



Determination of the Henry's constant and the mass transfer rate of VOCs in solvents

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ABSTRACT

Absorption of hydrophobic volatile organic compounds (VOCs): dimethylsulfide (DMS), dimethyldisulfide (DMDS) and toluene, in organic solvents: di-(2-ethyl)hexyladipate (DEHA), n-hexadecane, oleyl alcohol and PEG 400, was studied. In order to characterise the absorption capacity of various VOC/solvent systems, the Henry's constant (H) was determined. DMS was found to be the least absorbable in all the selected solvents. Amongst these solvents, DEHA was found to be the most efficient to absorb the considered VOCs. The effect of water addition to the considered solvents (emulsions) on the Henry's constants was examined and confirmed a decreasing VOC absorption for an increasing amount of water in solvent. Finally, to quantify the process rapidity, the absorption rate (N) and the overall liquid mass transfer coefficient ($K_L a$) were measured for some selected couples VOC/solvent and revealed a superior efficiency of DEHA compared to other solvents in trapping DMS, DMDS and toluene.

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1. Introduction

Nowadays, many industries generate malodorous and/or toxic volatile organic compounds (VOCs). Because the distance separating residential and industrial areas has been shortening, odour nuisance has grown. Thus authorities receive more and more complaints from communities. At present, several processes are available to remove odorous compounds at low concentration: chemical scrubbing [1], biological treatment [2] and adsorption. Despite being one of the most commonly used process in gas recovering, adsorption can not be considered as a final treatment but only as a pollution relocation and/or concentration step. Therefore, it requires additional treatments such as thermal desorption and thermal oxidation. Concerning the chemical way, scrubbing is mainly processed with an aqueous solution (acidic, basic, oxidant) because the targeted compounds are more or less soluble in water. The gaseous compound is transferred into the liquid scrubbing solution, and then removed by chemical reactions. The mass transfer rate is enhanced by the chemical reaction taking place in the liquid phase. However, some VOCs are not very soluble in water (called hydrophobic VOCs) and their mass transfer from the gas phase to the aqueous phase is not easy to achieve, even with the help of chemical reactions. As a consequence, the removal efficiencies remain very low. Because of their hydrophobic character, the

efficiency of biological treatment of such compounds is also limited. To the best of our knowledge, there is yet no process that can successfully remove hydrophobic VOCs at low concentration from exhausted industrial gas streams.

Amongst the family of water-insoluble VOCs, one can find dimethylsulfide (DMS), dimethyldisulfide (DMDS), and toluene. These compounds are often encountered in gaseous effluents issued from pulp and paper factories [3], composting facilities [4], food industries [5], etc. In order to remove such compounds, current processes must be improved. For this purpose, absorption by an organic solvent seems to be a promising alternative. Several solvents are available to absorb hydrophobic VOCs. Therefore, finding the best solvent in terms of absorption capacity and absorption rate, but also in terms of cost and recycling easiness, is an important task. In fact, solubility is a fundamental factor since it characterises the absorption capacity of a solvent versus a VOC. Besides, the absorption rate must not be neglected because the required time to absorb a known quantity of VOC is an important parameter in the process designing, directly related to the size of a plant. For that reason the mass transfer coefficient, $k_L a$ or $K_L a$, needs to be measured. Even though it is well-known that the physico-chemical properties of the liquid phase play an important role, the value of this parameter is not easily predictable. For example, Das et al. [6] found that the interfacial area " a " measured in an organic phase can differ from the one found in an aqueous phase using the same device. They suggested that the presence of an organic phase can limit the coalescence, but a high viscosity can also decrease turbulence, resulting in a less developed interfacial area. Moreover, Cents et al. [7] reported

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that the liquid film mass transfer coefficient “ k_L ” depends on the dissipated energy and hydrodynamics. Lekhal et al. [8] found that “ k_L ” can increase for low oil concentrations in water (3–4%). These results show that hydrodynamics plays an important role on the variations of $k_L a$, which implies that $k_L a$ and $K_L a$ values are difficult to compare from a study to another.

