Article

Mass Transfer in Multiphasic Gas/Liquid/Liquid Systems. K_La Determination Using the Effectiveness-Number of Transfer Unit Method

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Abstract: The Effectiveness-Number of Transfer Unit method (ε-NTU method) was applied to determine the overall mass transfer coefficient, K_La, of operating gas-liquid absorbers treating Volatile Organic Compounds (VOCs). This method requires the knowledge of the operating conditions (gas flow rate, Q_G; liquid flow rate, Q_L; scrubber volume V), the measurement of gaseous concentrations at the inlet, C_{Gin}, and at the outlet, C_{Gout}, of the contactor (in order to determine the effectiveness of the absorber ε) and the calculation of the Henry coefficient of the VOC between the gas and the liquid phases (H_{VOC}). Coupled with the "equivalent absorption capacity" concept, the ε-NTU method was used to determine K_La of absorbers contacting a gas and a mixture of water and a Non Aqueous Phase, successfully. The method, validated from literature data for configurations countercurrent scrubbers and stirred tank reactors, could be used to simply determine the overall mass transfer coefficient of systems for which the standard K_La determination methods still remain non-reliable or inaccurate (viscous solvents, mixture of immiscible liquids, fermentation broths ...).

Keywords: absorption; mass transfer; effectiveness-NTU method; TPPB; K_La; VOC

1. Introduction

The removal of volatile organic compounds (VOCs) in air can be achieved using bioscrubbers. However, some VOCs are poorly soluble in water leading to mass transfer limitations. In response to the low solubility of hydrophobic pollutants, a Non Aqueous Phase (NAP) can be added to water in order to improve the absorption of VOCs from air to water [1–3]. The addition of a third no miscible phase makes the system more heterogeneous and, obviously, more complex from the mass transfer point of view. Actually, when the liquid phase is a mixture of a NAP and water, the physico-chemical properties of the mixture are not sufficiently known to enable the design of the absorber to be carried out by classical procedure reported in Chemical Engineering books [4–6]. For instance, the overall mass transfer coefficient, K_La, cannot be determined by the current methods available in the literature because they are usually based on the measurement of VOC concentration in the liquid phase. Consequently, these methods are not relevant for mixtures of NAP and water and there is always a need to develop a simple, standard and reliable method for K_La determination adapted to multiphasic gas/liquid/liquid systems. For this purpose, the Effectiveness—Number of Transfer Units (ε-NTU) method usually applied to heat exchanger design has been adapted in order to determine K_La of absorbers implementing complex gas/liquid/liquid systems. The novelty of the study is to combine the ε-NTU method with the "equivalent absorption capacity" concept [2,3] enabling to calculate the physical properties (Henry coefficient, molecular weight and density) of water/NAP mixtures. In a first part of the paper, the ε-NTU method adapted to the configuration Countercurrent Scrubbers (CS) is introduced, and the "equivalent absorption capacity" concept is developed. It is then showed

that the ε-NTU method can be applied successfully to determine $K_L a$ of diversified countercurrent absorbers for various operating conditions. In a second part, it is demonstrated that the ε-NTU method can be also applied successfully to the Stirred Tank Reactors (STR) configuration.

2. ε-NTU Method for $K_L a$ Determination

2.1. Single Gas-Liquid Countercurrent Absorber

The ε-NTU method usually applied to heat exchanger design was adapted to gas-liquid countercurrent absorbers to describe the mass transfer of any VOC between a gas phase and a liquid phase. It was demonstrated that [7]:

$$\text{NTU} = \frac{K_L a \, V}{H_{VOC,L} \, Q_G} \tag{1}$$

The dimensionless number of transfer units (NTU) corresponds to the ratio between the gas residence time in the absorber (V/Q_G) and the time needed for the mass transfer of the VOC from the gas phase to the liquid phase ($H_{VOC,L}/K_L a$). As the Henry coefficient can be expressed using different definitions, it is necessary to apply the appropriate units. For the purposes of this work, the parameter $H_{VOC,L}$ is defined as the dimensionless air-to-liquid concentration ratio ($H_{VOC,L} = C_G/C_L$) which is the most convenient for mass distribution calculations (a reference state of infinite dilution is assumed). In the case where the inlet liquid concentration is VOC-free (case of industrial applications) the effectiveness of the absorber ($\varepsilon = (C_{Gin}-C_{Gout})/C_{Gin}$) can be expressed according to Equation (2) for the configuration Countercurrent Scrubbers (CS):

$$\varepsilon = \frac{1 - \exp\left(-\text{NTU}\left(\frac{A-1}{A}\right)\right)}{1 - \frac{1}{A}\exp\left(-\text{NTU}\left(\frac{A-1}{A}\right)\right)} \tag{2}$$

In Equation (2), A is the absorption factor ($Q_L/(H_{VOC,L} \, Q_G)$). The effectiveness vs. NTU is plotted in Figure 1 for various A values.

Consequently, the ε-NTU method can be used to determine simply the overall mass transfer coefficient, $K_L a$, of an operating absorber from the knowledge of the physical parameters: $H_{VOC,L}$, Q_G, Q_L, V, C_{Gin} and C_{Gout}. The determination procedure is as follows: (i) the efficiency ε of the absorber is determined from the measurement of the gaseous VOC concentrations at the inlet and outlet of the absorber, respectively; (ii) for a given VOC to be transferred, the absorption factor A is calculated; (iii) from the knowledge of ε and A, the NTU value is then obtained, either from Figure 1, or from Equation (3) deduced from Equation (2); (iv) finally, $K_L a$ value is calculated from Equation (4).

$$\text{NTU} = \frac{A}{1-A} \, \ln\left(\frac{\varepsilon - 1}{\varepsilon/A - 1}\right) \tag{3}$$

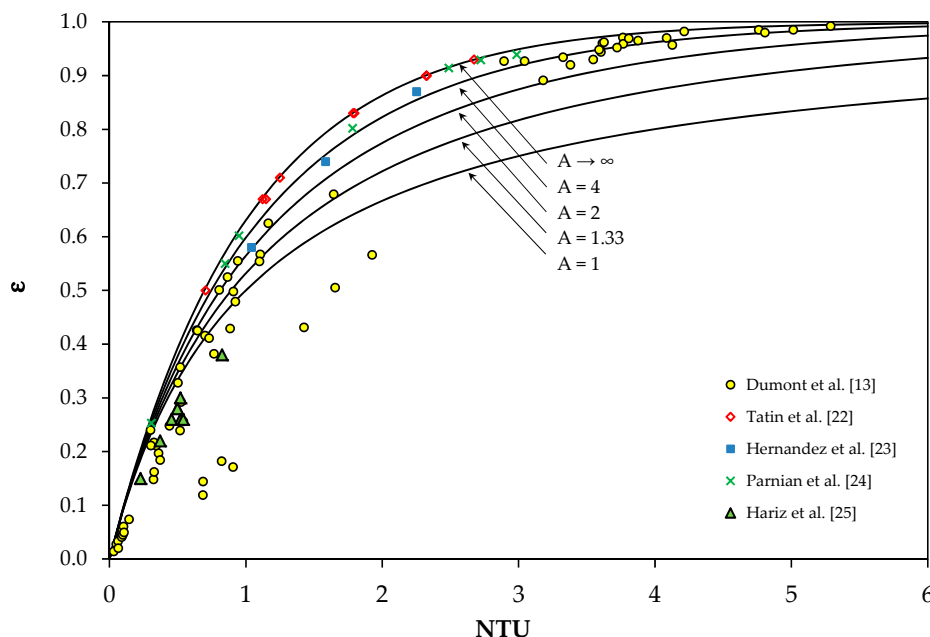$$K_L a = \frac{H_{VOC,L} \, Q_G \, \text{NTU}}{V} \tag{4}$$

