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# Study of mass transfer of VOCs into viscous solvents in a pilot-scale cables-bundle scrubber

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#### A R T I C L E I N F O

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#### ABSTRACT

A widely operated way to treat industrial air loaded with VOCs is the absorption technique. For this, the choice of a well-adapted solvent is obviously of prime importance. In the present work an absorption process using viscous organic absorbents, namely, phthalates was studied to scrub flue gases. A suitable thin film device, the cables-bundle contactor, was applied both to favor mass transfer and to limit the pressure drops, and various experiments were achieved at the pilot-scale. Correlations predicting hydrodynamic and mass transfer parameters (interfacial area, liquid hold-up, liquid phase mass transfer coefficients) essential for the design of industrial absorption units, were deduced from experimental results. A comparison of performances of the cables contactor and a packed bed scrubber of same void fraction was made for absorption of toluene into DEHP.

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# 1. Introduction

The reduction of volatile organic compounds (VOCs) contained in flue gases issued from many factories, chemical plants and petroleum facilities, is of significant concern for environmental purpose and human health. Different end-of-pipe techniques can be applied to control VOC emissions in process air/gas streams [1].

This work deals globally with the development steps of a regenerative and recuperative absorption process using heavy solvents, which appear to be very attractive in case of recovering of the VOCs is wanted.

Heavy solvents, namely, di-2-ethylhexyl phthalate (DEHP), diiso-heptyl phthalate and di-iso-nonyl phthalate were chosen as absorbents. These high viscosity agents require thin film contactors to reduce liquid phase mass transfer resistance and hydrodynamic conditions limiting the pressure drops. Toluene absorption in a packed column with a viscous absorbent (di(2-ethylhexyl) adipate) was experimented in terms of hydrodynamic and mass transfer results [2], showing that the solvent viscosity was not a technical obstacle to its implementation in an industrial column and that the pressure drops remain within acceptable levels. However, phthalates that are used here present higher viscosity values. Therefore, it was decided to achieve absorption of VOCs and regeneration of phthalates in a cables-bundle scrubber [3,4] which is particularly well suited to this kind of operation due to its ordered packing with a high void fraction and very low pressure drop.

This scrubber, developed in our laboratory, was patented [3] many years ago under the registered trademark Amazone<sup>®</sup> and its hydrodynamic characteristics were thoroughly studied [4]. Since then, it was used in various applications related to the flue gas treatment, namely, absorption processes using low viscosity aqueous solutions or suspensions. Our department has investigated the capture of sulphur dioxide into sodium sulphite solutions [5] and calcium sulphite slurries [6], of other acid pollutants: HCl and SO<sub>2</sub> with Mg(OH)<sub>2</sub> suspensions [7], organic sulphurs [8], HF and SiF4 [9] for very specific applications, and more recently of VOCs into aqueous suspensions of activated carbon [10,11].

In our study, three kinds of VOC were investigated: aromatic hydrocarbons (toluene, ethylbenzene and 1,2,4-trimethylbenzene), linear paraffins (hexane, heptane, octane and decane) and *iso* and/or cyclic paraffins (cyclohexane, methylcyclohexane and 2,2,4-trimethylpentane). These VOCs are especially present in white-spirit vapors emitted in our specific application.

As Henry's constants and liquid diffusion coefficients are absolutely essential to design any industrial gas–liquid mass transfer equipment, these parameters have to be known for each pair of VOC–phthalate. In a previous paper [12] we published results relative to the solubility of VOC in phthalates, including our own detailed experiments. Testing already published and our equilibrium data with different thermodynamical models, we showed that the UNIFAC-Dortmund modified (DMD) model allows to estimate Henry's constants with a mean relative deviation lower than 10% in the range 18–75 °C. The second part of our research [13] has



