



Determination of partition coefficients of three volatile organic compounds (dimethylsulphide, dimethyldisulphide and toluene) in water/silicone oil mixtures

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ABSTRACT

The main objective of this work was to propose a model able to predict the partition coefficient of odorous or toxic gaseous pollutants (dimethylsulphide, dimethyldisulphide and toluene) in water/silicone oil mixtures. Experimental measurements using a static headspace method were carried out for pure water ($H_{\text{voc,water}}$), for pure silicone oil ($H_{\text{voc,solvent}}$) and for mixtures of varying composition ($H_{\text{voc,mixture}}$). The dramatic decrease in the partition coefficient ($H_{\text{voc,mixture}}$) with oil addition clearly showed a deviation from linearity, which was more pronounced for increasing $H_{\text{voc,water}}/H_{\text{voc,solvent}}$ ratios. Moreover, experiments using a dynamic absorption method underlined that 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 solvent, and balanced using the “equivalent absorption coefficients” $H_{\text{voc,mixture}}/H_{\text{voc,water}}$ and $H_{\text{voc,mixture}}/H_{\text{voc,solvent}}$. An “equivalent absorption capacity” concept is then proposed, which should be useful to design absorption units using two-phase liquid mixtures for the treatment of industrial air loaded with volatile organic compounds.

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1. Introduction

Industrial treatment plants can generate gas emissions containing volatile organic compounds (VOCs) causing hazardous and/or malodorous air pollution. The removal of odours can be achieved using bioreactors, which are suitable for the treatment of low concentrations of waste gas pollutants [1]. However, some of these malodorous volatile organic compounds are scarcely soluble in water leading to limitations in bioreactor performance. In response to the low solubility of some pollutants, a water-immiscible organic solvent (typically silicone oil) can be added to water in order to improve mass transfer from the gas phase to the liquid phase [2], in a typically named two-phase partitioning bioreactor (TPPB) [3]. TPPBs have been demonstrated to be effective in degrading high levels of toxic organic compounds. However, the design of such bioreactors requires the knowledge of physical data, mainly

Henry's law constants (or partition coefficients) of VOCs in such mixtures, which are not available in the literature [4]. As Henry's constant represents the air–water equilibrium partition coefficient for a chemical compound present in a dilute aqueous solution [5], the term “partition coefficient” will be preferentially used to express the COV equilibrium between air and liquid mixture. Concerning a TPPB, the value of the partition coefficient must be known for each water/silicone oil ratio. It is not currently possible to estimate partition coefficients using computer models (such as Unifac and Uniquac) due to the physicochemical nature of the mixtures, which is not sufficiently well defined [6]. Consequently, experimental measurements are required. With the aim of treating hydrophobic volatile organic compounds in a two-phase partitioning bioreactor, the partition coefficients of three pollutants, dimethyldisulphide (DMDS), dimethylsulphide (DMS) and toluene, were measured in pure water, in pure silicone oil, and in water/silicone oil mixtures of varying composition. From these measurements, the objective of this work was to propose a model able to predict the partition coefficients of these pollutants in mixtures of immiscible liquids.

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Nomenclature

<i>A</i>	absorption factor
<i>C</i>	concentration (mol m^{-3})
E_{ff}	efficiency (–)
<i>G</i>	number of moles in the gas phase (mol)
<i>P</i>	partition coefficient (–)
<i>H</i>	dimensional form of the partition coefficient ($\text{Pa m}^3 \text{ mol}^{-1}$)
$K_{\text{L}a}$	volumetric mass transfer coefficient (s^{-1})
<i>L</i>	number of moles in the liquid phase (mol)
<i>M</i>	molecular weight (kg mol^{-1})
<i>m</i>	slope of the equilibrium line (–)
<i>n</i>	number of moles (mol)
<i>R</i>	ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
<i>T</i>	temperature (K)
<i>V</i>	volume (m^3)
<i>x</i>	molar fraction of VOC in the liquid phase (–)
<i>y</i>	molar fraction of VOC in the gas phase (–)

Greek letters

ϕ	silicone oil volume fraction (–)
η	dynamic viscosity (Pa s)
ρ	density (kg m^{-3})

Superscripts

G	gas phase
L	liquid phase

Subscripts

dam	dynamic absorption method
DMDS	dimethyldisulphide
DMS	dimethylsulphide
eq	equilibrium
end	relative to the final concentration (dynamic absorption method)
G, Gas	gas phase
L, Liquid	liquid phase
mixture	water/silicone oil mixture
shm	static headspace method
solvent	relative to silicone oil
VOC	volatile organic compound
water	water

2. Materials and methods

2.1. Chemical products

Silicone oil (dimethylpolysiloxane) Rhodorsil® fluids 47V5 with a viscosity of 5 mPa s was purchased from the Rhodia Company, France (density: 930 kg m^{-3} ; molecular weight: 740 g mol^{-1}).

Dimethylsulphide ($\text{CH}_3\text{--S--CH}_3$) and dimethyldisulphide ($\text{CH}_3\text{--S--S--CH}_3$) were chosen as sulphur target pollutants due to their known malodorous character and their slight solubility in water. Toluene (C_7H_8) was also chosen because it is a highly hydrophobic, widely used compound. Moreover, it is commonly used in laboratory-scale bioreactors and many solubility data are available, both in water and in silicone oil. Table 1 summarises the physical data of the three selected pollutants and Table 2 presents significant values of partition coefficients given in the literature. A data compilation is also available on the web for pure water (<http://webbook.nist.gov/>). For DMS and DMDS solubility in water, Iliuta and Larachi [7] provided an extensive review. According to these authors, the solubility data are quite scarce,

Table 1

Some physical data of the selected pollutants ($T = 20^\circ \text{C}$).

	DMDS	DMS	Toluene
Molecular weight (g mol^{-1})	94.2	62.1	92.1
Density (kg m^{-3})	1046	850	870
T_{eb} ($^\circ \text{C}$)	109	37.3	111
P_{sat} (Pa)	3813	53200	3800

while the experimental temperatures used differ greatly and cover a wide range. For both pollutants, however, they found a very good agreement between their measurements and the literature values with an average deviation of 2.6% for DMDS [8] and 0.77% for DMS [9]. For toluene in water, the literature values range from 562 to $779 \text{ Pa m}^3 \text{ mol}^{-1}$, whereas handbooks of physicochemical properties give an average value of $680 \text{ Pa m}^3 \text{ mol}^{-1}$ [10].