Figure 1. Effectiveness ε vs. Number Transfer Units for various A values (continuous lines) and for experimental data corresponding to the different countercurrent gas-liquid absorbers described in Table 1.

2.2. Gas/Liquid/Liquid Systems. Use of the "Equivalent Absorption Capacity" Concept

Determination of K_La using ε-NTU method requires only known operating parameters ($H_{VOC,L}$, Q_G, Q_L, V,) and gaseous concentrations (C_{Gin} and C_{Gout}) which can easily be measured. Consequently, the ε-NTU method appears to be a useful technique for K_La determination of systems applying water/NAP mixtures whose physical properties are difficult to describe and for which the measurements of liquid concentrations can be difficult or inaccurate. Moreover, in the presence of biomass (case of Two Phase Partitioning bioreactors, TPPB), the liquid phase becomes an even more heterogeneous complex system of water, NAP, microorganisms and surfactant molecules for which the ε-NTU method based only on the gaseous concentrations could represent a complementary tool to the different techniques available for K_La determination [8,9]. For water/NAP mixtures, the main difficulty lies in the knowledge of the Henry coefficient of the VOC to be transferred between the gas phase and the water/NAP mixture (i.e., $H_{VOC,L}$ = $H_{VOC,mix}$). As highlighted by the "equivalent absorption capacity" concept [3], $H_{VOC,mix}$ can be expressed as a function of the VOC Henry coefficients for air/water and air/NAP, respectively, and as a function of the NAP volume fraction in the mixture (ϕ_{NAP}).

$$\frac{1}{H_{VOC,mix}} = \frac{1 - \phi_{NAP}}{H_{VOC,W}} + \frac{\phi_{NAP}}{H_{VOC,NAP}} \tag{5}$$

Note that the "equivalent absorption capacity" concept is an empirical concept based on experimental mass transfer measurements carried out in batch reactor between air and various water/silicone oil mixtures [2,3,10] and successfully applied to a countercurrent gas-liquid contactor for the absorption of toluene and dimethyldisulphide (DMDS) [11]. The idea of this concept is based on the fact that the absorption capacity of a unit volume of water/NAP mixture is equivalent to the absorption capacity of a the same volume of a pseudo-homogeneous phase whose physical properties can be calculated as a function of the NAP volume fraction and from the physical properties of water and NAP, respectively

(mathematical expressions of the molecular weight and density of the mixture [3] are not used here). Equation (5) can be rewritten in the following form:

$$H_{VOC,mix} = \frac{H_{VOC,W}}{1 + \phi_{NAP}(m_R - 1)} \tag{6}$$

with:

$$m_R = \frac{H_{VOC,W}}{H_{VOC,NAP}} \tag{7}$$

The Henry coefficient of the VOC between the gas phase and the NAP ($H_{VOC,NAP}$) has to be significantly lower than the Henry coefficient of the VOC between the gas phase and the water ($H_{VOC,W}$) in order to obtain a large solubility ratio m_R. Depending on the NAP selected, the range of m_R reported in the literature is dramatically large, from 10 for moderately poor water-soluble compounds (dimethyldisulfide, dichloromethane...) to 100,000 for very-poorly water-soluble compounds (-pinene, hexane ...). Figure 2 highlights the significant influence of the m_R parameter on $H_{VOC,mix}$. It can be observed that $H_{VOC,mix}$ tends rapidly towards H_{NAP} with the addition of NAP; this trend being more pronounced for increasing m_R ratio.
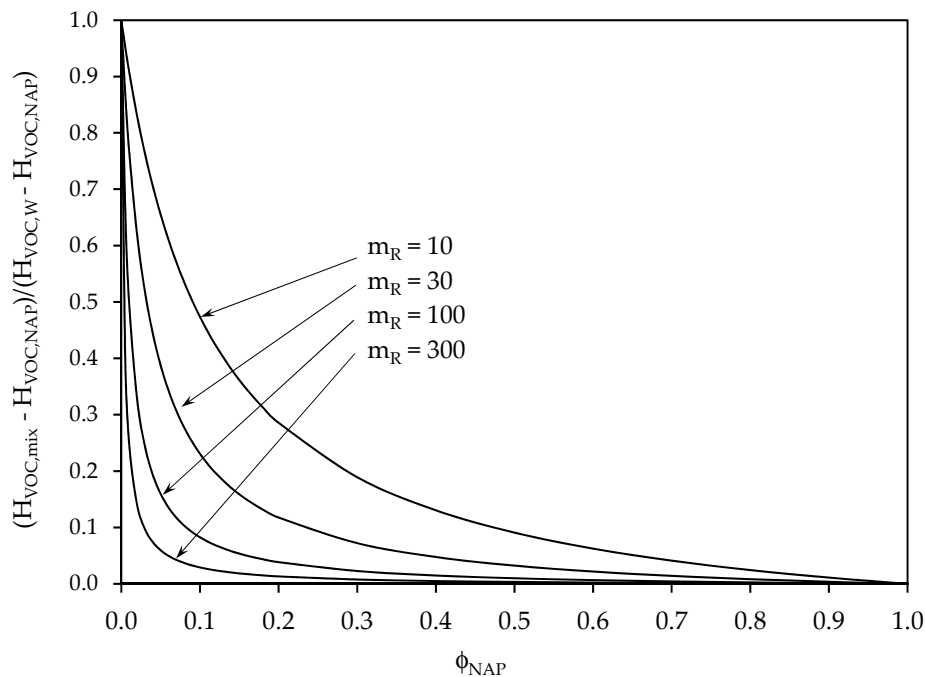

Figure 2. Henry coefficient of the VOC between air and the water/NAP mixture ($H_{VOC,mix}$) vs. NAP volume fraction (ϕ_{NAP}). Influence of the solubility ratio m_R.

