlighted the contradictions in the reported results of  $K_{L,a}$ . Moreover, these authors showed that no universally applicable relationship describing the influence of all NAPs in any volume fraction could be accurately used for  $K_{L,a}$  prediction. Lastly, in the recent review devoted to the latest advances in TPPBs, Munoz *et al.* [2] reinforced this point of view by demonstrating that the effect of NAP addition on mass transfer performance cannot be adequately characterized by means of  $K_{L,a}$  alone. It is clear that the main mistake which has been made is in trying to study the change in mass transfer rate for the same driving force. Because NAP

addition dramatically changes the absorption capacity of the liquid mixture, the driving force also changes, which has seldom been taken into account. In such gas/liquid/liquid systems, analogies should not have been made with the gas/liquid mass transfer intensified by the presence of small solid inert particles or with the gas/liquid mass transfer enhanced by a chemical reaction in the liquid phase.

Fig. 4

Fig. 5 gives the change in the dimensionless  $K_L a$  ratio determined in the present study compared with the results obtained for styrene [8], DMS and DMDS [9] using a similar measurement technique and the same silicone oil. Note that the data given in [8] were calculated using  $H_{oil} = 0.00044$  (or  $H'_{oil} = 1.1 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ ) and are presented here using  $H_{oil} = 0.00029$  (or  $H'_{oil} = 0.7 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ ) as discussed above. Fig. 5 reveals that the results reported in this study follow the same trend as those obtained for DMS and DMDS. Moreover, it appears that the decrease in the  $K_L a$  ratio is more pronounced for high  $m_R$  values ( $= H_{water}/H_{oil}$ ) i.e. the decrease in the  $K_L a$  ratio (which is a hydrodynamic parameter) could be related to the change in a thermodynamic parameter, which could be explained in two ways.

Fig. 5

The first explanation concerns the mechanisms involved in physical gas-liquid absorption. The significant decrease in  $K_L a$  due to silicone oil addition could be attributed to a simultaneous decrease in both the overall mass transfer coefficient “ $K_L$ ” and the interfacial area “ $a$ ”. In fact, the literature reports that the addition of a NAP can significantly affect both these parameters but there are substantial variations between results. For instance, Clarke and

Correia [16] emphasized, in an extensive literature review, that the interfacial area is highly dependent on the physicochemical properties of the liquid phase, such as surface tension and viscosity, which define bubble size through their influence on bubble break-up and coalescence. Although such remarks were clearly illustrated by Kundu *et al.* [17] and Dumont *et al.* [18] when reporting that the change in fluid properties could affect bubble size, gas hold up and consequently interfacial area, no relationship between these parameters can be used to predict any changes due to NAP addition. Moreover, the literature devoted to gas/liquid/liquid systems often presents contradictory results. For instance, Quijano *et al.* [19] reported that silicone oil addition increased the gaseous interfacial area whereas Basheva *et al.* [20] indicated that oil addition induced bubble coalescence. However, the change in the interfacial area should be the same for DMS, DMDS and styrene because it depends mainly on the properties of pure liquids, water and silicone oil, which remained the same for all experiments. As the results are different for these 3 VOCs, Fig. 5 clearly indicates that the change in the interfacial area cannot be used for this explanation.

Concerning the influence of NAP addition on  $K_L$ , Clarke and Correia [16] reported that it has generally been found to be negative. Several mechanisms can explain the decrease in  $K_L$  due to NAP addition (for example, change in surface tension, bubble mobility, increase in viscosity, physical-chemical interactions between oil and water). An analysis based on the film theory has been made by Dumont *et al.* [8] to explain the possible decrease in  $K_L$  due to silicone oil addition. It appeared that silicone oil addition could lead to a dramatic increase in the gas film resistance in relation to the decrease in the  $H_{mix}$  value (Fig. 1) because styrene solubility in the pseudo-homogeneous liquid increases greatly with oil addition. Moreover, oil addition could lead to a dramatic change in the value of the diffusion coefficient by increasing the liquid film resistance. However, the results from Fig. 5 clearly indicate that such an explanation should be particularly dependent on the change in the diffusion coefficient.