The purpose of this work was to find and to compare the efficiency of some solvents for their ability to absorb hydrophobic volatile compounds such as sulphur compounds and toluene. Absorption capacity and absorption rate were the sole criteria taken into account in this study. In a first step, the Henry’s constant was determined to quantify the absorbency (absorption capacity) of four selected solvents facing the three target VOCs. Then the mass transfer rate and the overall mass transfer coefficient were estimated for each VOC in two best solvents, DEHA (di-(2-éthyl)hexyladipate) and n-hexadecane. Due to the high VOC solubility in two of the selected solvents, mass transfer is very rapid and thus, not easily measurable in conventional scrubbers. As a consequence, the efficiencies of these solvents were compared using a non-optimised device. Since gaseous effluents often contain both hydrophobic and hydrophilic VOCs, an emulsion consisting of water and organic solvent may be more interesting to use than a pure solvent in certain cases. Therefore, some Henry’s constants were measured in emulsions in order to determine the effect of water on the absorption capacity.

2. Experimental

2.1. Henry’s constant determination (1/H)

The authors of this work were interested in solvents displaying the following properties: low viscosity (high mass transfer rate), low volatility (limitation of solvent losses due to evaporation) and density close to that of water (less energy required for recycling). The solvents chosen for this study were DEHA (di-(2-éthyl)hexyladipate), n-hexadecane, PEG 400 (polyethyleneglycol) and oleyl alcohol (cis-9-octadecen-1-ol; 70% purity). Their physico-chemical properties are reported in Table 1. Except for PEG 400, these solvents are not soluble in water.

Dimensionless Henry’s constants H were obtained using a static method. A known quantity of solvent (or emulsion) was introduced into a specific flask (vial), whose exact volume was measured. The flask was gas-tightly sealed and then a known quantity of VOC was added through the septum. The vial was shaken by a swivelling support during one night at 25 °C. Once the equilibrium was reached, revealed by a constant VOC concentration in the gas phase, the quantity of pollutant in the gas phase was measured using gas chromatography analysis: toluene with a GC-Flame Ionisation Detector from Fisons (with FFAP 25 m column, $T_{det} = 250$ °C, $T_{inj} = 200$ °C, $T_{oven} = 70$ °C), and sulphur compounds with a GC-Flame Photometry Detector from Agilent (with a GS-GASPRO 30 m column, $T_{det} = T_{inj} = 200$ °C, $T_{oven} = 180$ °C). Assuming the mass bal-

Table 1
Solvents’ and pollutants’ characteristics.

Solvent	MW (g mol ⁻¹)	Density	T_{eb} (K)	μ (Pa s)
DEHA	370.58	0.92	690	0.0125 [9]
n-hexadecane	226.44	0.77	560	0.0021
Oleyl alcohol (70%)	268.47	0.89	480 (13 mm Hg)	0.028
PEG 400	398–402	1.13	>523	0.1336 [9]
Pollutant	MW (g mol ⁻¹)	Density	T_{eb} (K)	P_{sat} (hPa)
DMS	62.1	0.846	311	505
DMDS	94.2	1.063	382	37
Toluene	92.1	0.867	389	38

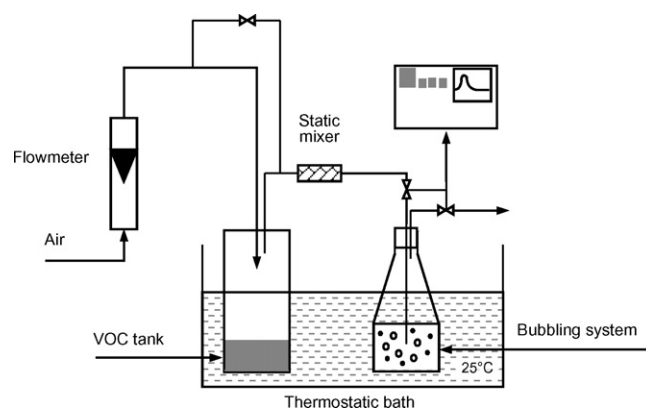


Fig. 1. Experimental set-up for mass transfer rate determination.

ance conservation, the liquid phase concentration can be calculated. The dimensionless constant H was obtained using Eq. (1). The same experiments were carried out with emulsions (5–100% (v/v) solvent in water).

$$HC_L = C_G \quad (1)$$

Throughout this study, each experimental point was calculated as the average of at least four measurements. The relative standard deviation was found in the range 0–8%.