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# Nomenclature

а	specific interfacial area (m <sup>2</sup> m <sup>-3</sup> scrubber)
at	specific area of dry packing (m <sup>-1</sup> )
$A_0$	fractional absorption = $(c_{G1}-c_{G2})/c_{G1}$
В	$= G/V_{\rm L} (m_{\rm C}^3  {\rm s}^{-1}  {\rm m}_{\rm L}^{-3})$
CC	VOC concentration in the gas phase $(\text{kg}\text{m}^{-3})$
CT CT	VOC concentration in the liquid phase $(kg m^{-3})$
D	diffusion coefficient ( $m^2 s^{-1}$ )
d	density of cables (15.625 cables $m^{-2}$ )
u <sub>c</sub>	density of cables $(13,023 \text{ cables III})$
g	standard gravity (in s <sup>-2</sup> )
G	total gas flow rate (m <sup>3</sup> s)
Н	Henry's coefficient $(m_L^2 m_G^{-3})$
$H_{G}$	gas phase height of transfer unit (m)
$H_{L}$	liquid phase height of transfer unit (m)
$H_{OG}$	overall gas height of transfer unit (m)
k	film mass transfer coefficient (m s <sup>-1</sup> )
Κ	overall mass transfer coefficient (m s <sup>-1</sup> )
L	liquid flow rate ( $m^3 s^{-1}$ or $Lmin^{-1}$ )
Lc	liquid flow rate on one cable $(m^3 s^{-1})$
_c M	molecular weight (g mol $^{-1}$ )
Na	(228) cables of the bundle
Noc	overall gas number of transfer unit
nsat	saturation vanor pressure (Pa)
p An	processing drop (Da)
Δp r	pressure drop (ra) absorption ratio $= U(UC)$
1 r	absorption ratio = $L/(HG)$
r <sub>c</sub>	equivalent cymunical cable radius (m or mm)
3	scrubber cross-section (m <sup>-2</sup> )
и	superficial velocity (m s <sup>-1</sup> )
$u_{\rm f}$	gas velocity at flooding $(m s^{-1})$
ν	liquid velocity $(m s^{-1})$
$V_{\rm L}$	total liquid volume (m³)
x	radial coordinate (m)
Ζ	vertical axis downwards (m)
Ζ	column height (m)
Greek le	tters
α	numerical coefficient in Eq. (20)
β.ν	numerical exponents in Eq. (20)
B	liquid hold-up in the cables-bundle $(m^3 m^{-3})$
δ	liquid sheath thickness (m)
e	nacking void fraction
n	dynamic viscosity (Pas)
ין ס	density $(k_{\alpha}m^{-3})$
р Д	time(s min or h)
0	contact time (s)
$\sigma_{c}$	contact time (s)
aubaan	ta
subscrip	
G	gas
L	liquia
1	scrubber inlet
2	scrubber outlet

consisted in the experimental determination of diffusivity data for different VOC-phthalate systems by means of absorption tests performed in a wetted-wall column. A preliminary literature review has indeed highlighted the lack of research works existing in this field. Moreover, classical empirical correlations [14] were found to be not adequate for the estimate of this property for such viscous solvents. Therefore, other original correlations for different classes of VOCs were developed.

Finally this third part of the study aims at analyzing the absorption performances of VOCs into phthalates (DEHP exclusively)



**Fig. 1.** Schematic diagram of the experimental set-up: (1) cables-bundle contactor; (2) air-VOC mixer; (3) VOC evaporator; (4) air compressor; (5) main air fan; (6, 7) flow meters; (8) VOC bottle; (9) gear pump (VOC); (10) thermostat; (12) phthalate feed; (13) gear pump (phthalate); (11, 14) three-way valves; (15, 16, 17) two-way valves.

in a single-stage pilot-scale cables-bundle scrubber, and particularly at determining the liquid phase mass transfer coefficients which are original in such a contactor operated with viscous fluids. Hydrodynamic parameters (interfacial area and liquid hold-up) and mass transfer coefficients were deduced from the experimental results.

# 2. Experimental

# 2.1. Experimental set-up

The absorption of airborne VOC vapors, in a currently observed concentration range  $0.5-1 \text{ g m}^{-3}$ , was carried out in a cables scrubber operating at ambient temperature and atmospheric pressure.

The cables scrubber is a gas-liquid contactor in which the packing is made of twisted polypropylene cables of mean cylindrical equivalent diameter 1.6 mm stretched vertically in parallel with a pitch of 8 mm. The absorbent flows down around the yarns in thin more or less cylindrical sheaths of high velocity, and thickness of some tenth of mm in case of low viscosity liquids. The gas phase was introduced at the bottom of the column generating a countercurrent contact between the two phases.