Indeed, even if the gas film resistance must be taken into account, its influence on the overall mass transfer coefficient  $K_L$  is not sufficient to explain alone the great difference observed between DMDS and styrene. Consequently, this explanation should be mainly supported by the change in the value of the diffusion coefficient, which has to be determined. The diffusion coefficient of styrene in water is  $D_{\text{water}} = 0.8 \cdot 10^{-9} \text{ m}^2/\text{s}$  [21] and, although there is no value available in the literature for the diffusion coefficient of styrene in the silicone oil used in this study, data from the literature devoted to the measurement of VOC diffusion coefficients in oils indicate that values could be lower than that for water by a factor of 10 [8] which could, however, be insufficient to explain the decrease in  $K_L$ . To conclude about this first explanation, it must be pointed out that the dramatic decrease in  $K_L a$  cannot be explained by a simultaneous decrease in both parameters  $K_L$  and  $a$ .

The second explanation concerns the mass transfer pathway between the gas and the liquid mixture for the operating conditions of this study. With the same methodology and the same silicone oil as those used in this study to characterize the mass transfer of DMS, DMDS and toluene into water/silicone oil mixtures, Dumont *et al.* [9] showed experimentally (at least for toluene) that the mass transfer between the gas and the mixture was in the order gas→water→oil. For styrene, the same conclusion could be made because silicone oil addition does not improve the mass transfer rate (the ratio of mass transfer rates ranges between 0.7 and 1; Fig. 4). Hence, silicone oil addition can moderately affect the mass transfer rate by modifying the physicochemical properties (surface tension, viscosity) which define a change in the bubble size distribution i.e. in the interfacial area. In other words, the droplet size could be much larger than the liquid boundary layer, making the effect of the dispersed phase on the absorption rate negligible [14-15]. For the experimental conditions corresponding to the present study, the mass transfer rate would be rather controlled by a thin

layer of water covering bubbles and representing a barrier between the air and the mixture. In such a way, this layer of water would be the bottleneck controlling the mass transfer rate whatever the silicone oil volume fraction i.e. whatever the  $H_{\text{mix}}$  value. To conclude, it appears that this explanation is linked to the analysis of the experimental results previously made in 2006 [10] based on the hypothesis of no contact between gas and silicone oil. In such a case,  $K_{\text{L}}a$  remains roughly constant with oil addition because the mass transfer is governed by  $H_{\text{water}}$ . Consequently, the drop in  $K_{\text{L}}a$  recorded (Fig. 5) would only be an apparent decrease, balancing the large increase in the driving force due to oil addition.

## 6. Conclusion

The volumetric mass transfer coefficients ( $K_{\text{L}}a$ ) of styrene in gas/water/silicone oil systems were measured experimentally using a dynamic method. Experimental results previously analyzed assuming no contact between gas and silicone oil [10] were reconsidered by applying the “equivalent absorption capacity” concept. It was shown that silicone oil addition slightly hinders the styrene mass transfer rate compared to the air/water system. Moreover, a significant decrease in  $K_{\text{L}}a$  values due to silicone oil addition is observed. In comparison with similar measurements carried out for other VOCs (DMS, DMDS and toluene), it is noted that this decrease in  $K_{\text{L}}a$  value could be related to the change in the partition coefficient ratio  $m_{\text{R}}$ . However, the relationship between the change in a hydrodynamic parameter ( $K_{\text{L}}a$ ) and that in a thermodynamic parameter ( $m_{\text{R}}$ ) had to be explained. In fact, the drop in  $K_{\text{L}}a$  recorded following silicone oil addition would only be an apparent decrease, balancing the large increase in the driving force due to oil addition. Finally,  $K_{\text{L}}a$  has to remain roughly constant whatever the silicone oil volume fraction (which corresponds to the results given in [10]) because the mass transfer is governed by the partition coefficient between gas and water ( $H_{\text{water}}$ ). The paper also highlighted that the study of the change in  $K_{\text{L}}a$  in terms of silicone oil

addition could be questionable because oil addition changes the partition coefficient value ( $H_{\text{mix}}$ ) which is not taken into account for  $K_L a$  determination.