2.2. Mass transfer rate determination (N)

Fig. 1 shows the experimental set-up of the dynamic method implemented in order to obtain the absorption rate N for six couples VOC/solvent (two solvents for each VOC). Rather than to determine the accurate values, the objective was to compare both solvents, and hence the gas-liquid contactor was not optimised. A polluted gas stream was generated by bubbling pure VOC with a carrier gas (air); then, this synthetic gas came into contact with the pure solvent ($Q_G = 3.6$ – 5 L min⁻¹). The evolution of the VOC concentration in the gas phase versus time was monitored by analysing inlet and outlet pollutant concentration. The high bubble velocity and the low value of liquid depth (around 5 cm) suggested that the liquid phase could be considered perfectly mixed. Using the integration of $C_{G,o}$ time-course in the transient regime and the mass balance between the inlet and the outlet, the liquid VOC concentration could be obtained (Eq. (2)).

$$Q_G \int_0^t (C_{G,i} - C_{G,o}) dt = C_L V_L \quad (2)$$

where V_L is the volume of liquid phase, C the VOC concentration, and the subscripts G, L, i, o correspond to gas, liquid, inlet and outlet. Then, the absorption rate N was calculated, for each selected couple VOC/solvent (Eq. (3)). The liquid VOC concentration at the end of the experiment, where $C_{G,i} = C_{G,o}$, can be used to reconfirm previously obtained H constant values.

$$N_t = \frac{C_{L,t+\Delta t} - C_{L,t-\Delta t}}{2\Delta t} V_L \quad (3)$$

The total volume of our experimental device was 2 L. As a consequence the renewal time for gas phase was about 30 s even with the least important flow of 3.6 L min⁻¹. Therefore the 10 min waiting time before the first inlet measurement could be considered much greater than the intrinsic response time of the system.

2.3. Overall volumetric mass transfer coefficient determination ($K_L a$)

Eq. (4) gives the relation between the overall mass transfer coefficient K_L and the film mass transfer coefficients k_L and k_G :

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{Hk_G} \quad (4)$$

When no term of this equation can be neglected, i.e. when mass transfer resistance cannot be attributed to the liquid phase only, the overall mass transfer coefficient K_L should be used instead of the liquid mass transfer coefficient k_L . The mass transfer rate (N_t) is related to this coefficient in Eq. (5):

$$N_t = K_L a V_L (\overline{C_{L,t}^E} - C_{L,t}) \quad (5)$$

where $\overline{C_{L,t}^E}$ is the VOC concentration in the liquid phase at equilibrium between the two phases at the film interface and a is the volumetric interfacial area.

The contact time between the two phases was supposed to be long enough to achieve equilibrium at the interface. By plotting values of N_t versus $V_L(\overline{C_{L,t}^E} - C_{L,t})$, straight lines were obtained.

3. Results and discussion

3.1. Henry's constants in pure solvents

The values of the Henry's constant for each couple VOC/solvent are reported in Table 2. The higher $1/H$ is, the more important the VOC solubility in the solvent is. As it can be observed, whichever the solvent, the DMS absorption was low: its $1/H$ values did not exceed 360, whereas values between 990 and 2820 were found for the two other VOCs. This can be attributed to the low boiling temperature of DMS, and its high saturation vapour pressure. In fact, among the three chosen pollutants, DMS is the most volatile (saturation vapour pressure = 505 hPa compared to 37 hPa and 38 hPa for DMDS and toluene, respectively), hence DMS should be the most difficult to trap into a liquid phase. Except for oleyl alcohol (which was not pure), the solubility of the sulphur VOCs varied in the same order according to the four solvents: DEHA > n-hexadecane > PEG 400 > water. Results were slightly different for toluene, but DEHA was still the best solvent for toluene absorption. Same conclusion had been made by Heymes et al. [9] and by Roizard et al. [10]. Differences among the VOC solubilities could be related to their polarity since toluene is the least polar compounds.