The laboratory scrubber used in the present work has a rectangular cross-section of  $0.096 \text{ m} \times 0.152 \text{ m}$  and 1 m of useful height. It includes 228 cables on which the liquid distribution is made through individual holes.

Besides its low pressure drop due to the high voidage, the main property of this type of scrubber is that, as for wetted wall columns, its specific interfacial area, *a*, is quite insensitive to the liquid flow rate. With aqueous solutions of low viscosities [3,4], this area is typically equal to about 95–100 m<sup>2</sup> m<sup>-3</sup> for the nominal irrigation rate of  $30-32 \text{ m}^3 \text{ h}^{-1} \text{ m}^{-2}$  of horizontal cross-section. In the case of high viscosity liquids of about 80 mPa s as investigated in this study the irrigation flow rate has to be reduced ten-fold to 2.6–3.75 m<sup>3</sup> h<sup>-1</sup> m<sup>-2</sup> in order to avoid too thick liquid sheaths and to limit the increase of pressure drops.

The experimental equipment is illustrated in Fig. 1.

#### 2.2. Experimental procedure

The major part of the airflow G' is mixed with a small airflow rate G'' which is saturated in VOC in an evaporator. The organic liquid is recycled to the saturator by a small pump and its temperature controlled by a thermostatic bath to fix its vapor pressure. The con-

448 Table 1

Operating conditions

1 6	
Liquid	0.6-0.75-0.9 (Lmin <sup>-1</sup> )
flow	$2.5-3.12-3.75 (m^3 h^{-1} m^{-2})$
rate Phthalate volume (semi-continuous test)	2.6 (L)
Gas flow rate	$\approx 50 (m^3 h^{-1})$
G'	≈49.5
G″	≈0.5
VOC concentration in the inlet gas	$0.5 \rightarrow 1 \ (g \ m^{-3})$
VOC consumption	$\approx 50 (mL h^{-1})$
Temperature	20–28 (°C)
Pressure	$\approx 10^5 (Pa)$
Duration of runs	$1 \rightarrow 4$ (h)

centration of VOC in the feed gas was varied by adjusting the liquid temperature and the flow rate *G*<sup>"</sup>.

A gear pump achieves the circulation or the feed of the solvent with a flow rate in the range of  $3.64 \times 10^{-2}$  to  $5.47 \times 10^{-2}$  m<sup>3</sup> h<sup>-1</sup> (±2.67–3.98 mLmin<sup>-1</sup> per cable). A constant gas flow rate of 50 m<sup>3</sup> h<sup>-1</sup> corresponding to a gas velocity of 0.96 m s<sup>-1</sup> was fixed for all absorption tests.

An on-line analysis of the gas at both ends of the scrubber was performed by a flame ionization detector, allowing to compute the fractional absorption.

The major part of the absorption test runs was achieved in a semi-continuous way, with recycled viscous solvents.

For all VOCs, continuous absorption test runs were also carried out and their results, in terms of heights of transfer units, were compared to the semi-continuous ones. In such cases, the solvent was continuously fed into the scrubber without recirculation, which consumed large quantities of product.

Operating conditions are summarized in Table 1.

#### 2.3. VOC and solvent characteristics

Table 2 summarizes the main properties of the four volatile organic compounds used in this study (toluene, *n*-hexane, *n*-octane, methylcyclohexane) at the temperature of 20 °C: it includes densities, vapor pressures, and essential data about solubilities: Henry's constants and liquid diffusivities in DEHP issued from our previous works [12,13]. Vapor pressures can be found in [15]. It can be seen that, for example, toluene is seventeen times more soluble than *n*-hexane but its diffusion coefficient is half. The two compounds toluene and methylcyclohexane present more similar solubility and diffusivity properties.

As to the physicochemical properties of DEHP, they are presented in Table 3.