### **Nomenclature**

a: interfacial area ( $\text{m}^{-1}$ )

C: concentration ( $\text{mol}/\text{m}^3$ )

D: diffusion coefficient ( $\text{m}^2/\text{s}$ )

H: partition coefficient (-)

H': partition coefficient ( $\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ )

$K_L$ : mass transfer coefficient ( $\text{m}\cdot\text{s}^{-1}$ )

$K_L a$ : volumetric mass transfer coefficient ( $\text{s}^{-1}$ )

$m_R$ : partition coefficient ratio (-)

R: universal gas constant ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ )

T: temperature (K)

$V_G$ : volume of the gas phase ( $\text{m}^3$ )

$V_L$ : volume of the emulsion ( $\text{m}^3$ )

### *Greek Letters*

$\delta$ : film thickness (m)

$\phi$ : dispersed liquid volume fraction (-)

$\tau$ : 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



## References

- [1] M.A. Deshusses, Biological waste air treatment in biofilter, *Environ. Biotechnol.* 8 (1997) 335-339.
- [2] R. Muñoz, A.J. Daugulis, M. Hernandez, G. Quijano, Recent advances in two-phase partitioning bioreactors for the treatment of volatile organic compounds, *Biotechnol. Adv.* 30 (2012) 1707-1720.
- [3] A.J. Daugulis, Two-phase partitioning bioreactors: a new technology platform for destroying xenobiotics, *Trends in Biotechnol.* 19 (2001) 457-462.
- [4] E. Dumont, G. Darracq, A. Couvert, C. Couriol, A. Amrane, D. Thomas, Y. Andrès, P. Le Cloirec, Determination of partition coefficients of three volatile organic compounds (dimethylsulfide, dimethyldisulfide and toluene) in water/silicone oil mixtures, *Chem. Eng. J.* 162 (2010) 927-934.
- [5] M. Hernandez, G. Quijano, R. Munoz, S. Bordel, Modeling of VOC mass transfer in two-liquid phase stirred tank, biotrickling filter and airlift reactors, *Chem. Eng. J.* 172 (2011) 961-969.
- [6] E. Dumont, G. Darracq, A. Couvert, C. Couriol, A. Amrane, D. Thomas, Y. Andrès, P. Le Cloirec, VOC absorption in a countercurrent packed-bed column using water/silicone oil mixtures: Influence of silicone oil volume fraction, *Chem. Eng. J.* 168 (2011) 241-248.
- [7] E. Dumont, G. Darracq, A. Couvert, C. Couriol, A. Amrane, D. Thomas, Y. Andrès, P. Le Cloirec, Hydrophobic VOC absorption in two-phase partitioning bioreactors; influence of silicone oil volume fraction on absorber diameter, *Chem. Eng. Sci.* 71 (2012) 146-152.
- [8] E. Dumont, Y. Andrès, Styrene absorption in water/silicone oil mixtures, *Chem. Eng. J.* 200-202 (2012), 81-90.
- [9] E. Dumont, G. Darracq, A. Couvert, C. Couriol, A. Amrane, D. Thomas, Y. Andrès, P. Le Cloirec, Volumetric mass transfer coefficients characterising VOC absorption in water/silicone oil mixtures, *Chem. Eng. J.* 221 (2013) 308-314.
- [10] E. Dumont, Y. Andrès, P. Le Cloirec, Mass transfer coefficients of styrene and oxygen into silicone oil emulsions in a bubble reactor, *Chem. Eng. Sci.* 61 (2006) 5612-5619.
- [11] G. Quijano, A. Ordaz, R. Munoz, F. Thalasso, New insights on O<sub>2</sub> uptake mechanisms in two-phase partitioning bioreactors, *Biotechnol. Letters* 32 (2010) 223-228.