The combination of Equations (3), (4) and (6) gives:

$$K_L a|_\phi = \frac{H_{VOC,W}}{[1 + \phi_{NAP}(m_R - 1)]} \frac{Q_G}{V_P} \frac{A}{1 - A} \ln\left(\frac{\varepsilon - 1}{\varepsilon/A - 1}\right) \tag{8}$$

and:

$$\frac{K_L a|_\phi}{K_L a|_{\phi=0}} = \frac{1}{[1 + \phi_{NAP}(m_R - 1)]} \frac{A(1 - A_0)}{A_0(1 - A)} \frac{\ln\left(\frac{\varepsilon - 1}{\varepsilon/A - 1}\right)}{\ln\left(\frac{\varepsilon_0 - 1}{\varepsilon_0/A_0 - 1}\right)} \tag{9}$$

where A_0 and ε_0 are the absorption factor and the absorber efficiency in the absence of NAP (i.e., $\phi_{NAP} = 0$), respectively.

As Q_G/V_p is the reciprocal of the gas EBRT (Empty Bed Residence Time), Equation (8) can be rewritten as follows:

$$K_L a|_\phi = \frac{H_{VOC,W}}{[1 + \phi_{NAP}(m_R - 1)]} \frac{1}{EBRT} \frac{A}{1 - A} \ln\left(\frac{\varepsilon - 1}{\varepsilon/A - 1}\right) \tag{10}$$

As highlighted by Equation (8), $K_L a$ depends on numerous parameters including reactors properties and operating conditions, through parameters V, Q_G, Q_L and ε. However, $K_L a$ can also be influenced significantly by thermodynamic properties such as $H_{VOC,W}$ and $H_{VOC,NAP}$, respectively (Equations (6) and (7) and Figure 2). The possible influence of the solubility ratio m_R on the change in $K_L a$ was evidenced during the experimental absorption of toluene, dimethylsulphide and dimethyldisulphide by various water/silicone oil mixtures [12].

The mathematical study of Equations (8)–(10) is complex due to the fact that the relation between the absorption efficiency, ε, and the NAP volume fraction, ϕ_{NAP}, cannot be predicted. However, it may be possible to demonstrate numerically that the 3 behavioral identified trends in $K_L a$ change due to the addition of NAP (i.e., (i) $K_L a$ increase to a maximum, with subsequent decrease; (ii) $K_L a$ increase to a maximum with no decrease; (iii) no increase in $K_L a$ or decrease in $K_L a$) can be described by Equation (8). Nonetheless, according to Figure 2, it is clear that the main change in $K_L a$ occurs for NAP volume fractions ranged from 0 to 0.3 in agreement with the significant drop in $H_{VOC,mix}$, especially for VOCs characterized by m_R larger than 100. For such NAP volume fractions, the change in the absorption efficiency is substantial, leading to a dramatic change in $K_L a$ evolution with the addition of NAP. Incidentally, all experimental results converge to indicate that the change in $K_L a$ occurs for this range of NAP volume fractions [13]. Beyond $\phi_{NAP} = 0.3$, the change in the Henry coefficient, $H_{VOC,mix}$, is more insignificant (Figure 2), which can explain the fact that the experimental enhancement factor reaches a plateau with increasing the volumetric fraction of NAP [14].

Coupled with the "Equivalent Absorption Capacity" concept, the $K_L a$ determination of operating absorbers using the ε-NTU method could be the expected tool to explain certain results reported in the current literature concerning gas/liquid/liquid systems and TPPB. According to Equation (4), it is clear that the Henry coefficient, $H_{VOC,mix}$, is the most sensitive of all parameters. As $H_{VOC,mix}$ depends on ε and the Henry coefficients $H_{VOC,W}$ and $H_{VOC,NAP}$ which are significantly affected by the temperature, its determination must be as accurate as possible. The Henry coefficients $H_{VOC,W}$ can be found in the literature [15,16]. For $H_{VOC,NAP}$ values, new determination techniques have been developed recently [17–19]. Concerning the influence of the temperature, an example from data reported in Tatin et al. can be given [20]. For toluene absorption in silicone oil Rhodorsil® 47V340 (Bluestar Silicones Company, Lyon, France) used as NAP, these authors determined the change in $H_{VOC,NAP}$ related to temperature. Between 18 °C and 22 °C, the $H_{VOC,NAP}$ value varies from 7.0×10^{-4} to 8.28×10^{-4}, i.e., a 15% difference. Taking also into account the influence of temperature on the change in the Henry coefficient of toluene between air and water, the order of magnitude in the change in $H_{VOC,mix}$ for a water/silicone oil mixture ($\phi_{NAP} = 10\%$ *v/v*) calculated according to Equation (5) is also 15% ($H_{VOC,mix} = 0.0068$ at 18 °C and $H_{VOC,mix} = 0.0080$ at 22 °C). As a result, the measurement of the temperature throughout the height of the absorber is an important parameter to consider for accurate $K_L a$ determination.

3. Validation of the ε-NTU Method for Countercurrent Scrubbers (CS)

The $K_L a$ determination procedure using the ε-NTU method was applied to various cases of countercurrent scrubbers (CS) reported in the literature. As observed in Table 1, experimental data are diversified in terms of NAP used, VOCs to be transferred and operating conditions.

3.1. Data from Tatin et al.

This study outlined the toluene removal by a spray tower consisting of an empty cylindrical vessel and nozzles spraying various water/silicone oil mixtures ($\phi_{NAP} = 10\%$ and 20%) into the

vessel. From experimental data summarized in Table 1, $K_L a$ were obtained from the ε-NTU method (Table 2). For all experiments reported in this table, absorption factors were dramatically large, beyond values usually applied in industrial cases. For a (90/10 *v/v*) water/silicone oil mixture sprayed at a constant liquid flow-rate, $K_L a$ was not influenced by the change in the gas flow-rate for the range of applied flow-rates. Moreover, for ϕ_{NAP} = 10%, at constant gas and liquid flow-rates, the increase in temperature had a negative impact on toluene absorption in relation with the increase in the Henry coefficient. However, the impact is positive on the change in $K_L a$. A 2.7-fold increase is calculated for the 5–50 °C range. This finding is consistent with results deduced from the literature [11,21] indicating the influence of the Henry coefficient on $K_L a$. Lastly, the influence of the silicone oil volume fraction in the mixture on toluene removal was studied. Authors reported that results were not significant: when the silicone oil volume fraction was doubled (from ϕ_{NAP} = 10% to ϕ_{NAP} = 20%), efficiency was improved by only 3%. This very interesting result could be explained as follows: although the increase in the NAP volume fraction significantly improves the mixture absorption capacity (the Henry coefficient $H_{VOC,mix}$ decreases from 0.0041 to 0.0021, i.e., a 2-fold decrease), this positive effect is limited by the significant decrease in $K_L a$ in the same proportion (Table 2). The $K_L a$ decrease is obviously due to the increase in the viscosity of the liquid mixture in relation to the doubling of silicone oil volume, but also to the fact that $K_L a$ is intrinsically dependent on the NAP volume fraction as highlighted by Equation (8) as well as of the Henry coefficient as explained above.