#### 3. Model development

#### 3.1. Absorption test runs

To determine the overall gas–liquid height of transfer unit  $H_{OG}$  of the absorption column from the results of the semi-continuous experiments, a model was developed on the basis of the following assumptions [10]:

#### Table 2

Physicochemical properties of the VOC used at 20 °C

## Table 3

Physicochemical properties of DEHP C24H38O4 at 20 °C

CAS	$M(\operatorname{g}\operatorname{mol}^{-1})$	$ ho_{\rm L}({\rm kg}{ m m}^{-3})$	$\eta_{\rm L}$ (mPas)
117-81-7	390.56	983	76

 a Henry's law for the gas-liquid equilibrium of the organic compounds:

$$c_{\rm G} = H c_{\rm L} \tag{1}$$

This is a reasonable assumption for small liquid concentrations, especially valid in the initial times of the runs;

• a total liquid volume contained in the scrubber (the majority being in the sump) perfectly mixed.

Neglecting the hold-up of solvent on the cables with respect to the total liquid volume, the instantaneous mass balance for a semi-continuous absorption test run can be written as:

$$V_{\rm L} \frac{{\rm d}c_{\rm L2}}{{\rm d}\theta} = G(c_{\rm G1} - c_{\rm G2}) \tag{2}$$

At a given time, with the same assumption of negligible holdup and for the very low concentrations existing in both phases, the instantaneous mass balance of the cables-bundle alone is:

$$G(c_{\rm G1} - c_{\rm G2}) = L(c_{\rm L1} - c_{\rm L2}) \tag{3}$$

The number of transfer units of the cables-bundle is given by the classical relation:

$$N_{\rm OG} = \frac{r}{r-1} \ln \frac{c_{\rm G1} - Hc_{\rm L1}}{c_{\rm G2} - Hc_{\rm L2}} \tag{4}$$

with the absorption ratio *r*:

$$r = \frac{L}{HG}$$
(5)

Eliminating  $c_{L1}$  between Eqs. (3) and (4) results in:

$$(c_{\rm G1} - c_{\rm G2}) = (c_{\rm G1} - Hc_{\rm L2})A_0 \tag{6}$$

where

$$A_0 = \frac{1 - \exp[-N_{\text{OG}}(r-1)/r]}{1 - (1/r)\exp[-N_{\text{OG}}(r-1)/r]}$$
(7)

Substituting  $c_{G1} - c_{G2}$  from (6) in Eq. (2) and integrating from 0 to  $\theta$  leads finally to:

$$c_{G2} = c_{G1} [1 - A_0 \exp(-A_0 B H \theta)]$$
(8)

with

$$B = \frac{G}{V_{\rm L}} \tag{9}$$

Eq. (8) involves a variation of the output concentration of VOC in the gas phase which reaches the input concentration at high values of time.

If  $\ln(c_{G1}-c_{G2})$  is plotted versus time, a straight line is obtained, with a slope and an intercept (for  $\theta = 0$ ) equal to the product  $A_0BH$ and  $\ln(A_0 c_{G1})$ , respectively. According to Eq. (6), the parameter  $A_0$ appears to be the initial fractional absorption. The slope and the intercept are determined for all runs by linear regression. Given  $A_0$ 

VOC	Formule	CAS	$ ho_{\rm L}({\rm kg}{ m m}^{-3})$	p <sup>sat</sup> (kPa)	$H  m_L^3  m_G^{-3}$	$D_{\rm L} ({\rm m}^2{\rm s}^{-1})$
Toluene n-Hexane n-Octane	C <sub>7</sub> H <sub>8</sub> C <sub>6</sub> H <sub>14</sub> C <sub>9</sub> H <sub>16</sub>	108-88-3 110-54-3 111-65-97	865 659 700	2.92 16.15 1.4	$3.19 \times 10^{-4}$ $4.74 \times 10^{-3}$ $4.40 \times 10^{-4}$	$5.51 \times 10^{-11}$ $1.16 \times 10^{-10}$ $6.23 \times 10^{-11}$
Methylcyclohexane	$C_7H_{14}$	108-87-2	770	4.83	$9.79 \times 10^{-4}$	$4.24 \times 10^{-11}$

from the intercept and *B* from the measured *G* and  $V_L$  the particular value of the Henry's constant *H* can be obtained from the slope. This is an appreciable advantage of the semi-continuous runs over the continuous ones. In case *H* is known by previous solubility measurements, the slope also allows to calculate  $A_0$  which constitutes a practical way to validate the data given by the semi-continuous runs and the model assumptions. When a small difference between the two values of  $A_0$  is found, the mean is calculated otherwise the results are discarded. Then, from  $A_0$  and *r*,  $N_{OG}$  is drawn by solving Eq. (7) and finally  $H_{OG}$  is obtained by  $h/N_{OG}$  with a column height *h* equal 1 m.