- [12] G. Darracq, A. Couvert, C. Couriol, A. Amrane, D. Thomas, E. Dumont, Y. Andrès, P. Le Cloirec, Silicone oil: an effective absorbent for the removal of hydrophobic volatile organic compounds, *J. Chem. Technol. Biotechnol.* 85 (2010) 309-313.
- [13] Kirk-Othmer, *Encyclopedia of chemical technology*, New York, Wiley & Sons, 3<sup>rd</sup>, Vol 21 (1983).
- [14] D.W.F. Brillman, M.J.V. Goldschmidt, G.F. Versteeg, W.P.M. van Swaaij, Heterogeneous mass transfer models for gas absorption in multiphase systems, *Chem. Eng. Sci.* 55 (2000) 2793-2812.
- [15] E. Dumont, H. Delmas, Mass transfer enhancement of gas absorption in oil-in-water systems: a review, *Chem. Eng. Process.* 42 (2003) 419-438.
- [16] K.G. Clarke, L.D.C. Correia, Oxygen transfer in hydrocarbon-aqueous dispersions and its applicability to alkane bioprocesses: a review, *Biochem. Eng. J.* 39 (2008) 405-429.
- [17] A. Kundu, E. Dumont, A.M. Duquenne, H. Delmas, Mass transfer characteristics in gas-liquid-liquid systems, *Can. J. Chem. Eng.* 81 (2003) 640-646.
- [18] E. Dumont, Y. Andrès, P. Le Cloirec, Effect of organic solvents on oxygen mass transfer in multiphase systems: Application to bioreactors in environmental protection, *Biochem. Eng. J.* 30 (2006) 245-252.
- [19] G. Quijano, J. Rocha Rios, M. Hernandez, S. Villaverde, S. Revah, R. Muñoz, F. Thalasso, Determining the effect of solid and liquid vectors on the gaseous interfacial area and oxygen transfer rates in two-phase partitioning bioreactors, *J. Hazard. Mat.* 175 (2010) 1085-1089.
- [20] E.S. Basheva, S. Stoyanov, N.D. Denkov, K. Kasuga, N. Satoh, K. Tsujii, Foam boosting by amphiphilic molecules in the presence of silicone oil, *Langmuir* 17 (2001) 969-979.
- [21] US EPA 1996 - Soil Screening Guidance: Technical Background Document - Publication 9355.4-17A -EPA/540/R-95/128-PB96-963502. US Environmental Protection Agency (1996) <http://www.epa.gov>.

**Figures caption**

Fig. 1: Change in  $H_{\text{mix}}$  values versus silicone oil volume fraction ( $H_{\text{mix}}$  is calculated using Eq. (3) with  $H_{\text{water}} = 0.1130$ ).