For pure silicone oil, few data are available. De Guardia et al. [11] reported values for DMS and DMDS at various temperatures; the values for $T = 25^\circ \text{C}$ are reported in Table 2. For toluene, some data correlated to the oil dynamic viscosity are available in the literature. Values range from 1.75 to $7.07 \text{ Pa m}^3 \text{ mol}^{-1}$.

To summarise the data presented in Table 2 for the selected pollutants, values of 60, 20 and 300 are found for the ratios of solubility in silicone oil and in water for DMDS, DMS and toluene, respectively.

2.2. Experimental

Partition coefficients were obtained using a static headspace method at $T = 25^\circ \text{C}$. A known amount of pure liquid (or mixture) was introduced into a specific flask (vial) whose exact volume was measured. After closing it and making it gas-tight, a known quantity of pollutant was added through the septum. The vial was shaken, using a swivel support, for three days. Once equilibrium was reached (checked by a constant VOC concentration in the gas phase), the VOC concentration in the gas phase (C_{eq}^{G}) was measured by gas chromatography (flame ionisation detector type focus). The gas chromatography conditions used in this work are given in Table 3. The VOC concentration in the liquid phase (C_{eq}^{L}), and consequently the partition coefficient, could be deduced from the mass balance according to Eq. (1):

$$P_{\text{VOC}} = \frac{C_{\text{eq}}^{\text{G}}}{C_{\text{eq}}^{\text{L}}} \left[\frac{\text{mole}_{\text{VOC,Gas}}/m_{\text{Gas}}^3}{\text{mole}_{\text{VOC,Liquid}}/m_{\text{Liquid}}^3} \right] \quad (1)$$

P_{VOC} represents the dimensionless concentration ratio. The alternative dimensional form of partition coefficients generally used in

Table 2

Partition coefficient for pure water ($H_{\text{VOC,water}}$) and pure silicone oil ($H_{\text{VOC,solvent}}$) at $T = 298 \text{ K}$.

	H_{VOC} ($\text{Pa m}^3 \text{ mol}^{-1}$)	Reference
DMDS		
In water	111.9	Iliuta and Larachi [8]
In silicone oil	$1.9_{(\eta = 3 \text{ mPa s})}$	De Guardia et al. [11]
DMS		
In water	182.1	Iliuta and Larachi [9]
In silicone oil	$8.1_{(\eta = 3 \text{ mPa s})}$	De Guardia et al. [11]
Toluene		
In water	640	Staudinger and Roberts [5]
	670	Mackay and Shiu [12]
	680	Mackay et al. [10]
In silicone oil	$7.07_{(\eta = 50 \text{ mPa s})}$	Poddar and Sirkar [6]
	$2.74_{(\eta = 10 \text{ mPa s})}$	Muzenda et al. [13]
	$1.76_{(\eta = 20 \text{ mPa s at } T = 20^\circ \text{C})}$	Heymes et al. [14]
	$2.43_{(\eta = \text{not indicated})}$	Heymes et al. [15]

Table 3
Analytical conditions implemented to determine the pollutant concentration in the gas phase.

Pollutant	Apparatus	Column	Detector	T_{inj}	T_{oven}	T_{det}	Carrier gas
DMDS	Thermo	RTx ⁻¹	FID	150 °C	50 °C (1.2 min) 50 °C/min → 200 °C (3 min)	250 °C	N ₂ 3.3 mL/min
DMS	focus-GC	15 m × 0.32 mm			100 °C (1.4 min) 50 °C/min → 200 °C (3 min)		N ₂ 3.2 mL/min
Toluene					100 °C (1.5 min) 20 °C/min → 180 °C (0 min)		

this paper is:

$$H_{voc} = RT P_{voc} \left[\frac{\text{mole}_{voc,Gas}/\text{mole}_{Gas}}{\text{mole}_{voc,Liquid}/m^3_{Liquid}} (\text{Pa}) \right] = \left[\frac{\text{Pa } m^3_{Liquid}}{\text{mole}_{voc,Liquid}} \right] \quad (2)$$

Each experimental value was calculated from the average of at least four measurements. The relative standard deviation ranged from 0 to 8%.

To confirm the measurements obtained by means of the static headspace method, partition coefficients were also deduced from the absorption kinetics of pollutants in water/silicone oil mixtures. These measurements were carried out using a method developed for the measurement of mass transfer coefficients at the laboratory-scale [16]. In this method, a known gas volume polluted with VOC was continuously flowed, via a circulating loop, through the water/silicone oil mixture. The operation was batch-wise with respect to the liquid system and the decrease in the VOC concentration in the gas phase was measured over time. Fig. 1 presents a schematic overview of the experimental set-up used. A glass reactor filled with 1 L (V_{Liquid}) of mixture was connected to

a 216-l tank allowing a known volume of polluted air to be prepared (total air volume $V_{Gas} = 217$ L). For the preparation of waste air, pollutant was directly injected into the tank with a syringe and a continuous circulation of the laden air in a closed loop enabled the gas phase to mix thoroughly (dashed envelope in Fig. 1). The VOC concentration was continuously measured in the tank using a flame ionisation detector (Cambustion HFR 400 FFID) calibrated from standards before each experiment. After confirming that the VOC concentration was constant, three-way diverting valves were simultaneously hand-operated in order to flow the polluted gas through the liquid mixture (gas flow rate: 1 m³/h). The pressure changes in the gas circuit and the decrease in the VOC concentration in the gas phase were monitored and recorded as a function of time for further analysis. During absorption, the mass balance of the pollutant between the gas and liquid phases was used to calculate the VOC concentration in the water/silicone oil mixture. When equilibrium was reached (Fig. 2), the measured value C_{eq}^G and the calculated value C_{eq}^L led to the partition coefficient according to Eq. (1). All the experiments were carried out in triplicate at a constant temperature of 25 °C inside the reactor and at room temperature