3.2. Henry's constants in emulsions

Figs. 2–4 show the results obtained for experiments carried out with emulsions. As expected, the value of $1/H$ (absorption capacity) linearly increased with the percentage of solvent in water, except for PEG 400 that seemed to follow an exponential trend.

The miscibility of PEG 400 in water could explain this difference, but this assumption should be subsequently confirmed by considering other experiments with some miscible solvents. Extrapolation of the $1/H$ value for a nil value of solvent in water led to the solubility of each VOC in water (values of 9, 17 and 12 for DMS, DMDS and

Table 2
Henry's constant of the three VOCs chosen in the different solvents.

$1/H$	DMS	DMDS	Toluene
DEHA	127	2338	2821
n-Hexadecane	114	1425	990
Oleyl alcohol (70%)	360	1250	1637
PEG 400	108	1344	1645
Water	12 [11]	23 [12]	4 [13]

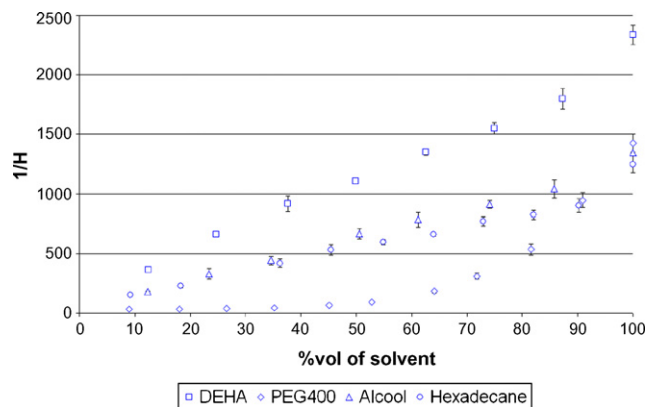


Fig. 2. $1/H$ values versus the volume percentage of solvent in water (DMDS).

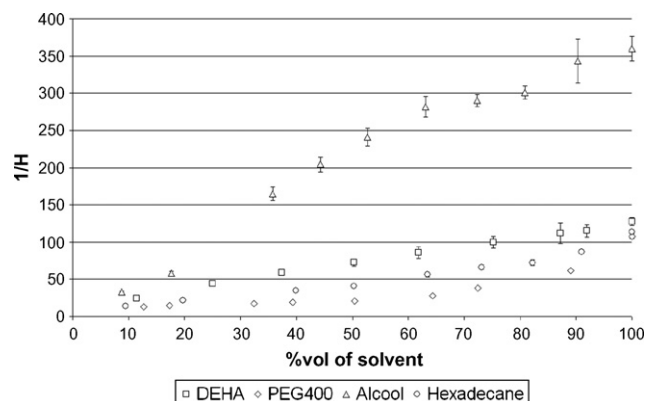


Fig. 3. $1/H$ values versus the volume percentage of solvent in water (DMS).

toluene, respectively), which appeared rather close to the values given in the available literature (Table 2). The experimental error between experimental values and those found in the available literature, especially for toluene, can be attributed to the low $1/H$ values in water.

3.3. Mass transfer rate and overall mass transfer coefficient

The first solvent chosen for mass transfer rate experiments was DEHA owing to its high absorption capacity towards all the target pollutants. However, despite being more efficient than n-hexadecane for toluene absorption, PEG 400 was not selected because of its solubility in water, which would make the solvent recycling difficult. n-Hexadecane was therefore chosen instead.