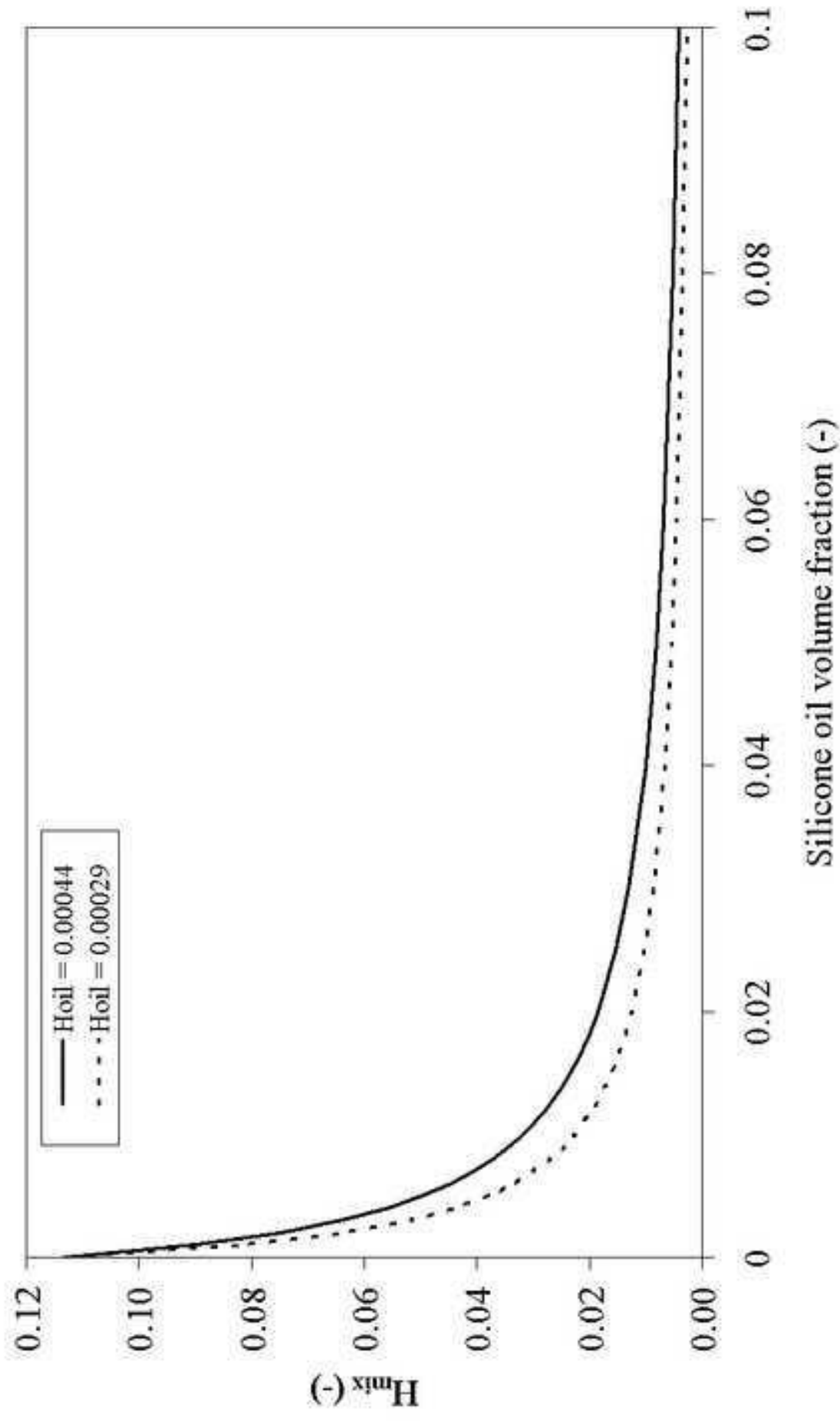
Fig. 2: Absorption of styrene - Example of  $K_L a$  determination according to Eq. (8). (+): gas/water system; (O): gas/water/oil system.

Fig. 3: Validation of the time constant values  $\tau$  for gas/water and gas/water/oil systems (gray line: monitored decrease in styrene in the gas phase relative to the initial concentration; black line: model corresponding to Eq. (9)/  $C_{t=0}^G$ ).