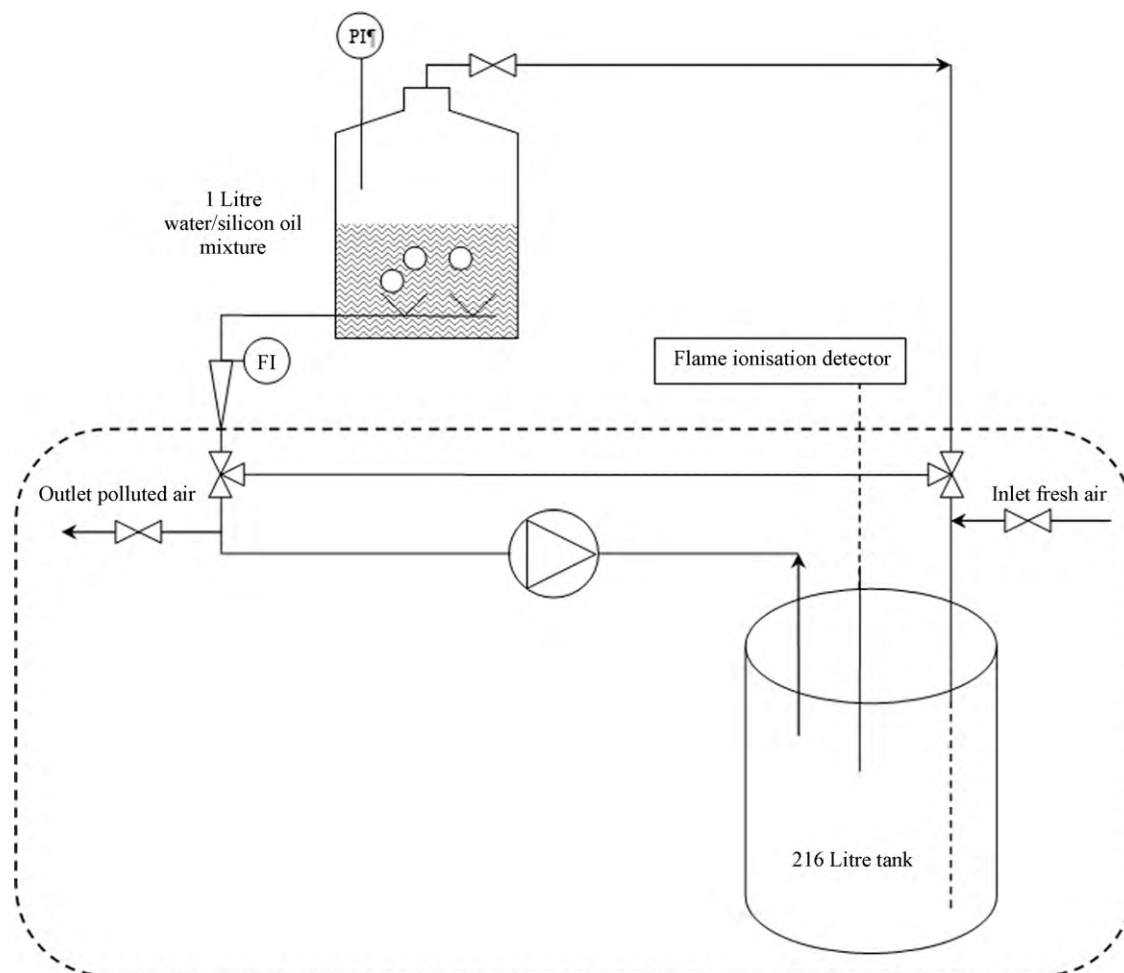


Fig. 1. Schematic overview of the experimental set-up implemented for kinetic absorption of pollutants in water/silicone oil mixtures (dashed envelope: circuit for polluted air preparation).

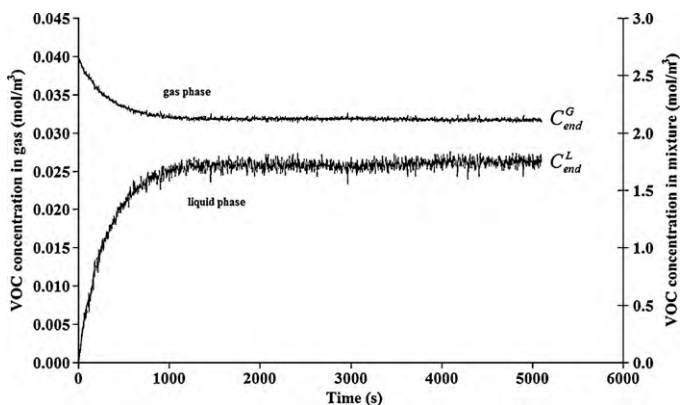


Fig. 2. Dynamic absorption method; example of DMDS mass transfer between the gas phase and a water/silicone oil mixture (5% silicone oil).

varying slightly around 20 °C inside the tank. Between each experiment, the reactor was washed with alcohol, and then with distilled water.

3. Results and discussion

3.1. Static headspace method (H_{shm})

The partition coefficient values obtained from the static headspace method are reported in Table 4.

Concerning DMDS and toluene, the experimental measurements for water were in good agreement with the literature data (Table 2). In the case of silicone oil, and taking the oil viscosity into account, partition coefficient was of the same order of magnitude as those reported in the literature (Table 2).

Accurate measurements were more difficult to perform for DMS due to the high volatility of this compound (saturation vapour pressure = 53,200 Pa; see Table 1). Indeed, the value for water was 32% lower than that proposed by Iliuta and Larachi [9], whereas that obtained for silicone oil ($17.7 \text{ Pa m}^3 \text{ mol}^{-1}$) was roughly twice the value ($8.1 \text{ Pa m}^3 \text{ mol}^{-1}$) recorded by De Guardia et al. [11], even if the difference between the viscosities of the silicone oils used (5 and 3 mPa s, respectively) can account, at least partially, for these differences.

Generally speaking, it appears that partition coefficient drops dramatically with the silicone oil volume fraction (ϕ). For data analysis, a mathematical expression of partition coefficient was developed assuming that the mixture of water and an immiscible solvent can be considered as a pseudo-homogeneous phase [17]. In such a case, partition coefficient can be defined as:

$$H_{\text{voc,mixture}} = RT \frac{C_{\text{gas}}}{C_{\text{mixture}}} \quad (3)$$

Table 4

Results from the static headspace method (shm): partition coefficients for the three considered pollutants in water/silicone oil mixtures ($T=298\text{K}$; H_{shm} in $\text{Pa m}^3 \text{ mol}^{-1}$).