Table 1. Literature data used for K_La determination using ε-NTU method (Countercurrent Scrubbers (CS) configuration).

COVs	NAP	$H_{VOC,W}$	$H_{VOC,NAP}$	m_R	Operating Conditions	Ref
Hexane	Silicone oil 190 mPa s	61	5.8×10^{-3}	$10,500_{(30\,°C)}$	$V = 2 \times 10^{-3}$ m^3 $Q_L = 3.01 \times 10^{-6}$ m^3/s Q_G: 1.67×10^{-5}; 3.33×10^{-5}; 5.00×10^{-5} m^3/s (gas EBRT: 120; 60; 40 s) ϕ_{NAP}: 0; 20%	[22]
Toluene	Silicone oil 340 mPa s	2.69×10^{-4} T^2 + 3.83×10^{-4} T + 9.1×10^{-2} (5–50 °C)	6.35×10^{-7} T^2 + 6.63×10^{-6} T + 3.75×10^{-4} (5–60 °C)	$235_{(5\,°C)}$ $261_{(17\,°C)}$ $341_{(50\,°C)}$	$V = 5.52 \times 10^{-1}$ m^3 $Q_L = 5.0 \times 10^{-3}$; 7.22×10^{-3} m^3/s Q_G: 2.78×10^{-2}; 5.56×10^{-2}; 9.72×10^{-2} m^3/s (gas EBRT: 20; 10; 6 s) ϕ_{NAP}: 10; 20%	[20]
Styrene	Silicone oil 10 mPa s	$0.153_{(NaCl\ solution)}$	6.0×10^{-4}	$255_{(30\,°C)}$	$V = 2 \times 10^{-3}$ m^3 Q_G: 1.67×10^{-5} m^3/s (gas EBRT: 120 s; Q_G/Q_L = 7.5 and 16) Q_G: 3.33×10^{-5} m^3/s (gas EBRT: 60 s; Q_G/Q_L = 32) ϕ_{NAP}: 0; 5; 10; 20%	[23]
Toluene DMDS	Silicone oil 5 mPa s	0.274 0.045	1.09×10^{-3} 1.37×10^{-3}	$252_{(25\,°C)}$ $33_{(25\,°C)}$	$V = 1.13 \times 10^{-2}$ m^3 $Q_L = [2.67 \times 10^{-5} – 1.39 \times 10^{-4}]$ m^3/s Q_G: 5.25×10^{-3}; 7.30×10^{-3}; 9.25×10^{-3} m^3/s (gas EBRT: 2.2; 1.6; 1.3 s) ϕ_{NAP}: 0; 10; 100%	[11]
Toluene	HOSO (sunflower oil) 77 mPa s Commercial sunflower oil 57 mPa s	0.274	0.0147 0.017	$19_{(24\,°C)}$ $16_{(24\,°C)}$	$V = 2.2 \times 10^{-2}$ m^3 $Q_L = [1.33 \times 10^{-5} – 2.07 \times 10^{-5}]$ m^3/s Q_G: 2.33×10^{-4}; 3.00×10^{-4}; 3.83×10^{-4} m^3/s (gas EBRT: 94; 73; 57 s) ϕ_{NAP}: 5%	[24]

Table 2. K_La determination using the data reported in Tatin et al. [20] (toluene absorption in silicone oil 340 mPa s; $Q_L = 7.22 \times 10^{-3}$ m³/s; $V = 5.52 \times 10^{-1}$ m³).

T (°C)	ϕ_{NAP}	$H_{VOC,mix}$	Q_G (m³/s)	A	ε	NTU	K_La (s⁻¹)	EBRT (s)
5	0.1	0.0041	2.78×10^{-2}	63.7	0.90	2.325	4.78×10^{-4}	20
			5.56×10^{-2}	31.8	0.67	1.123	4.61×10^{-4}	10
			9.72×10^{-2}	18.2	0.50	0.704	5.06×10^{-4}	6
5	0.1	0.0041	2.78×10^{-2}	63.7	0.90	2.325	4.78×10^{-4}	20
17		0.0065		40.1	0.83	1.796	5.86×10^{-4}	
50		0.0224		11.6	0.67	1.148	1.29×10^{-3}	
5	0.1	0.0041	2.78×10^{-2}	63.7	0.90	2.325	4.78×10^{-4}	20
	0.2	0.0021		124.7	0.93	2.673	2.80×10^{-4}	

3.2. Data from Hariz et al.

The toluene removal by a spray tower was also studied by Hariz et al. [24]. Two kinds of vegetable oils (a commercial sunflower oil and a High Oleic Sunflorer Oil, HOSO), were selected as NAPs (Table 1). As indicated in this table, Henry coefficient values of toluene between air and vegetable oils are significantly higher than the value reported for silicone oil [20] which explained the large difference between m_R values. K_La results obtained from the ε-NTU method are given in Table 3. In spite of large EBRT values of the gas in the scrubber, weak efficiencies were reported in relation with low absorption factor values. Nonetheless, K_La are of the same order of magnitude as those reported by Tatin et al. [20]. Moreover, it appears that the increase in the liquid flow-rate leads to an increase in K_La but results are lower for HOSO. Difference between oils could be due to the viscosity which is greater for HOSO than for the commercial oil. Concerning the influence of the gas flow-rate, no conclusion can be drawn from experimental results.

Table 3. K_La determination using the data reported in Hariz et al. [24] (toluene absorption in HOSO, a sunflower oil (77 mPa s) and in a commercial sunflower oil (57 mPa s); $V = 2.2 \times 10^{-2}$ m³).

NAP	ϕ_{NAP}	$H_{VOC,mix}$	Q_L (m³/s)	Q_G (m³/s)	A	ε	NTU	K_La (s⁻¹)	EBRT (s)
HOSO	0.05	0.146	1.33×10^{-5}	2.33×10^{-4}	0.392	0.22	0.371	5.72×10^{-4}	
			1.92×10^{-5}		0.564	0.30	0.520	8.04×10^{-4}	94
			1.67×10^{-5}		0.491	0.28	0.498	7.69×10^{-4}	
			1.67×10^{-5}	2.33×10^{-4}	0.491	0.28	0.498	7.69×10^{-4}	94
				3.00×10^{-4}	0.382	0.26	0.520	1.03×10^{-3}	73
				3.83×10^{-4}	0.299	0.15	0.228	5.78×10^{-4}	57
Commercial oil	0.05	0.156	1.33×10^{-5}	2.33×10^{-4}	0.366	0.26	0.541	8.96×10^{-4}	
			1.67×10^{-5}		0.458	0.26	0.454	7.52×10^{-4}	94
			2.07×10^{-5}		0.568	0.38	0.826	1.37×10^{-3}	

