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**Reversible absorption of volatile organic compounds by switchable-hydrophilicity solvents: a case study of toluene with N,N-dimethylcyclohexylamine**

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**Text S1. Chemicals**

N,N-Dimethylcyclohexylamine (CyNMe<sub>2</sub>) and N,N-dimethylbenzylamine (BDMA) were purchased from Chemical Reagent Co. Ltd.. Washing oil (WO) was obtained from Kunming Iron Co., Ltd. Both benzene and toluene were of analytical grade from Aldrich Chemical Co. CO<sub>2</sub> (with purity of 99.999%) and N<sub>2</sub> (with purity of 99.998%) were from GRD Ltd, Kunming. Ultrapure water was obtained from an Agilent purification system. Other chemical reagents were of analytical grade and were used as received without further purification.

**Text S2. Theory****S2.1 Henry's law constants, activity coefficient and viscosity**

Concentrations of toluene in absorbent and the Henry's law constant of toluene were determined by headspace gas chromatography.<sup>1,2</sup> The liquid phase was analyzed by GC-FID. According to the mass balance, toluene concentration in the liquid phase was calculated by the following equation:

$$C_L = C_S - C_G \quad (1)$$

Then, the dimensionless Henry's law constant  $H$ ,  $H_C$  and  $E$  could be calculated by equations (2)、(3) and (4), respectively:

$$H = C_G / C_L \quad (2)$$

$$H_C = HRT \quad (3)$$

$$E = P_G / x_G \quad (4)$$

The effect of temperature upon Henry's law constant is great at a constant pressure. At different temperature, two empirical equations were obtained by experiment, and that are the linear relationship between the natural logarithm of the Henry constant and the reciprocal of the absolute equilibrium temperature. The temperature dependence of Henry constant can be described by the Van' t Hoff equation,

$$\ln H = -A_H + B_H / T \quad (5)$$

$$\ln E = -A_E + B_E / T \quad (6)$$

Heymes<sup>3</sup> gave an equation relating the Henry's law constant ( $E$ ) to the activity coefficient ( $\gamma$ ) which was used to calculate the activity coefficient of toluene in different absorbents (equation 7).

$$\gamma = E / P^{sat} \quad (7)$$

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Viscosities were obtained from Lange's Handbook of Chemistry<sup>4</sup> or determined using an NDJ Series Digital Viscometer.

## S2.2 Evaluation criteria for absorption performance

Evaluation criteria for absorption performance of CyNMe<sub>2</sub> and other solvents include thermodynamic equilibrium parameters, such as Henry constant ( $E$ ), activity coefficient ( $\gamma$ ) and viscosity ( $\eta$ ) values for the gas-liquid absorption system. Absorbents with lower  $E$  (or higher  $\gamma$ ) and lower  $\eta$  are expected to have superior absorption performance. Because the overall absorption coefficient,  $K$ , is mainly determined by  $E$ , while  $E$  determines the absorption capacity and thus is related to  $\gamma$ , lower  $E$  or lower  $\gamma$  mean higher absorption capacity<sup>3</sup>. The diffusion coefficient ( $D_{AB}$ ) is inversely proportional to the viscosity ( $\eta$ ) of absorbent according to the relation:  $D_{AB} = f(1/\eta)$ .  $D_{AB}$  determines the gas-liquid mass transfer rate, so low  $\eta$  means relative high absorption. Because no accurate thermodynamic data were found in the literature for toluene gas-liquid phase equilibrium in selected absorbents, experimental were performed to obtain this data.

## S2.3 Mass transfer

Because adequate mass transfer is crucial to this process, the mass transfer mechanism was studied for the absorption step, including whether the mass transfer resistance is mainly located in the gas or liquid film. This information is of practical significance for scale-up of this method in industry.

Experiments on gas liquid mass transfer of VOC into the SHS were carried out in a double-stirred reactor (Fig. S3), including evaluation of the diffusion of gaseous component from the bulk gas phase, the diffusion through the gas interface to liquid interface, dissolution into liquid absorbent, and liquid phase diffusion. The liquid phase diffusion exhibits the inverse direction relative to gas phase diffusion. For gas-liquid absorbing processes, the resistance of mass transfer is used to describe the mass transfer mechanism (Lu et al., 2008).<sup>5</sup> The mass transfer coefficients,  $K_L$  and  $K_G$ , can be expressed as shown in Eq. (15) and (20) in the section below.

### S2.3.1 $K_L$ calculations

$K_L$  was determined as described in previous papers.<sup>6,7</sup> It was assumed that the mixing of the gas and the liquid phases was ideal. Henry's law constant was the main parameter for the

$K_L$  calculation. In the present work, the VOC absorption is physical absorption and the pressure is low, so the ideal gas law is applicable for the absorption system.