Silicone oil volume fraction	DMDS H_{shm}	DMS H_{shm}	Silicone oil volume fraction	Toluene H_{shm}
0.00	121.8	124.1	0.00	615.0
0.08	26.8		0.02	66.8
0.24	12.1	42.8	0.04	44.0
0.48	6.6		0.09	18.3
0.69	4.7		0.24	10.1
0.84	4.0		0.49	4.8
1.00	3.4	17.7	0.70	3.6
			0.85	2.7
			1.00	2.3

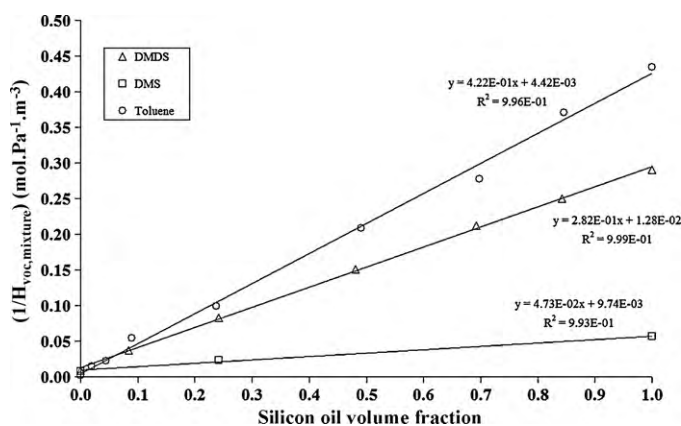


Fig. 3. Linear evolution of $1/H_{\text{voc,mixture}}$ versus ϕ for the three pollutants.

with the following expression of the solute concentration (Eq. (4)):

$$C_{\text{mixture}} = \frac{n_{\text{water}} + n_{\text{solvent}}}{V_{\text{mixture}}} \quad (4)$$

The number of moles of solute in both liquid phases is given by Eqs. (5) and (6):

$$n_{\text{water}} = C_{\text{water}}(1 - \phi)V_{\text{mixture}} \quad (5)$$

$$n_{\text{solvent}} = C_{\text{solvent}}\phi V_{\text{mixture}} \quad (6)$$

where C_{water} and C_{solvent} can be linked to their partition coefficients following Eqs. (7) and (8), respectively:

$$H_{\text{voc,water}} = RT \frac{C_{\text{gas}}}{C_{\text{water}}} \quad (7)$$

$$H_{\text{voc,solvent}} = RT \frac{C_{\text{gas}}}{C_{\text{solvent}}} \quad (8)$$

Combining Eqs. (3)–(8) give:

$$\frac{1}{H_{\text{voc,mixture}}} = \frac{(1 - \phi)}{H_{\text{voc,water}}} + \frac{\phi}{H_{\text{voc,solvent}}} \quad (9)$$

A similar expression of the evolution of partition coefficient has been experimentally validated by Davison et al. [18] to determine alkane solubility in water in the presence of high-density biomass. Eq. (9) can be rewritten as a linear equation expressing $1/H_{\text{voc,mixture}}$ versus ϕ (Fig. 3). Moreover, as expected, $1/H_{\text{voc,mixture}}$ linearly increased with the silicone oil volume fraction, indicating a good agreement between the mathematical model and the experimental results. Such an evolution has also been observed by Vuong et al. [19] for the absorption of DMS, DMDS and toluene in various mixtures of immiscible liquids i.e. water/di-(2-ethyl)hexyladipate, water/n-hexadecane and water/oleyl alcohol. In Fig. 4, the predicted evolution of the partition coefficient versus ϕ according to Eq. (9) is compared with the experimental results obtained from both static and dynamic methods, and with the linear evolution occasionally used to model mass transfer in mixtures of water

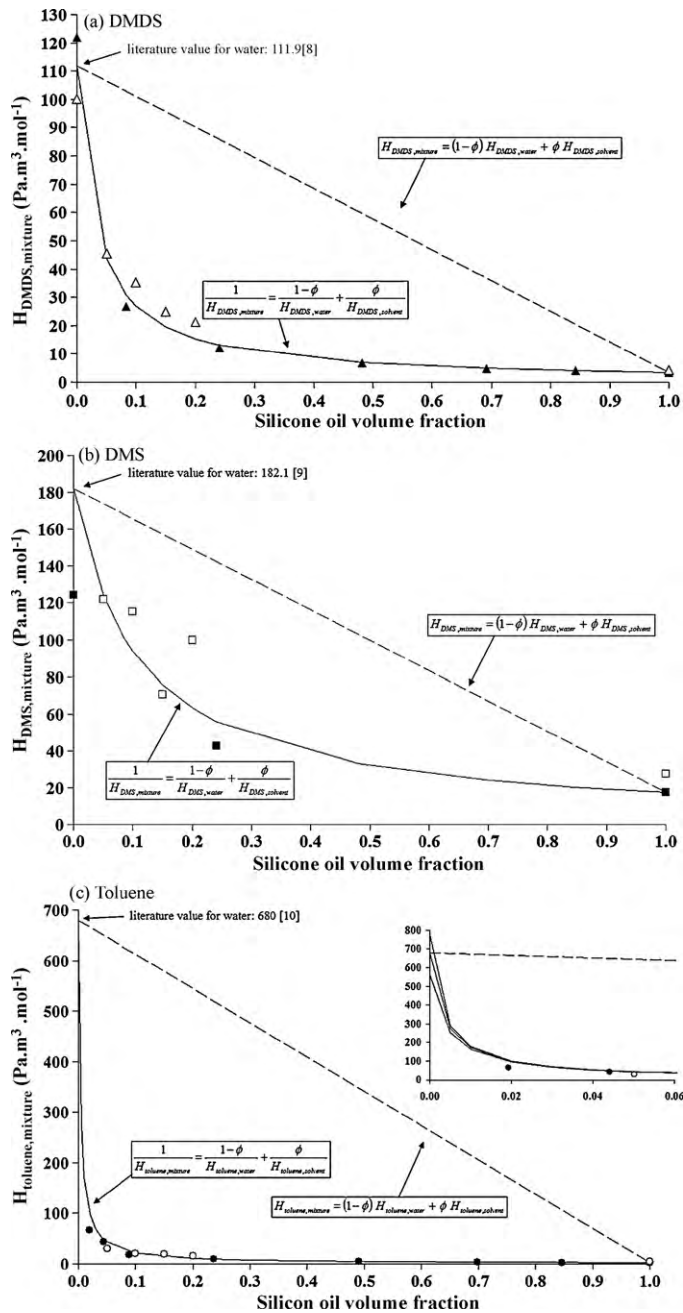


Fig. 4. Evolution of partition coefficients versus silicone oil volume fraction for the three pollutants; comparison between experimental data (closed symbols: static headspace method; open symbols: dynamic absorption method) and models (dashed line: linear model; black line: model corresponding to Eq. (9)). Insert for toluene: influence of the $H_{\text{voc,water}}$ value on the predicted $H_{\text{voc,mixture}}$ value calculated according to Eq. (9); $H_{\text{voc,water}} = 680$ from Mackay et al. [10] and extreme values reported in the literature $H_{\text{voc,water}} = 562$ and $H_{\text{voc,water}} = 779 \text{ Pa m}^3 \text{ mol}^{-1}$.