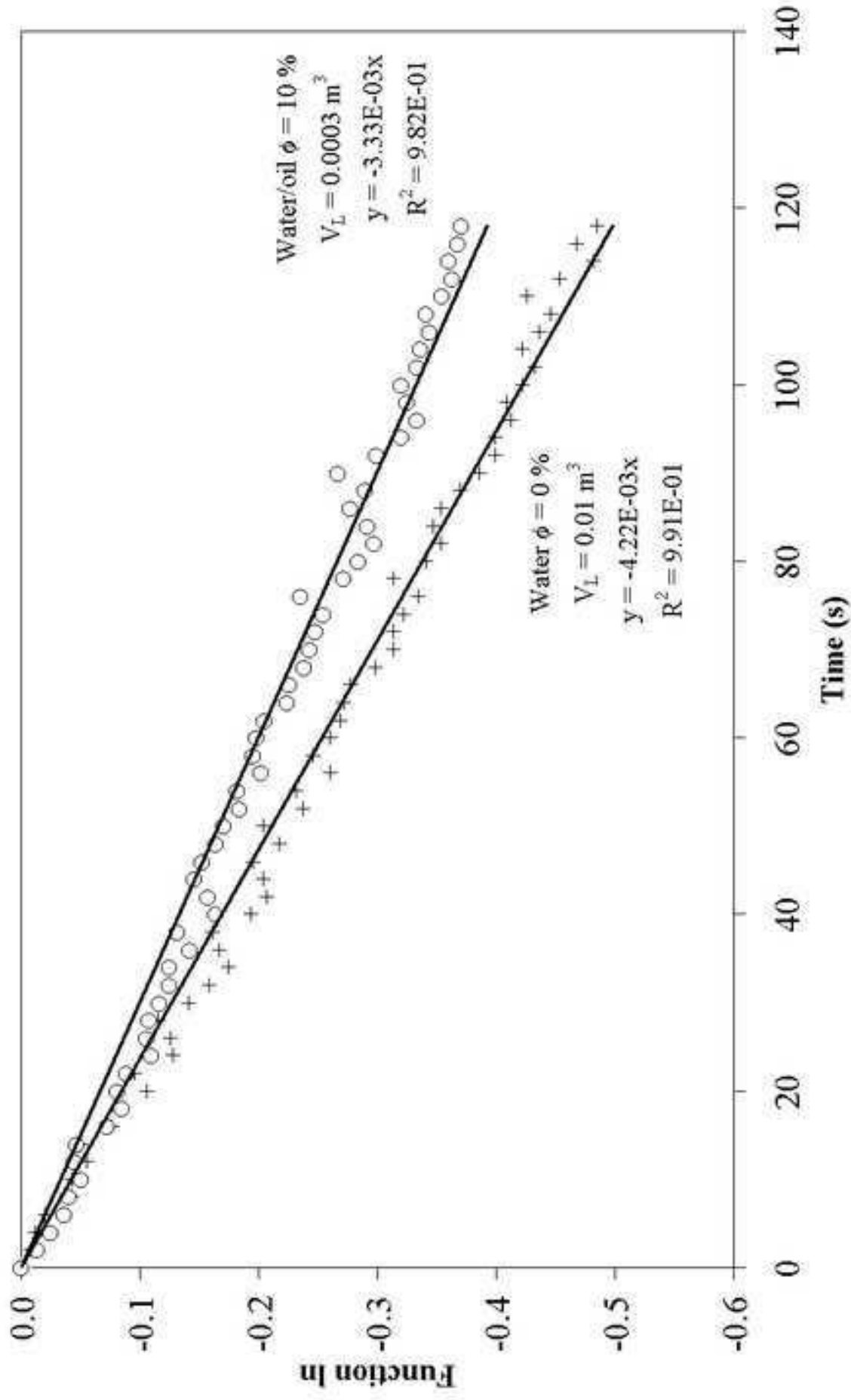
Fig. 4: Change in  $K_L a$  ratio (circles); liquid side driving force ratio (triangles) and styrene mass transfer rate ratio (squares) versus silicone oil volume fraction. Each ratio is described by Eq. (10).

Fig. 5: Change in  $K_L a$  ratio versus silicone oil volume fraction for three VOCs.