3.3. Data from Dumont et al.

Absorption experiments were carried out in a countercurrent gas–liquid absorber filled with Raschig rings as packing material. Three absorbing liquids: (i) water; (ii) pure silicone oil; and (iii) a mixture of water/silicone oil ($\phi_{NAP} = 10\%$) were used to transfer toluene and DMDS selected as VOC targets. Gas EBRT (2.2, 1.6 and 1.3 s) were relatively short in comparison with values applied by others studies (Table 1). For some operating conditions, absorption factors could then be significantly lower than 1 as illustrated in Figure 1. K_La results obtained from the ε-NTU method are reported in Figure 3 for a gas EBRT = 1.6 s (similar trends were obtained for gas EBRT 2.2 s and 1.3 s; not shown). For pure silicone oil, K_La ranged from 1.5×10^{-3} to 5.4×10^{-3} s⁻¹ which is around one order of magnitude lower than the values determined for pure water. The influence of the liquid viscosity is therefore confirmed by the data. Moreover, for pure silicone oil, a slight increase in K_La with the liquid flow-rate was observed for the range of the studied liquid flow-rates. This finding is in agreement with results reported in Bourgois et al. [25] who studied the absorption of four hydrophobic compounds (hexane, toluene, octane and methylcyclohexane) in a viscous solvent (DEHP, i.e., di-2-ethylhexylphtalate; dynamic viscosity: 76 mPa s). Conversely, for pure

water and for the water/silicone oil mixture, $K_L a$ were significantly affected by the liquid flow-rate. Such a result is consistent with data usually reported in the literature and with the sensitivity analysis reported by Hernandez et al. [22]. Additionally, Figure 4 highlights that $K_L a$ also depends on $H_{VOC,mix}$ which is in agreement with data reported in the literature [12,21,26]. Such an expected result is consistent with the mathematical expression of $K_L a$ given by Equation (9). Therefore, all findings highlight that, for a given VOC to be transferred using a given NAP (i.e., a given m_R value), $K_L a$ depend on the complex interactions that occur between the influent parameters Q_L, gas EBRT, ε and ϕ_{NAP}. As a result, it is confirmed that $K_L a$ for such complex systems could not be easily predicted. Although the ratio $K_L a|_{\phi_{NAP}} / K_L a|_{\phi_{NAP}=0}$ cannot be calculated strictly in the present case (in relation with the change in the range of the liquid flow-rates applied according to the liquid used), it is clear from Figure 3 that $K_L a$ drops with the addition of silicone oil. The most significant decrease is obtained for a 10% addition of silicone oil in water; the difference between ratio $K_L a|_{\phi_{NAP}=0.1}$ and $K_L a|_{\phi_{NAP}=1}$ being marginal. Such a result is mainly due to the change in the Henry coefficient which is significant between $\phi_{NAP} = 0\%$ and $\phi_{NAP} = 10\%$ as highlighted in Figure 2. According to this figure, the decrease in $H_{VOC,mix}$ is all the more pronounced as the m_R ratio is high. Differences observed in Figure 3 between $K_L a$ obtained for toluene and DMDS are therefore clearly explained by the difference between m_R values measured for these compounds (252 and 33, respectively; Table 1).
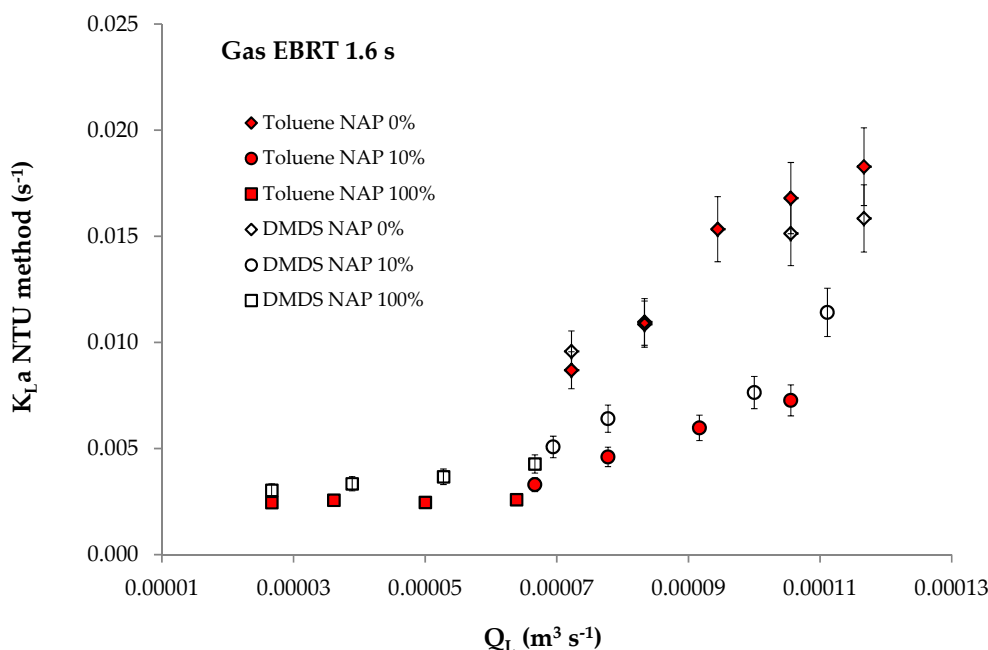

Figure 3. $K_L a$ vs. liquid flow-rate from data reported in Dumont et al. [11] (gas flow-rate = 7.3×10^{-3} m^3/s; V = 1.13×10^{-2} m^3; T = 25 °C).
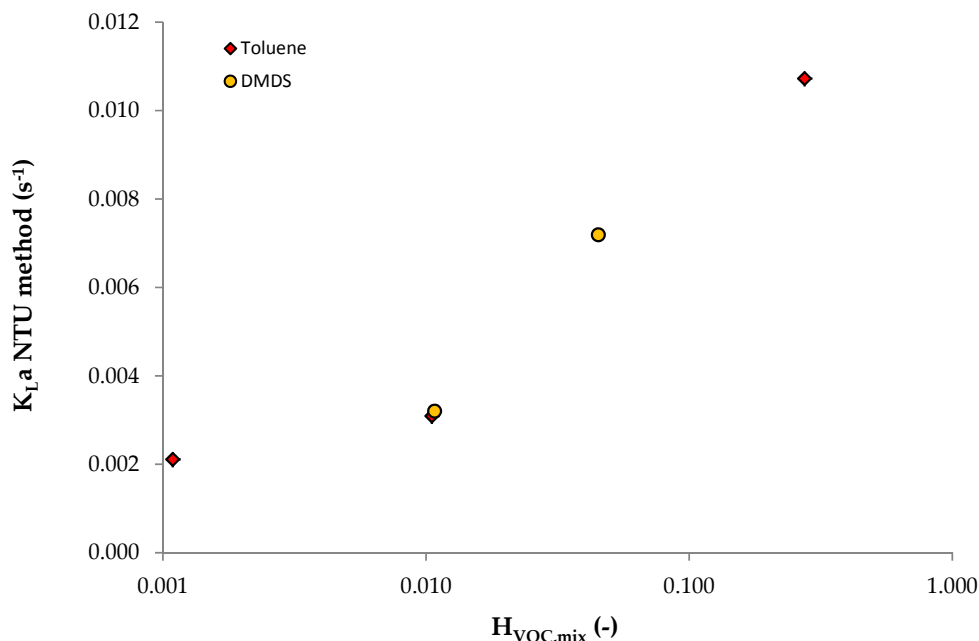
Figure 4. K_La vs. Henry coefficient from data reported in Dumont et al. [11] (gas flow-rate = 5.19 × 10^{-3} m^3/s; gas EBRT = 2.2 s; liquid flow-rate = 10^{-4} m^3/s; V = 1.13 × 10^{-2} m^3; T = 25 °C).