Table 5

Comparison between results from the dynamic absorption method H_{dam} and predicted values $H_{\text{voc,mixture}}$ calculated according to Eq. (9). $H_{\text{voc,mixture}}$ for the three pollutants are calculated using the following values: $H_{\text{DMDS,water}} = 111.9$; $H_{\text{DMDS,solvent}} = 3.4$; $H_{\text{DMS,water}} = 182.1$; $H_{\text{DMS,solvent}} = 17.7$; $H_{\text{toluene,water}} = 680$; $H_{\text{toluene,solvent}} = 2.3$ (H_{voc} in $\text{Pa m}^3 \text{ mol}^{-1}$; $T = 298 \text{ K}$. Note that: $P_{\text{voc,mixture}} = H_{\text{voc,mixture}}/RT$, dimensionless).

Silicone oil volume fraction	DMDS				DMS				Toluene			
	H_{dam}	$H_{\text{voc,mixture}}$	Difference	$P_{\text{voc,mixture}}$	H_{dam}	$H_{\text{voc,mixture}}$	Difference	$P_{\text{voc,mixture}}$	H_{dam}	$H_{\text{voc,mixture}}$	Difference	$P_{\text{voc,mixture}}$
0.05	45.6	43.4	5.0	0.01753	122	102.0	19.4	0.04115	30.6	43.2	-29.2	0.01745
0.10	35.3	26.9	31.0	0.01088	115	93.9	22.8	0.03791	21.0	22.3	-5.9	0.00901
0.15	24.9	19.5	27.5	0.00788	70.7	75.6	-6.5	0.03052	19.6	15.0	30.3	0.00607
0.20	21.4	15.3	39.7	0.00618	99.7	63.3	57.5	0.02554	15.5	11.3	36.6	0.00458
1.00	4.3	3.4	25.0	0.00139	27.4	17.7	54.8	0.00714	5.1	2.3	121.7	0.00093

and immiscible solvents [20,21]. The predicted evolution is calculated using the $H_{\text{voc,water}}$ value given in the literature (Table 2), and our experimental $H_{\text{voc,solvent}}$ measurements. A clear deviation from linearity of the experimental data appears, which is more pronounced for increasing $H_{\text{voc,water}}/H_{\text{voc,solvent}}$ ratios (for instance, toluene: $H_{\text{toluene,water}}/H_{\text{toluene,solvent}} = 680/2.3 = 295$). Moreover, in the case of toluene where the $H_{\text{toluene,water}}$ value is relatively inaccurate (from 562 to 779 $\text{Pa m}^3 \text{ mol}^{-1}$ according to the literature), it can be observed that the $H_{\text{toluene,water}}$ value has no influence on the $H_{\text{toluene,mixture}}$, since the silicone oil volume fraction is greater than 2% (inserted in Fig. 4c). Consequently, adding silicone oil to improve the absorption of scarcely soluble pollutants in water appears significantly useful, even for very low values of the oil volume fraction (a few percent). However, it must be mentioned that the dramatic decrease in partition coefficient following oil addition could modify the volumetric mass transfer coefficient $K_L a$. Indeed, according to the two-film theory, mass transfer, which is controlled by the liquid film resistance for scarcely soluble solutes, i.e. in the case of water or water/silicone oil mixtures at low volume fractions, could be controlled by both the liquid film resistance and the gas film resistance when the silicone oil volume fraction increases. Some peculiar behaviour of the volumetric mass transfer coefficient reported in the literature, especially at low volume fractions of solvent [22,23], could be explained by the decrease in partition coefficient (complementary to explanations attributed to surface tension and viscosity).

3.2. Dynamic absorption method (H_{dam})

For the three target pollutants, the results from the dynamic absorption method confirmed the trend revealed by the static headspace method (Fig. 4), even in the case of DMS, despite the difficulties of obtaining accurate measurements. Values deduced from dynamic measurements are nonetheless higher than those obtained with the static method, indicating that the dynamic absorption method cannot be used for an accurate determination of partition coefficients. However, these results give interesting information for the design of two-phase partitioning absorbers as demonstrated below. The non-negligible calculated difference (Table 5) between the results drawn from dynamic absorption and the predicted values given by Eq. (9), or values of static measurements, cannot be explained solely by the inaccuracy of the operating parameters, mainly the temperature control of the mixture. Although a dynamic equilibrium between phases was reached (Fig. 2), it could be assumed that the continuous gas flow in the mixture caused a stripping of pollutant. Consequently, the pollutant concentration was lower in the liquid phase and higher in the gas phase than expected, leading to higher H_{voc} values than those obtained by the static method. Basically, the dynamic absorption experiments carried out in this study could correspond to an ideal stage whose graphical construction is given in Fig. 5. The equilibrium line between the gas phase and the liquid phase is

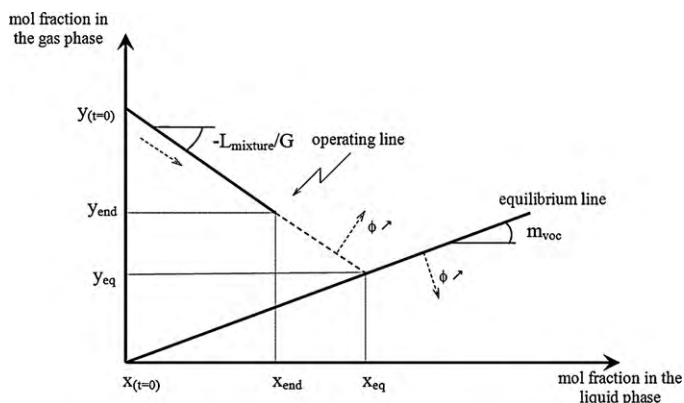


Fig. 5. Relationship between the equilibrium line and the operating line corresponding to the absorption stage displays in Fig. 1.