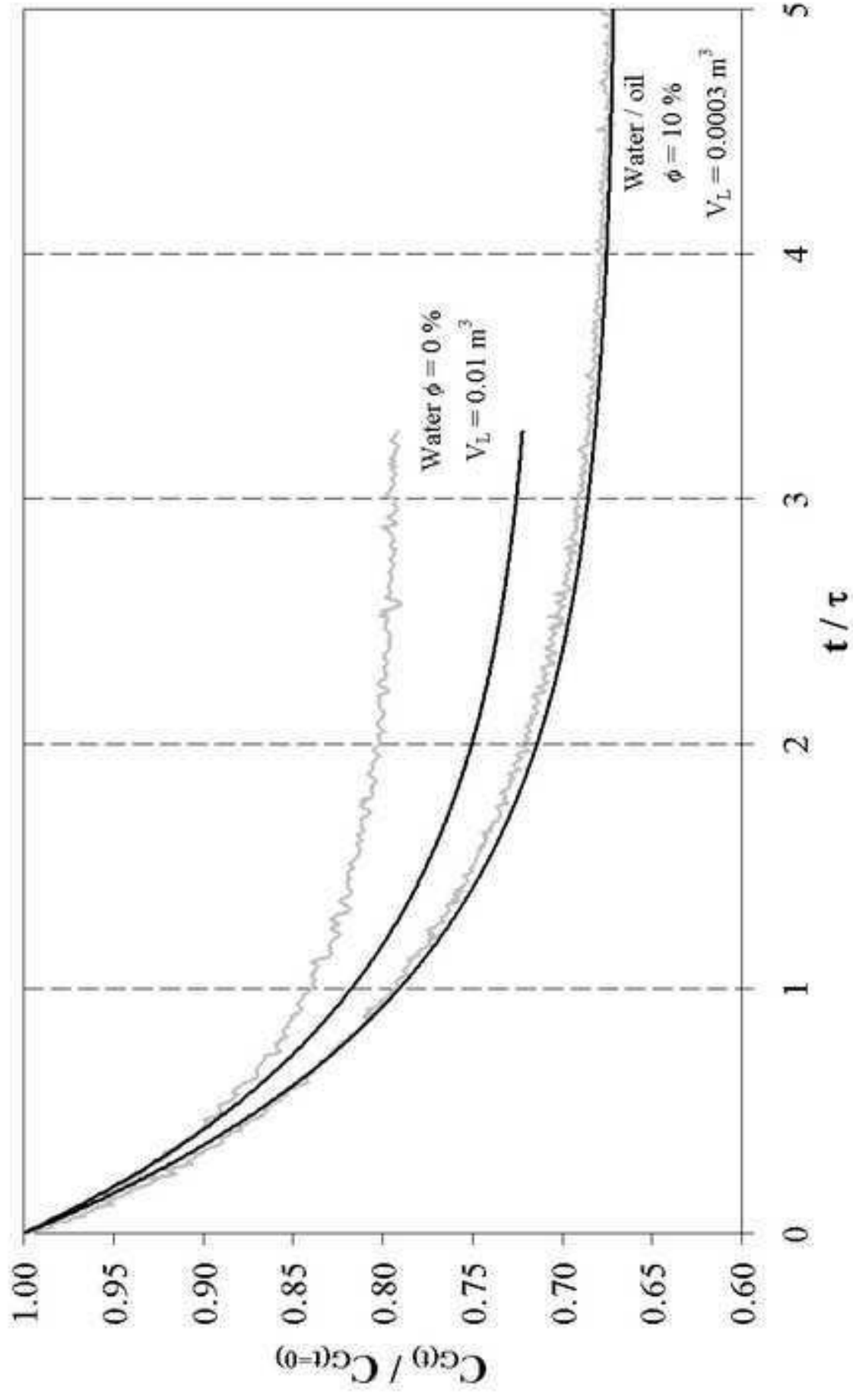
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