3.4. Data from Hernandez et al. and from Parnian et al.

These studies investigated the hexane removal [22] and the styrene removal [23] by water/silicone oil volume fractions on biotrickling filters packed with polyurethane foam cubes [22] (ϕ_{NAP} = 20%), and with a mixture of pumice and steel pall rings [23] (ϕ_{NAP} ranged from 0 to 20%), respectively. For both studies, K_La for pure water cannot be calculated from the ε-NTU method in relation with the unrealistic values of the removal efficiencies reported by these authors. As a result, all data reported in these studies could be considered as erroneous. Nonetheless, assuming that reported ε values are accurate for the other cases, K_La were calculated using the ε-NTU method (Table 4). Values are of the same order of magnitude as values calculated from Tatin et al. [20] using silicone oil as NAP. The three values obtained from the data of Hernandez et al. [22] for ϕ_{NAP} = 20% (K_La = 5.44 × 10^{-4} s^{-1}; 7.66 × 10^{-4} s^{-1} and 7.55 × 10^{-4} s^{-1} for gas EBRT: 120; 60 and 40 s, respectively; Table 1) indicate that the mass transfer coefficient was only slightly impacted by the change in the gas flow-rate. This finding is in agreement with the sensitivity analysis conducted by these authors.

Studying the effect of the addition of NAP for three liquid flow-rates at a constant gas EBRT, results from the data of Parnian et al. [23] (Figure 5) show that the change in K_La with the addition of silicone oil corresponds to the type 1 behavior reported in the literature [13] for Q_G/Q_L ratio of 7.5 and 16 (i.e., K_La increase to a maximum, with subsequent decrease). Such findings can be explained by the fact that an increase of at least 10% in silicone oil improved the styrene absorption significantly, whereas a subsequent addition up to 20% had no further effect on ε (in relation with the moderated change in the Henry coefficient between ϕ_{NAP} = 10% and ϕ_{NAP} = 20% relatively to ϕ_{NAP} = 0%, as already explained above from the data of Tatin et al. [20]). However, such an explanation is not valid for the Q_G/Q_L ratio of 32. In this case, the removal efficiency increased regularly with the addition of silicone oil, as well as K_La. Therefore, these results need to be confirmed by additional measurements.

Table 4. $K_L a$ determination using the data reported in Parnian et al. [23] (styrene absorption in water/silicone oil mixtures; silicone oil 10 mPa s; EBRT = 60 s; $V = 2 \times 10^{-3}$ m^3).

ϕ_{NAP}	$H_{VOC,mix}$	Q_L (m^3/s)	Q_G (m^3/s)	A	ε	NTU	$K_L a$ (s^{-1})
0	0.1530			0.87	0.999	no calculable	
0.05	0.0112			11.94	0.602	0.95	1.77×10^{-4}
0.1	0.0058	4.44×10^{-6}	3.33×10^{-5}	23.01	0.929	2.72	2.63×10^{-4}
0.2	0.0030			45.14	0.914	2.49	1.22×10^{-4}
0	0.1530			0.41	0.972	no calculable	
0.05	0.0112			5.60	0.802	1.78	3.32×10^{-4}
0.1	0.0058	2.08×10^{-6}	3.33×10^{-5}	10.78	0.999	7.51	7.25×10^{-4}
0.2	0.0030			21.16	0.999	7.20	3.54×10^{-4}
0	0.1530			0.20	0.815	no calculable	
0.05	0.0112			2.80	0.253	0.31	5.70×10^{-5}
0.1	0.0058	1.04×10^{-6}	3.33×10^{-5}	5.39	0.55	0.85	8.19×10^{-5}
0.2	0.0030			10.58	0.939	2.99	1.47×10^{-4}

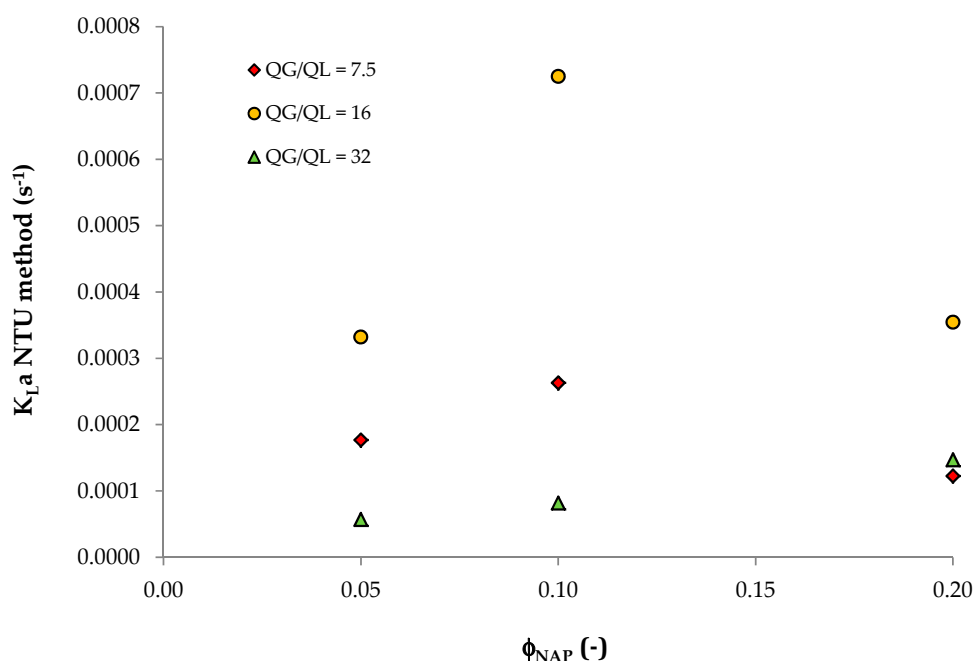**Figure 5.** $K_L a$ vs. NAP volume fraction from data reported in Parnian et al. [23] ($V = 2 \times 10^{-3}$ m^3; for $Q_G/Q_L = 7.5$ and 16, $Q_G = 1.67 \times 10^{-5}$ m^3/s, i.e., gas EBRT: 120 s; for $Q_G/Q_L = 32$, $Q_G = 3.33 \times 10^{-5}$ m^3/s, i.e., gas EBRT: 60 s; T = 30 °C).