(Eq. (10)):

$$y = m_{\text{voc}}x \left[\frac{\text{mole}_{\text{voc,Gas}}/\text{mole}_{\text{Gas}}}{\text{mole}_{\text{voc,Liquid}}/\text{mole}_{\text{Liquid}}} \right] \quad (10)$$

where y and x are the molar fractions of the pollutant in the gas phase and in the liquid phase, respectively; m_{voc} is the slope of the equilibrium line and corresponds to the partition coefficient calculated with the appropriate units. The relation between m_{voc} and H_{voc} is given by Eq. (11):

$$m_{\text{voc}} = H_{\text{voc}} \left(\frac{1}{RT} \right) \left(\frac{M_{\text{Gas}} \rho_{\text{Liquid}}}{M_{\text{Liquid}} \rho_{\text{Gas}}} \right) \quad (11)$$

At the start of the experiment, the pollutant was only present in the gas phase ($y = y_{(t=0)}$ and $x_{(t=0)} = 0$). During the absorption step, the pollutant was transferred from the gas phase (G moles) to the liquid mixture (L_{mixture} moles) and the composition of each phase was deduced from the operating line whose slope is $(-L_{\text{mixture}}/G)$. Assuming an ideal stage, the final composition of each phase (y_{end} and x_{end}) should be given by the intersection between the operating line and the equilibrium line (y_{eq} and x_{eq}). However, the gas flow rate across the liquid, similar to a “blowing regime” described in tray towers, resulted in a decrease in the efficiency of this stage. Consequently, the point (y_{eq} , x_{eq}) could not be reached. The efficiency of the actual stage (E_{ff}) corresponds to the change in the gas composition during the experiment divided by the change that would have occurred if the gas phase had really been in equilibrium with the liquid phase (Eq. (12)):

$$E_{\text{ff}} = \frac{y_{(t=0)} - y_{\text{end}}}{y_{(t=0)} - y_{\text{eq}}} \quad (12)$$

$y_{(t=0)}$ and y_{end} can be experimentally deduced since the pollutant concentration in the gas phase was continuously monitored and since it can reasonably be assumed that the number of gas moles G was constant during absorption. Unfortunately, y_{eq} was not *a priori* calculable (except for pure solvents) because the number of moles corresponding to the liquid phase L_{mixture} varied according to the composition of the water/silicone oil mixtures. For a unit volume of the mixture ($V_{\text{Liquid}} = 1$ L in the conditions of the experiment), L_{mixture} decreases from 55.55 mol for pure water to 1.26 mol for pure silicone oil in relation to the difference between the molecular weights of water and the oil (18 g/mol versus 740 g/mol). Consequently, an increase in the silicone oil percentage in the mixture corresponded to a decrease in the slope of the operating line $(-L_{\text{mixture}}/G)$ in Fig. 5. However, except for pure liquids, L_{mixture} was unknown because both M_{mixture} and ρ_{mixture} were unknown; the simple calculation of L_{mixture} versus ϕ corresponding to a summation of the numbers of moles of water and solvent ($n_{\text{water}} + n_{\text{solvent}}$)

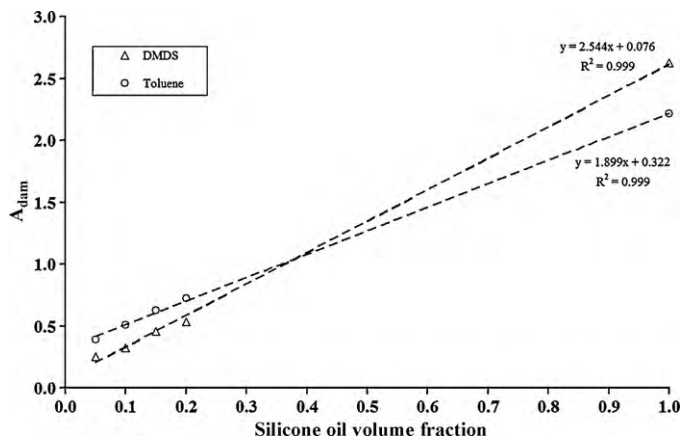


Fig. 6. Experimental absorption factor A_{dam} versus ϕ for DMDS and toluene (dynamic absorption method).

in the mixture gave erroneous results from the absorption point of view. In the same way, the increase in the silicone oil percentage led to a decrease in the slope of the equilibrium line (m_{voc}) according to Eq. (9) and Fig. 4. It resulted in a change of the intersection of both operating and equilibrium lines in relation to the silicone oil percentage. Nevertheless, it is possible to determine L_{mixture} and E_{ff} as a function of the silicone oil percentage as described below.

An experimental dimensionless absorption factor A_{dam} corresponding to the dynamic absorption method can be calculated. Between the start and the end of the experiment, the mass balance can be written:

$$V_{\text{Gas}} (C_{(t=0)}^G - C_{\text{end}}^G) = V_{\text{Liquid}} C_{\text{end}}^L \quad (13)$$

corresponding to (in molar units):

$$G(y_0 - y_{\text{end}}) = Lx_{\text{end}} \quad (14)$$

The introduction of Eq. (1) into Eq. (13) and Eq. (10) into Eq. (14) gives two expressions of the absorption factor (Eqs. (15) and (16)):

$$A_{\text{dam}} = \frac{V_{\text{Liquid}}}{P_{\text{voc}} V_{\text{Gas}}} = \frac{C_{(t=0)}^G - C_{\text{end}}^G}{C_{\text{end}}^G} \quad (15)$$

$$A_{\text{dam}} = \frac{L}{m_{\text{voc}} G} = \frac{y_0 - y_{\text{end}}}{y_{\text{end}}} \quad (16)$$

A_{dam} can be easily determined using $C_{(t=0)}^G$ and C_{end}^G in Eq. (15).

According to Fig. 6, A_{dam} followed a linear trend for silicone oil addition for both DMDS and toluene. The DMS trend is not given due to inaccurate measurements by both the static headspace and the dynamic absorption methods. It is also possible to estimate the absorption factor A that would have occurred if the gas phase and the liquid phase had really been in equilibrium, by replacing C_{end}^G by C_{eq}^G in Eq. (15) and y_{end} by y_{eq} in Eq. (16):

$$A = \frac{V_{\text{Liquid}}}{P_{\text{voc}} V_{\text{Gas}}} = \frac{C_{(t=0)}^G - C_{\text{eq}}^G}{C_{\text{eq}}^G} = \frac{L}{m_{\text{voc}} G} = \frac{y_0 - y_{\text{eq}}}{y_{\text{eq}}} \quad (17)$$

A was calculated using V_{Liquid} and V_{Gas} and from the partition coefficient values P_{voc} determined using the predicted model corresponding to Eq. (9) and whose values are reported in Table 5. Since V_{Liquid} and V_{Gas} were constant during the absorption step and $1/P_{\text{voc}}$ was a linear function of the silicone oil percentage (Fig. 3), the absorption factor was obviously a linear function of ϕ , i.e. $A = a\phi + b$. Furthermore, it must be considered that the linear trend of $1/H_{\text{voc}}$ versus ϕ was valid whatever the expression of the partition coefficient ($1/P_{\text{voc}}$ or $1/m_{\text{voc}}$). As G was constant, it appears that $1/(m_{\text{voc}} G)$ was also a linear function of ϕ , i.e. $(1/m_{\text{voc,mixture}} G) = c\phi + d$. The linear evolution of $1/(m_{\text{voc,mixture}} G)$ versus ϕ can only be determined