As shown in Eq. (10) the overall gas–liquid height of transfer unit  $H_{OG}$  of the absorption column is a function of the gas-film and liquid-film heights of transfer unit according to:

$$H_{\rm OG} = \frac{G}{K_{\rm G}aS} = \frac{G}{k_{\rm G}aS} + \frac{HG}{L}\frac{L}{k_{\rm L}aS} = H_{\rm G} + \frac{1}{r}H_{\rm L}$$
(10)

The determination of the liquid-film mass transfer  $k_{\rm L}$  requires a prior estimate of the gas-film height of transfer unit  $H_{\rm G}$ .

In the case of a continuous absorption test run, the number of transfer units of the cables scrubber is simply computed thanks to the relation (4) but this needs the value of *H*. The fed liquid is VOC-free,  $c_{L2} = 0$ . The concentration  $c_{L1}$  can be obtained from the classical stationary mass balance (3) written for the contactor.

#### 3.2. Gas phase mass transfer characteristics of the column

To estimate the gas-film height of transfer unit  $H_{\rm G}$ , absorption experiments of *n*-pentylbenzene ( $\rho_{\rm Pentbenz}$  = 860 kg m<sup>-3</sup>;  $p^{\rm sat}$  (20 °C) = 0.029 kPa) in DEHP were specifically performed for different gas and liquid flow rates, the inlet gas concentration in VOC being fixed. With a Henry's constant of  $5.35 \times 10^{-6}$  m<sub>L</sub><sup>2</sup> m<sub>G</sub><sup>-3</sup> at 20 °C for *n*-pentylbenzene in DEHP, the very high solubility of this component relatively to other volatile organics led to the assumption of the complete cancellation of the liquid phase resistance.

The experimental procedure was similar to the one used in the determination of  $H_{OG}$  presented previously for other VOCs; it involved the measurement of absorption rates for various operating conditions in different semi-continuous absorption tests.

By fitting all results of these runs, a relation was obtained for the influence of liquid and gas superficial velocities on the gas-film height of transfer unit.

$$H_{\rm Gpenthenz} = 1.09 \, u_{\rm G}^{0.252} u_{\rm I}^{-0.228} \tag{11}$$

#### 4. Results and discussion

## 4.1. Gas-film height of transfer unit $H_G$

A classical correction of the  $H_G$  values taking into account the ratio of gas phase diffusivities can be applied:

$$H_{G_{\text{VOC}}} = H_{G_{\text{Pentbenz}}} \left(\frac{D_{G_{\text{Pentbenz}}}}{D_{G_{\text{VOC}}}}\right)^{2/3}$$
(12)

The diffusivities relative to VOC in the gas phase were estimated by means of the correlation of Fuller, Schettler and Giddings [16].

#### 4.2. Effective interfacial area a

The determination of the effective interfacial area by unit volume of the scrubber was based on the theoretical application of the gravitational flow of viscous liquids, at the stationary state in the laminar regime, assuming that the solid support and the liquid-films are perfectly cylindrical. The velocity profile (Fig. 2) was



Fig. 2. Liquid sheath and liquid velocity profile on the cables.

obtained by integration of the Navier–Stokes equations, expressed in cylindrical coordinates.