3.5. Conclusions

Coupled with the "equivalent absorption capacity" concept, the ε-NTU method was applied successfully to determine $K_L a$ of diversified countercurrent gas-liquid contactors for various operating conditions (i.e., at different reactor scales, Table 1), NAP and organic compounds characterized by a very large range of Henry coefficients calculated according to Equation (5) (around five orders of magnitude between extreme values). The calculation procedure highlighted that $K_L a$ is sensitive to $H_{VOC,mix}$ and depends on the complex interactions that occur between the influent parameters Q_L, gas EBRT, ϕ_{NAP} and ε. However, the experimental determination of the change in $K_L a$ versus NAP volume fraction in countercurrent absorbers requires expensive apparatus and large NAP amounts. Consequently, there is a need to reduce operating costs by using cheaper devices such as stirred tank reactors requiring small NAP quantities.

4. Validation of the ε-NTU Method for Stirred Tank Reactor (STR)

For the Stirred Tank Reactors (STR) configuration, the gas flow-rate is dispersed through a known volume of a well-mixed liquid phase, and consequently $Q_L = 0$. In this case, it can be demonstrated that the effectiveness of the absorber is [7]:

$$\varepsilon = 1 - \exp(-\text{NTU}) \tag{11}$$

$$\text{NTU} = -\ln(1 - \varepsilon) \tag{12}$$

Although the parameter stirring rate is known to influence significantly the mass transfer in water/NAP system [13,27], it is not directly considered in Equation (11). The K_La determination procedure using the ε-NTU method was applied to data from two studies which considered the mass transfer performance of a very hydrophobic VOC, hexane, in various water/silicone oil mixtures (Table 5). As indicated in this table, the system hexane/water/NAP is characterized by a very large value in the solubility ratio ($m_R = 10{,}500$ at 30 °C). The ε-NTU method was applied successfully to all experimental data reported in Bordel et al. [28] (Table 6 and Figures 6 and 7) and in Hernandez et al. [22].

Table 5. Literature data used for K_La determination using ε-NTU method (Stirred Tank Reactors (STR) configuration).

VOCs	NAP	$H_{VOC,W}$	$H_{VOC,NAP}$	m_R	Operating Conditions	Ref
Hexane	Silicone oil 190 mPa s	61	5.8×10^{-3}	10,500 (30 °C)	$V = 2 \times 10^{-3} \text{ m}^3$ $Q_G = 1.67 \times 10^{-5} \text{ m}^3/\text{s}$ Stirring rates: 100; 200; 300 rpm ϕ: 5; 7.5; 10; 20%	[28]
Hexane	Silicone oil 190 mPa s	61	5.8×10^{-3}	10,500 (30 °C)	$V = 2 \times 10^{-3} \text{ m}^3$ Q_G: 1.67×10^{-5}; 3.33×10^{-5}; $5.00 \times 10^{-5} \text{ m}^3/\text{s}$ (EBRT: 120; 60; 40 s) Stirring rates: 200 rpm ϕ: 0; 20%	[22]

Table 6. K_La determination using the data reported in Bordel et al. [28] (hexane absorption in water/silicone oil mixtures; silicone oil 190 mPa s; $V = 2 \times 10^{-3} \text{ m}^3$).

ϕ_{NAP}	$H_{VOC,mix}$	100 rpm			200 rpm			300 rpm		
		ε	NTU	K_La (s^{-1})	ε	NTU	K_La (s^{-1})	ε	NTU	K_La (s^{-1})
0.05	0.116	0.53	0.755	7.29×10^{-4}	0.64	1.022	9.86×10^{-4}	0.64	1.022	9.86×10^{-4}
0.075	0.077	0.52	0.734	4.72×10^{-4}	0.69	1.171	7.54×10^{-4}	0.76	1.427	9.19×10^{-4}
0.1	0.058	0.50	0.693	3.35×10^{-4}	0.73	1.309	6.32×10^{-4}	0.79	1.561	7.54×10^{-4}
0.2	0.029	0.89	2.207	5.33×10^{-4}	0.93	2.659	6.42×10^{-4}	0.86	1.966	4.75×10^{-4}
0.3	0.019	0.64	1.022	1.65×10^{-4}	0.92	2.526	4.07×10^{-4}	0.88	2.120	3.42×10^{-4}

Figure 6 confirms that K_La depends on $H_{VOC,mix}$ which is in agreement with results obtained from countercurrent gas-liquid absorbers (see Section 3). Moreover, the influence of the stirring rate on K_La is clearly evidenced in this figure. However, at 200 and 300 rpm, the change in K_La vs. $H_{VOC,mix}$ seems partially inconsistent at first glance since there is a discontinuity in the trend describing the change in K_La. This discontinuity is also evidenced in Figure 7 for the silicone volume fraction $\phi_{NAP} = 20\%$. According to the authors, an increase in the silicone oil volume fraction of up to 20% enhanced the effectiveness whereas no significant variations were recorded for an increase of up to 30% (Table 6). At a stirring rate of 300 rpm, the increase in the effectiveness with the addition of oil was gradual, whereas at 100 rpm the effectiveness recorded between $\phi_{NAP} = 10\%$ and $\phi_{NAP} = 20\%$ jumped from $\varepsilon = 50 \pm 4\%$ to $\varepsilon = 89 \pm 3\%$ (Table 6). For the stirring rate of 200 rpm, the jump was less significant. In terms of the change in K_La, the jump in

the effectiveness at ϕ_{NAP} = 20% leads to an increase in the K_La. Consequently, it can be evidenced that the coupled interaction between the parameters, stirring rate and NAP volume fraction, on the effectiveness of the absorption is complex. At 300 rpm, the overall mass transfer coefficient decreases continuously with the addition of silicone oil whereas at 100 rpm, K_La decreases then increases and decreases again with the addition of NAP. Such changes in K_La vs. ϕ_{NAP} is reported in the literature [1]. Consequently, these findings confirm that the empirical correlations reported in the literature for the prediction of K_La are therefore limited to the operating conditions applied for their determination [27].

For the STR configuration, the combination of Equations (4), (6) and (12) gives:

$$\frac{K_La|_{\phi_{NAP}}}{K_La|_{\phi_{NAP}=0}} = \frac{\ln(1-\varepsilon)}{[1+\phi_{NAP}(m_R-1)]\ln(1-\varepsilon_0)} \tag{13}$$

where ε_0 is the absorber efficiency in the absence of NAP (i.e., ϕ_{NAP} = 0). Using the data reported in Hernandez et al. [22] (Table 5), the ratio $K_La|_{\phi_{NAP}=0.2}/K_La|_{\phi_{NAP}=0}$ are calculated to be 3.1×10^{-3} and 3.0×10^{-3} for gas EBRT of 120 and 40 s, respectively. These very low values are due to the high m_R value which leads to a dramatic decrease in the Henry coefficient with the addition of NAP (Figure 2). In the present case, $H_{VOC,mix}$ drops from 61 in the absence of NAP (i.e., $H_{VOC,W}$) to 0.029 for a water/silicone oil mixture with 20% of silicone oil. As a result, the 2100-fold decrease in $H_{VOC,mix}$ directly impacts the K_La. Such finding confirms the influence of the Henry coefficient already highlighted from the absorption of styrene by water/silicone oil mixtures in a bubble reactor [29].