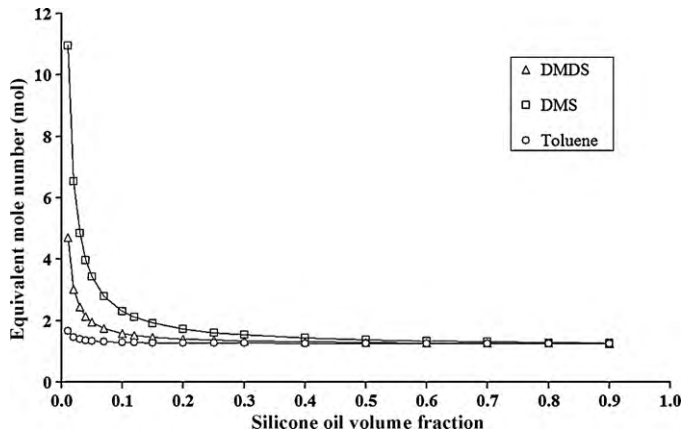


Fig. 7. L_{mixture} versus ϕ for the three pollutants. Open symbols: values calculated with Eq. (18). Black line: L_{mixture} model corresponding to Eq. (19).

from the two known points, $1/(m_{\text{voc,water}}G)$ corresponding to $\phi = 0$ and $1/(m_{\text{voc,solvent}}G)$ corresponding to $\phi = 1$. From Eq. (17), L_{mixture} values can consequently be deduced for the three pollutants (Eq. (18)):

$$L_{\text{mixture}} = \frac{A}{1/m_{\text{voc,mixture}}G} = \frac{a\phi + b}{c\phi + d} \quad (18)$$

L_{mixture} values for DMDS, DMS and toluene are given in Table 6. They can be compared to the number of liquid moles ($n_{\text{water}} + n_{\text{solvent}}$) actually present in the mixture. Thus, it appears that L_{mixture} values tend rapidly towards n_{solvent} ; this trend was more pronounced for increasing $H_{\text{voc,water}}/H_{\text{voc,solvent}}$ ratios. Consequently, it can reasonably be considered that the mixture had an absorption capacity equivalent to that of a pseudo-homogeneous phase in which the number of moles (L_{mixture}) given in Table 6 can be expressed as a function of ϕ . The “equivalent absorption capacity” of the mixture towards the pollutant transfer depends mainly on the ability of both liquids to absorb the pollutant, which must be balanced according to $H_{\text{voc,water}}$ and $H_{\text{voc,solvent}}$. In the same way, if the mixture can be considered as a pseudo-homogeneous phase from the absorption point of view, it can be characterised by an equivalent density (ρ_{mixture}) and an equivalent molecular weight (M_{mixture}). If L_{mixture} is considered, its trend versus ϕ , calculated using Eq. (18) and modelled values obtained from Eq. (19), is displayed in Fig. 7. To improve the representation, L_{mixture} is not given in the case of pure water ($\phi = 0$). It can be observed that the mole number of the pseudo-homogeneous phase is satisfactorily expressed by Eq. (19), based on the actual number of moles of both water and solvent present in the mixture, i.e. n_{water} and n_{solvent} . It appears that the mole number of the pseudo-homogeneous phase, having an absorption capacity equivalent to that of the mixture, depends on

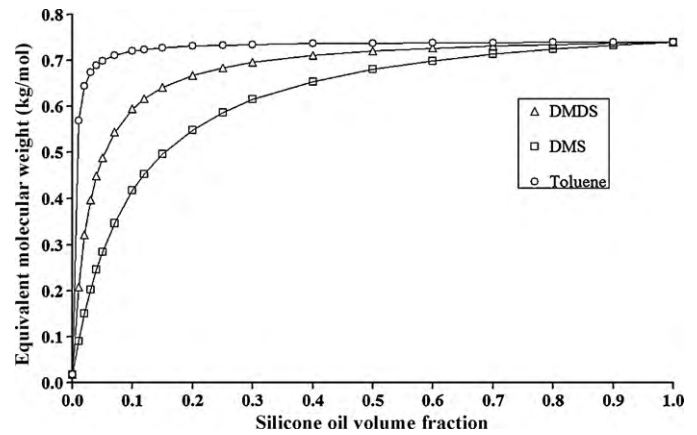


Fig. 8. M_{mixture} versus ϕ for the three pollutants. Open symbols: values calculated with Eq. (20). Black line: M_{mixture} model corresponding to Eq. (22).

$H_{\text{voc,water}}$ and $H_{\text{voc,solvent}}$ towards the “equivalent absorption coefficients” $H_{\text{voc,mixture}}/H_{\text{voc,water}}$ and $H_{\text{voc,mixture}}/H_{\text{voc,solvent}}$ applied to water and solvent volumetric fractions, respectively.

$$\frac{1}{L_{\text{mixture}}} = \frac{(1-\phi)^2}{n_{\text{water}}} \frac{H_{\text{voc,mixture}}}{H_{\text{voc,water}}} + \frac{\phi^2}{n_{\text{solvent}}} \frac{H_{\text{voc,mixture}}}{H_{\text{voc,solvent}}} \quad (19)$$

In Eq. (19), $H_{\text{voc,mixture}}$ is given by Eq. (9). The equivalent molecular weight related to the mole number of the pseudo-homogeneous phase can be determined from Eqs. (19) and (20):

$$M_{\text{mixture}} = V_{\text{liquid}} \frac{\rho_{\text{mixture}}}{L_{\text{mixture}}} \quad (20)$$

with:

$$\rho_{\text{mixture}} = (1-\phi)\rho_{\text{water}} \frac{H_{\text{voc,mixture}}}{H_{\text{voc,water}}} + \phi\rho_{\text{solvent}} \frac{H_{\text{voc,mixture}}}{H_{\text{voc,solvent}}} \quad (21)$$