Assuming an uniform distribution of the liquid on the cablesbundle the mean liquid flow rate on one cable

$$L_{\rm c} = \frac{L}{N_{\rm c}} \tag{13}$$

is related to the velocity profile by the relation

$$L_{\rm c} = \int_{r_{\rm c}}^{r_{\rm c}+o} 2\pi r v(x) \,\mathrm{d}x \tag{14}$$

with 
$$v(x) = \frac{gr_c^2 \rho_L}{4\eta_L} \left( 1 - \frac{x^2}{r_c^2} + 2\frac{(r_c + \delta)^2}{r_c^2} \ln \frac{x}{r_c} \right)$$
  
and  $r_c \le x \le r_c + \delta$  (15)

From Eqs. (14) and (15), the radius of the liquid-film  $(r_c + \delta)$  was computed for each absorption test and led to the specific interfacial area a (m<sup>-1</sup>):

$$a = d_{\rm c} 2\pi (r_{\rm c} + \delta) \tag{16}$$

The liquid hold-up  $\beta_L$  (m<sup>3</sup> m<sup>-3</sup>) was calculated as follows:

$$\beta_{\rm L} = d_{\rm c} \pi ((r_{\rm c} + \delta_{\rm c})^2 - r_{\rm c}^2) \tag{17}$$

Values of *a* and  $\beta_{\rm L}$ , function of the liquid flow rate, are reported in Table 4.

**Table 4**Effective interfacial area a and liquid hold-up  $\beta_L$ 

$L(Lmin^{-1})$	$\delta$ (10 <sup>-3</sup> m)	$a (m^2 m^{-3})$	$\beta_{\rm L} ({ m m}^3{ m m}^{-3})$
0.6	0.860	123.6	0.046
0.75	0.891	126.7	0.050
0.9	0.918	129.3	0.054

#### Table 5

Semi-continuous absorption test runs of VOC in DEHP

VOC	$L(L\min^{-1})$	<i>t</i> (°C)	<i>A</i> <sub>0</sub>	r	N <sub>OG</sub>	H <sub>OG</sub> (m)	$k_{\rm L} (10^{-6}{ m ms^{-1}})$
	0.6	22	0.345	2.111	0.465	2.149	1.887
	0.6	23.5	0.335	1.945	0.451	2.218	1.955
	0.75	25.5	0.346	2.083	0.467	2.143	2.264
Talaaaa	0.75	23.5	0.351	2.301	0.473	2.116	2.071
loluene	0.75	23.5	0.350	2.353	0.469	2.133	1.986
	0.9	26	0.367	2.458	0.498	2.007	2.438
	0.9	25	0.386	2.581	0.531	1.884	2.539
	0.9	24	0.386	2.700	0.530	1.887	2.406
	0.6	25.5	0.059	0.127	0.082	12.264	3.978
	0.75	28	0.068	0.140	0.097	10.331	5.187
n-Hexane	0.75	28	0.067	0.140	0.095	10.489	5.103
	0.9	24	0.051	0.192	0.061	16.411	2.634
	0.9	24	0.083	0.192	0.114	8.774	5.122
	0.6	26	0.272	1.253	0.361	2.771	2.389
	0.6	20	0.284	1.657	0.369	2.710	1.787
n Ostana	0.75	21	0.304	1.917	0.396	2.522	2.009
n-Octane	0.75	22	0.286	1.832	0.368	2.716	1.904
	0.9	22	0.298	2.176	0.382	2.619	1.937
	0.9	22	0.298	2.170	0.382	2.616	1.948
	0.6	24	0.144	0.635	0.176	5.676	1.849
	0.6	25	0.131	0.610	0.158	6.326	1.710
	0.75	23	0.158	0.798	0.192	5.198	1.894
Methylcyclohexane	0.75	26	0.143	0.708	0.173	5.774	1.935
	0.75	24	0.166	0.915	0.201	4.978	2.040
	0.9	25	0.163	0.883	0.197	5.068	2.081
	0.9	25	0.164	0.885	0.198	5.040	2.090

### 4.3. Overall gas-liquid height of transfer unit H<sub>OG</sub>

Experiments of VOC absorption in DEHP were performed for the three different liquid flow rates, at ambient temperature, in order to determine the overall gas–liquid height of transfer unit  $H_{OG}$ . Experimental results are summarized in Table 5.

Fig. 3a shows the asymptotic evolution of the output concentration of toluene in the gas phase, during a semi-continuous absorption test run, tending to the input concentration. Fig. 3b illustrates the interpretation of this absorption test leading to the determination of the initial fractional absorption  $A_0$  and hence to the overall gas-liquid height of transfer unit  $H_{OG}$ .