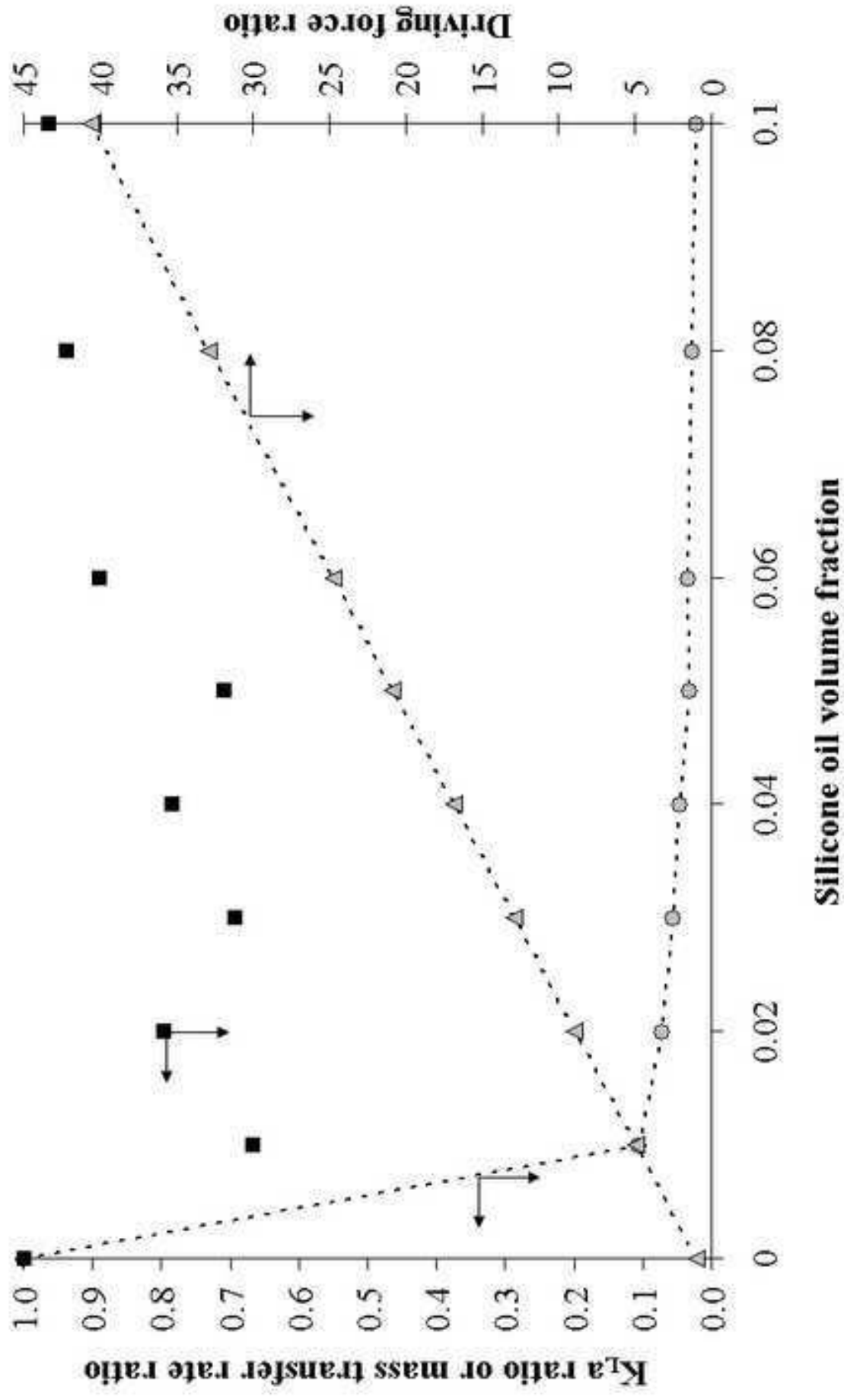
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