The “equivalent absorption coefficients” $H_{\text{voc,mixture}}/H_{\text{voc,water}}$ and $H_{\text{voc,mixture}}/H_{\text{voc,solvent}}$ must also be used to express satisfactorily the equivalent density of the pseudo-homogeneous phase, based on both water and solvent densities. If the “equivalent absorption coefficients” are not used to balance the relative importance of water and solvent, Eq. (20) can lead to M_{mixture} values higher than M_{solvent} for some values of ϕ . Fig. 8 presents the evolution of M_{mixture} versus ϕ calculated using Eq. (20) and the modelled values obtained from Eq. (22).

$$M_{\text{mixture}} = (1-\phi)M_{\text{water}} \frac{H_{\text{voc,mixture}}}{H_{\text{voc,water}}} \frac{\rho_{\text{mixture}}}{\rho_{\text{water}}} + \phi M_{\text{solvent}} \frac{H_{\text{voc,mixture}}}{H_{\text{voc,solvent}}} \frac{\rho_{\text{mixture}}}{\rho_{\text{solvent}}} \quad (22)$$

Table 6

Left: mole numbers actually present in the mixture for a liquid volume: $V_L = 1 \text{ L}$ ($L = n_{\text{water}} + n_{\text{solvent}}$). Right: equivalent mole number values (L_{mixture}) calculated according to Eq. (18) with the following expressions: DMDS, $A = 3.256\phi + 0.1020$, $1/(m_{\text{voc,mixture}}G) = 2.671\phi + 0.0018$; DMS, $A = 0.582\phi + 0.0627$, $1/(m_{\text{voc,mixture}}G) = 0.513\phi + 0.0011$; toluene, $A = 4.947\phi + 0.0168$, $1/(m_{\text{voc,mixture}}G) = 3.949\phi + 0.0003$.

Silicone oil volume fraction	n_{water} (mol)	n_{solvent} (mol)	$L = n_{\text{water}} + n_{\text{solvent}}$ (mol)	L_{mixture} (mol)		
				DMDS	DMS	Toluene
0.00	55.556	0.000	55.556	55.550	55.550	55.550
0.01	55.000	0.013	55.013	4.714	10.964	1.665
0.02	54.444	0.025	54.470	3.024	6.526	1.460
0.05	52.778	0.063	52.841	1.956	3.428	1.336
0.10	50.000	0.126	50.126	1.590	2.306	1.294
0.15	47.222	0.189	47.411	1.467	1.921	1.280
0.20	44.444	0.251	44.696	1.406	1.727	1.274
0.50	27.778	0.628	28.406	1.293	1.273	1.261
1.00	0.000	1.257	1.257	1.256	1.254	1.257

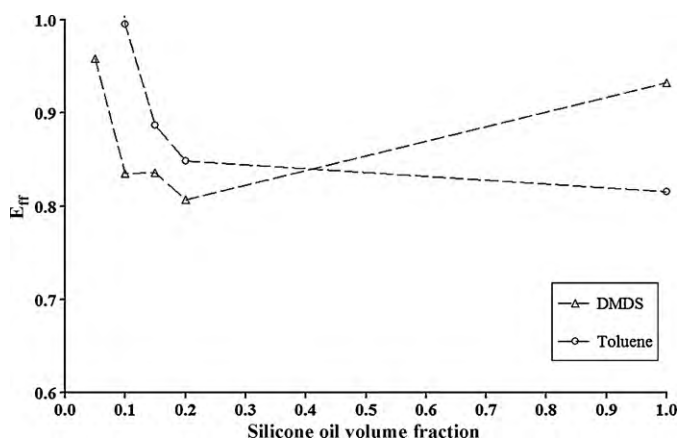


Fig. 9. Absorption efficiency E_{ff} versus ϕ for DMDS and toluene (dynamic absorption method).

To summarise the concept of “equivalent absorption capacity” of a two-phase mixture using an example, one can say that 1 L of a water/silicone oil mixture (90:10 v/v) has an absorption behaviour equivalent to that of a pseudo-homogeneous phase with the following characteristics:

- For DMDS: $L = 1.590 \text{ mol}$; $H = 26.7 \text{ Pa m}^3 \text{ mol}^{-1}$; $\rho = 945 \text{ kg m}^{-3}$; $M = 594 \text{ g mol}^{-1}$.
- For DMS: $L = 2.310 \text{ mol}$; $H = 94.4 \text{ Pa m}^3 \text{ mol}^{-1}$; $\rho = 963 \text{ kg m}^{-3}$; $M = 417 \text{ g mol}^{-1}$.
- For toluene: $L = 1.294 \text{ mol}$; $H = 22.3 \text{ Pa m}^3 \text{ mol}^{-1}$; $\rho = 932 \text{ kg m}^{-3}$; $M = 720 \text{ g mol}^{-1}$.

These results are important for the design of an absorption column and similar studies must be undertaken in order to determine other parameters needed for correlations, mainly diffusion coefficient, surface tension, and dynamic viscosity.

To complete the analysis of the results obtained from the dynamic absorption method, an arrangement of Eq. (17) gives E_{ff} :

$$E_{ff} = \frac{A_{dam}}{A} \frac{y_{end}}{y_{(t=0)}} (A + 1) \quad (23)$$

Fig. 9 presents the variations in the absorption efficiency for DMDS and toluene related to silicone oil addition. A rapid decrease followed by a progressive increase can be observed for both pollutants. These changes were most likely caused by the variation in the viscosity of the mixture and by the increase in the mass transfer resistance related to the variation in the slope “ m_{voc} ” with silicone oil addition. A specific analysis of the impact of the mixture composition on the $K_L a$ could help identify the resistance to mass transfer. Such an analysis would simply be based on the pseudo-homogeneous phase with the appropriate value of the partition coefficient $H_{voc,mixture}$.

4. Conclusion

A simple predictive model has been experimentally checked for the determination of partition coefficients of VOCs in water/silicone oil mixtures. This study has highlighted the dramatic decrease in partition coefficient with oil addition and it can be concluded that the actual value deviates further from linearity as the ratio $H_{voc,water}/H_{voc,solvent}$ increases. Moreover, the partition coefficients expressed by Eq. (9) confirm that the mixture can reasonably

be considered as a pseudo-homogeneous phase. The dynamic absorption method analysis demonstrated that a given volume of a water/silicone oil mixture shows an “absorption capacity” equivalent to the same volume of a pseudo-homogeneous phase whose physical properties (number of moles, density and molecular weight) can be expressed from the physical properties of water and solvent, and balanced using the “equivalent absorption coefficients” $H_{voc,mixture}/H_{voc,water}$ and $H_{voc,mixture}/H_{voc,solvent}$ (Eqs. (19), (21) and (22)).

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