To conclude, it has to be pointed out that the ε-NTU method applied to STR data could be used to describe accurately the K_La behavior with the addition of NAP. However, taking into account that the strongest changes in K_La occur for a NAP volume fraction ranged between 0 and 20%, a lot of experiments will have to be carried out in order to study carefully the influence of this parameter. A number of NAP volume fractions as large as possible, and as close as possible to ϕ_{NAP} = 0, should be considered, especially for very hydrophobic VOCs characterized by high m_R values.
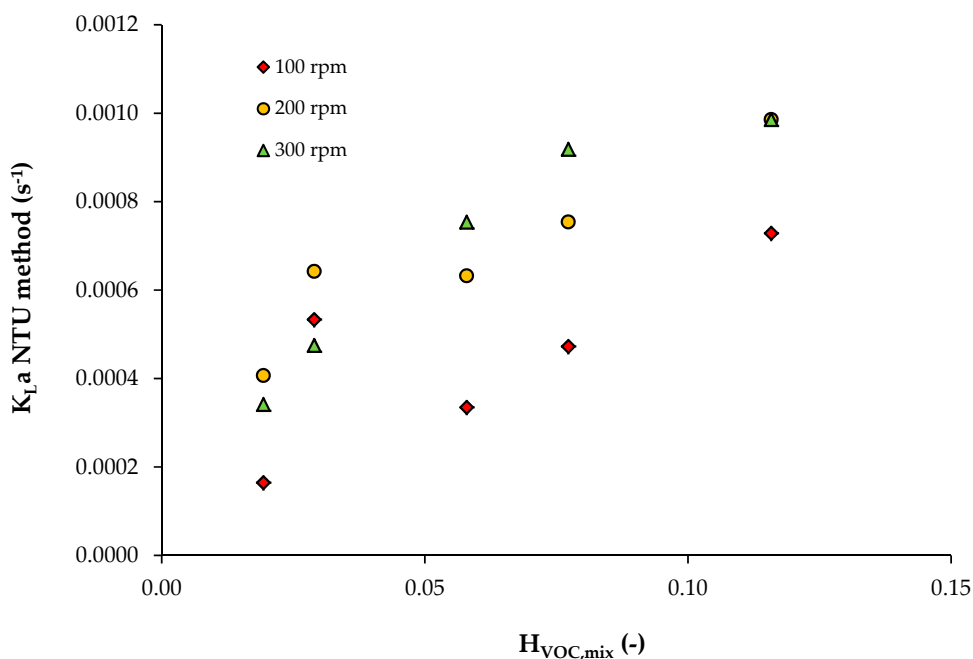

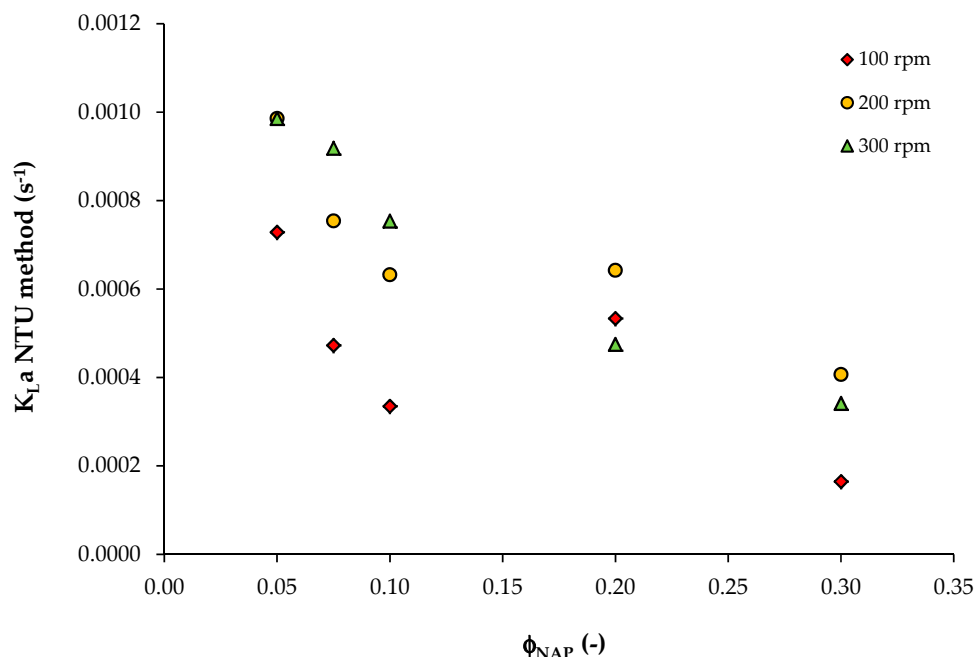**Figure 6.** K_La vs. Henry coefficient from data reported in Bordel et al. [28].

Figure 7. K_La vs. silicone oil volume fraction from data reported in Bordel et al. [28].

5. Conclusions

It was evidenced that the ε-NTU method can be used successfully to simply determine the overall mass transfer coefficient, K_La, of gas/liquid/liquid absorbers (countercurrent and stirred tank reactors). This method requires the knowledge of the operating conditions (Q_G, Q_L, V), the measurement of gaseous concentrations at the inlet and at the outlet of the contactor, and the calculation of the Henry coefficient of the VOC between the gas and the liquid phase. The ε-NTU method, validated from literature data, appears as a robust and reliable tool for K_La determination of complex systems. Coupled with the "equivalent absorption capacity" concept, this method can be used for environmental applications in treating the removal of air pollutants by means of Two-Phase Partitioning Bioreactors contacting a gas and a mixture of water and NAP. Moreover, the ε-NTU method could be used adequately to establish new empirical correlations for the prediction of K_La for heavy viscous solvents and for fermentation broths.

Conflicts of Interest: The author declares no conflict of interest.

Nomenclature

A	absorption factor
C_G	gaseous concentration (mol/m^{-3})
H	Henry coefficient
K_La	overall mass transfer coefficient (s^{-1})
m_R	solubility ratio
NTU	Number of Transfer Unit
Q_G	gas flow rate (m^3/s)
Q_L	liquid flow rate (m^3/s)
V	absorber volume (m^3)
Greek Letters	
ε	absorber effectiveness
ϕ	NAP volume fraction

Subscripts

in	inlet
L	liquid
mix	water/NAP mixture
NAP	Non Aqueous Phase
out	outlet
VOC	Volatile Organic Compound
W	water

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