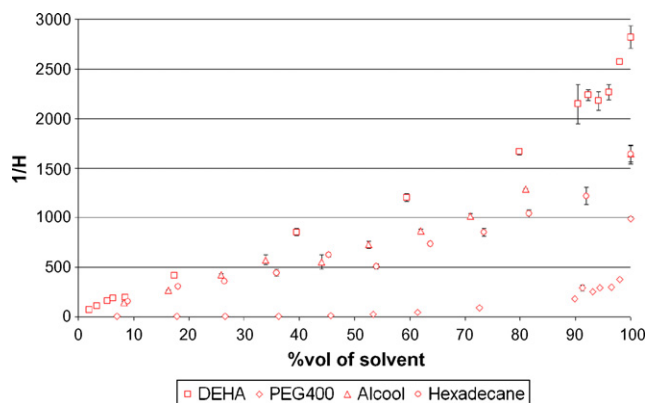


Fig. 4. $1/H$ values versus the volume percentage of solvent in water (toluene).

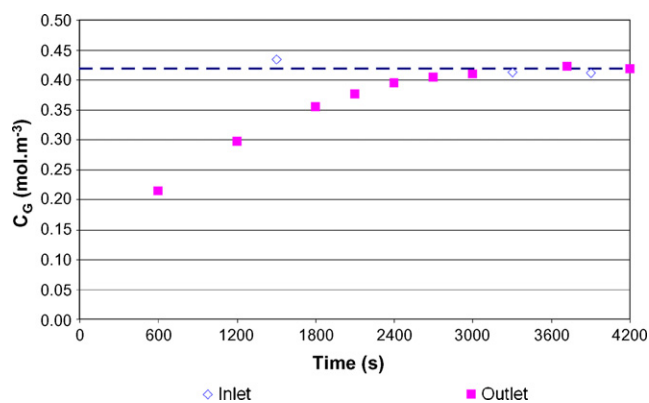


Fig. 5. Inlet and outlet DMS concentration in the gas phase versus time.

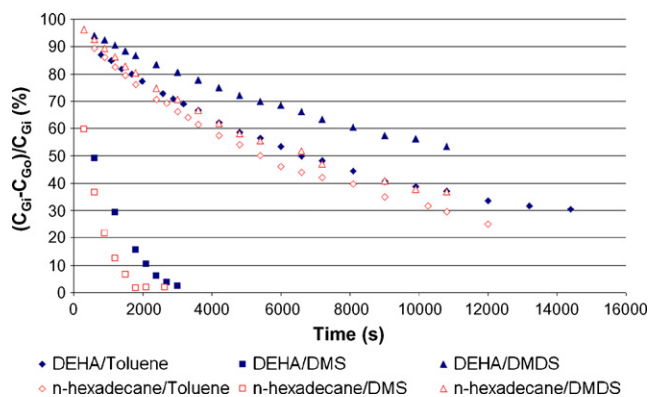


Fig. 6. $(C_{Gi} - C_{Go})/C_{Gi}$ versus time during the absorption of DMS, DMDS and toluene in DEHA and n-hexadecane.

Fig. 5 shows the variation of the outlet DMS concentration in the gas phase using DEHA as the solvent phase. The solvent was gradually loaded with DMS until its saturation, obtained when the outlet concentration reached the inlet value. At this moment, equilibrium between inlet gas and bulk liquid phase was achieved and Henry's constant can be reconfirmed. The value of $1/H$ found for the couple considered in Fig. 5 (DMS/DEHA) was found equal to 124, close to the value found with the static method (Table 2). It was also confirmed for the couple DMS/n-hexadecane, since the $1/H$ value was 114, irrespective of the method used, static (Table 2) or dynamic.

In order to take the inlet concentration effect into account (since inlet concentrations were not the same for all experiments), results were considered in terms of dimensionless absorption rate. Time-courses of $(C_{Gi} - C_{Go})/C_{Gi}$ values for the couples VOC/solvent selected are displayed in Fig. 6.