A satisfactory agreement between results of  $H_{OG}$  for semicontinuous and continuous test runs allowed us to validate the experimental procedure.

# 4.4. Liquid-film mass transfer coefficients k<sub>L</sub>

The liquid phase mass transfer coefficient  $k_L$  (Table 5), relative to each absorption test run, was calculated by means of the following equation:

$$k_{\rm L} = \frac{1}{(H_{\rm OG_{\rm VOC}} - H_{\rm G_{\rm VOC}})(aS/HG)}$$
(18)

using the corresponding values of a,  $H_{\rm G}$  and  $H_{\rm OG}$ .

Taking into account that the interfacial areas were only estimated theoretically, and that  $k_L a$  values only are important for design of industrial scrubbers including bundles of cables, the  $k_L$  were calculated to obtain good orders of magnitude which allowed to better characterize the liquid flow and the variables of influence as will be seen here after.

From our experimental results, we can highlight that, in spite of very different solubilities, the same order of magnitude of  $k_{\rm L}$  (2 × 10<sup>-6</sup> m s<sup>-1</sup>) has been observed for all investigated VOCs, and that it is very low for viscous solvents. This finding confirms that it is essential to carry out absorption with these solvents in thin film scrubbers.

We can claim a quite precise determination of the volumetric mass transfer coefficients  $k_L a$  as the liquid mass transfer resistance equals approximately 70% of the overall mass transfer resistance, which seems coherent and can be expected in case of a heavy viscous absorbent.



**Fig. 3.** (a) Variation with time of the gas outlet concentration in a semi-continuous absorption, (b) semi-logarithmic plot of the gas concentrations difference versus time (absorption run of toluene in DEHP).

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Results of the compariso	n

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	$a_t (m^{-1})$	ε	$\beta_{L}$	$a(m^{-1})$	$k_{\rm L} ({ m ms^{-1}})$	H <sub>OG</sub> (m)	$\Delta p/Z$ (Pa m <sup>-1</sup> )
Pall metal ring	139	0.965	0.0347	20.7	$1.5  imes 10^{-5}$	2.33	86
Cables-bundle	100	0.968	0.054	129	$2.5\times10^{-6}$	1.88	13

Moreover, a  $k_{\rm L}$  value increasing with the liquid flow rate was obtained for all the VOCs investigated.

The values of  $k_{\rm L}$  were analyzed according to the well-known relation given by the penetration theory of mass transfer:

$$k_{\rm L} = 2\sqrt{\frac{D_{\rm L}}{\pi\theta_{\rm c}}}\tag{19}$$

First of all, it was observed [17] that for all experiments the contact time deduced by Eq. (19) from the diffusivity and the experimental  $k_{\rm L}$  is always lower than the total fall time (for a height = 1 m) of liquid at the interface.

This was calculated with the liquid velocity  $v(r_c + \delta)$  given by Eq. (14) assuming a perfect gravitational laminar flow in the annular cylindrical film around the cables. Actually the contact times range approximately between one third and one half the fall time, which means that, despite the fact the flow is laminar and even "waves-free" owing to the very low Reynolds numbers [16], the liquid interface undergoes 2–3 renewals during its fall. This is due probably to the cables twisting.

This finding is important from a practical point of view because the  $k_{\rm L}$  will not depend on the contactor height which is generally greater than the actual liquid phase transfer contact height.

The falling velocity of the liquid being a function of its flow rate and its kinematic viscosity for the given cables diameter (Eq. (14)), all influence variables are identified.

So, our experimental values of  $k_L$  were related to these variables and  $D_L$  by means of a multidimensional regression in the form:

$$k_{\rm L} = \alpha u_{\rm L}^{\beta} \left(\frac{\eta_{\rm L}}{\rho_{\rm L}}\right)^{\gamma} D_{\rm L}^{0.5} \tag{20}$$

The exponent 0.5 of  $D_{\rm L}$  was fixed a priori according to the penetration theory.

Other numerical coefficient and exponents of the correlation must remain confidential.

It was found, however, that actual exponents  $\beta$  and  $\gamma$  were very close to those which were obtained by regression of the  $k_L$  values computed by Eqs. (19) and (14) for constant diffusivity and constant contact height by varying  $\eta_L/\rho_L$  and  $u_L$ , respectively. As for these computations, the model of a perfect laminar gravitational flow in the annular space of liquid around cables of 1.6 mm of equivalent cylindrical diameter was used, this confirms that the flow is quite laminar.

# 4.5. Comparison of the cables contactor with a conventional scrubber

To compare the performances of the cables-bundle absorber with those of a conventional packed bed scrubber, a packing of metal Pall rings 35 mm which has the same void fraction as the cables scrubber was chosen.

Comparison was made for absorption of toluene into DEHP and the same operating conditions ( $20 \,^{\circ}$ C, 1 atm,  $u_{G} = 0.96 \,\text{m s}^{-1}$ , the higher  $u_{L} = 0.001028 \,\text{m s}^{-1}$ ) as in our experimental work. The solvent properties, the Henry constant and the liquid phase diffusion coefficient are given above (Tables 2 and 3).

Recent works on packed columns including viscous absorbents were used in order to estimate hydrodynamic (wetted area, liquid hold-up, pressure drop) and mass transfer ( $k_L$ ,  $k_G$ ) parameters,

the Billet and Schultes correlations [18,19] being particularly recommended in the range of viscosity 0.2–200 mPa s. The general pressure drop correlation [16] allowed to estimate the packing flooding point:  $u_f = 2.76 \text{ m s}^{-1}$ . In this correlation, the influence of the liquid viscosity is important, giving  $u_f = 2.21 \text{ m s}^{-1}$  for an exponent of  $\eta_L$  equal to 0.2 (as in the original correlation of Eckert [Perry VI]) instead of 0.1.

The pressure drop of the cables scrubber was appraised from the value relative to aqueous solutions at the nominal liquid velocity  $(\Delta p/Z = 10\rho_G u_G^2)$  corrected by taking account, in case of the viscous absorbent, of the increase of liquid hold-up (from 0.023 to 0.054) and the subsequent increase of interstitial gas velocity.

The results of the comparison are summarized in Table 6.

They confirm that the pressure drop is drastically lower for the cables scrubber.

It appears, moreover, that the  $H_{OG}$  are of the same order of magnitude for both scrubbers, though a little worse for the packed column, despite a six times higher  $k_L$ . This can be explained easily by the penetration theory (Eq. (19)), the contact time being obviously lower for the Pall rings due to higher frequency of surface renewals. Actually, the estimated bad  $H_{OG}$  of the packed bed is due to the very low contact area, the ratio  $a/a_t$  for the Pall ring given by the correlation of wetting being likely greatly underestimated.

We are convinced that, at the present time, the standard design methods still remain non-reliable for viscous liquids. We showed in Ref. [14] that the existing relations allowing to estimate the liquid phase diffusion coefficients provide strongly erroneous values. Thus, the greatest care should be taken in the use of these design equations and correlations for industrial applications with viscous solvents and experimental or pilot runs should be carried out to check the results.

# 5. Conclusions

This study examined hydrodynamics and mass transfer in a cables-bundle scrubber fed with DEHP to remove VOCs from a low-concentration air effluent  $(0.5-1 \text{ g m}^{-3})$ . It has given a first insight of the conditions which allow the use of high viscosity solvents to carry out this operation in such a specific contactor with a view to scaling up the system for industrial application. Experimental data were obtained from semi-continuous absorption tests achieved at the pilot-scale. These data were analyzed by a model leading to the determination of the liquid side mass transfer coefficients and a semi-empirical correlation was derived for their estimation. These parameters together with previously determined solubilities and liquid diffusion coefficients in the VOC-phthalate systems are essential in the design steps.

An effective regeneration process is also essential in order to make the process technically feasible: it is, therefore, suggested to use the same contactor for the stripping of VOCs out of the phthalates. Since stripping will be made at higher temperatures (about 100 °C) than absorption, this operation should not raise particular difficulties because the solvent viscosity will fall to about a few mPa s.

Moreover, the overall process has to be studied from an economical point of view in order to compare it to other existing technologies and to prove if it could be implemented in a real industrial operation.

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