This dimensionless mass transfer rate decreased with time, due to the gradual VOC loading. Besides, mass transfer rate can be related to $1/H$ values, since the solvent that showed the best absorption capacity corresponded to the solvent showing the higher absorption rates (DEHA).

Mass transfer rates in DEHA determined for 50% of VOC transferred (data calculated from the equilibrium data, when time tends

Table 3

Values of mass transfer rate (N) and overall volumetric mass transfer coefficient ($K_L a$) for three VOCs in DEHA at 25 °C.

	DMS	DMDS	Toluene
N (mol s ⁻¹)	1.8×10^{-5}	6.7×10^{-6}	6.5×10^{-6}
$K_L a$ (s ⁻¹)	4.68×10^{-4}	1.04×10^{-4}	2.5×10^{-4}

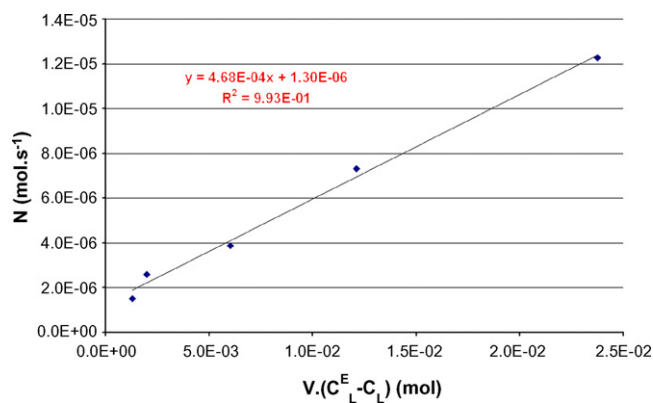


Fig. 7. Determination of $K_L a$ by linear fitting of experimental data (DMS/DEHA).

toward infinity) are reported in Table 3. DMS absorption was more rapid than the two other VOCs. This can be related to its molecular weight (62 g mol^{-1}), lower than those of DMDS and toluene (94 and 92 g mol^{-1} , respectively). A slight difference between toluene and DMDS could be observed: absorption of DMDS was faster, most likely because of its higher polarity. Nevertheless, the very close values suggested the same behaviour facing DEHA. Concerning experiments carried out with n-hexadecane, the same remarks could be made.

The values of $K_L a$ for the three VOCs selected in DEHA, which seems to be the best solvent to perform VOC absorption, are presented in Table 3. Fig. 7 shows a fitting example for the couple DMS/DEHA.

Once again, DMS could be considered as the most rapidly absorbed VOC. The values of $K_L a$ (about 10^{-4} s^{-1}) determined in these experiments were lower than those obtained ($k_L a$ about 10^{-2} s^{-1}) by Dumont et al. [14,15], as well as Cents et al. [7], but close to those reported for the couple Toluene/DEHA by Bourgois et al. [16] ($2.6 \times 10^{-4} \text{ s}^{-1}$). However, both $k_L a$ and $K_L a$ depend on the design of the reactor used to perform the experiments and regarding Eq. (4), k_L will certainly be higher than K_L .

4. Conclusion

Static and dynamic experiments were carried out in order to quantify the absorption capacity of four solvents (DEHA, n-hexadecane, oleyl alcohol and PEG 400) regarding three hydrophobic VOCs (DMS, DMDS and toluene) and to select the most relevant solvent to be implemented in an absorption process. High $1/H$ values were found, suggesting that the studied solvents were effective absorbing phases for hydrophobic VOCs. DMS was found to be the least absorbable compound, but showed the higher absorption rates while DMDS and toluene had similar behaviours. According to the study of mass transfer rate, DEHA appears to be the most efficient solvent in terms of both capacity and rate of VOCs absorption. Furthermore, $K_L a$ was evaluated and values about 10^{-4} s^{-1} were found. These results would be confirmed by implementing the solution in a scrubber, such as a packed column. Moreover, economical and environmental considerations must be taken into account (cost of the solvent as well as its recycling) in a further study. However, in order to completely mineralise the absorbed VOCs, an integrated process involving subsequent biological treatment will have to be considered.

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