Though the experiment was semi continuous, in order to maintain the volume constant, absorbent was added continuously into reactor in each 10min, the conservation of mass can be expressed by:

$$V_G C_{AG}^0 + V_L C_{AL}^0 = V_G C_{AG}^t + V_L C_{AL}^t \quad (8)$$

As no VOC was present in the absorbent at  $t = 0$  ( $C_{AL}^0 = 0$ ), equation (8) can be rearranged as:

$$C_{AL}^t = \frac{V_G}{V_L} (C_{AG}^0 - C_{AG}^t) \quad (9)$$

The time derivative of the available concentration is

$$\frac{dC_{AL}^t}{dt} = -\frac{V_G}{V_L} \frac{dC_{AG}^t}{dt} \quad (10)$$

According to the two-film theory, the VOC absorption rate in the liquid phase is given as follows:

$$N_A = \frac{V_L}{A} \frac{dC_{AL}^t}{dt} = K_L (C_{AL}^* - C_{AL}^t) \quad (11)$$

A combination of equation (10) and (11) leads to:

$$-\frac{V_G}{A} \frac{dC_{AG}^t}{dt} = K_L (C_{AL}^* - C_{AL}^t) \quad (12)$$

Using the Henry constant, the  $C_{AL}^*$  can be expressed as

$$C_{AL}^* = \frac{C_{AG}^\infty}{H} \quad (13)$$

At equilibrium, the gas concentration between toluene and absorbent can be expressed as:

$$C_{AG}^\infty = \frac{H V_G}{V_L + H V_G} C_{AG}^0 \quad (14)$$

A combination of equation (9) (12) (13) and (14) leads to a linear equation:

$$\ln \frac{C_{AG}^t - C_{AG}^\infty}{C_{AG}^0 - C_{AG}^\infty} = -\frac{A}{V_L} K_L t \quad (15)$$

By plotting  $\ln \frac{C_{AG}^t - C_{AG}^\infty}{C_{AG}^0 - C_{AG}^\infty}$  against  $\frac{A}{V_L} t$ , a straight line was obtained whose slope gives the mass transfer coefficient  $K_L$ .

### S2.3.2 $K_G$ calculations

According to the two-film theory, the VOC absorption rate in the gas phase is given by:

$$N_A = -\frac{V_G}{A} \frac{dC_{AG}^t}{dt} = K_G (P_{AG}^t - P_{AG}^*) \quad (16)$$

Because the absorption pressure is low, the ideal gas law is applicable, according to the Amagat law  $P_{AG}^t$  and  $P_{AG}^*$  can be expressed by:

$$P_{AG}^t = C_{AG}^t RT \quad (17)$$

$$P_{AG}^* = C_{AG}^\infty RT \quad (18)$$

A combination of equations (16), (17), and (18), leads to a linear equation:

$$-\frac{V_G}{A} K_G dt = \frac{1}{RT} \frac{dC_{AG}^t}{C_{AG}^t - C_{AG}^\infty} \quad (19)$$

After integration, this leads to a linear equation:

$$\ln \frac{C_{AG}^t - C_{AG}^\infty}{C_{AG}^0 - C_{AG}^\infty} = -\frac{ART}{V_G} K_G t \quad (20)$$

It should be noted that when  $C_{AG}^t > C_{AG}^\infty$ , calculated  $K_L$  and  $K_G$  value could be reasonable and valid.

## Text S3. The effect of water

### S3.1 The effect of water content in CyNMe<sub>2</sub>

The solubility (mass%) of water in CyNMe<sub>2</sub> is 5.0% (at 30°C), 8.0% (40°C), 11.3% (50°C), and 13.8% (60°C).<sup>8</sup> These mixtures containing different concentrations of water were obtained by addition of 0.849 mL water into 19 mL CyNMe<sub>2</sub> (5%), 1.358 mL water into mL CyNMe<sub>2</sub> (8%), 1.919 mL water into 17.74 mL CyNMe<sub>2</sub> (11.3%), and 2.343 mL water into 17.22 mL CyNMe<sub>2</sub> (13.8%). The absorption processes of different absorption system were performed at 430 mL/min N<sub>2</sub> carried 27 g/m<sup>3</sup> toluene.

### S3.2 The effect of a CO<sub>2</sub>-containing gas mixture on wet CyNMe<sub>2</sub>

A mix of 8.1 wt% water in CyNMe<sub>2</sub> was prepared as representative of the recycled amine that would be received from the separator if the separator were being maintained at 40 °C. The water/amine liquid mixture was maintained at 25 °C in a constant-temperature water bath. A

gas mixture of 10 wt% CO<sub>2</sub> in N<sub>2</sub> was bubbled through this liquid mixture for 2 h. Within 10 min of the onset of bubbling, the monophasic mixture split into two liquid phases, the lower (aqueous) phase being approximately 1/10<sup>th</sup> the volume of the liquid mixture. A similar experiment but having 7.9 wt% water, 89.4 wt% CyNMe<sub>2</sub>, and 1.3 wt% toluene gave the same result.

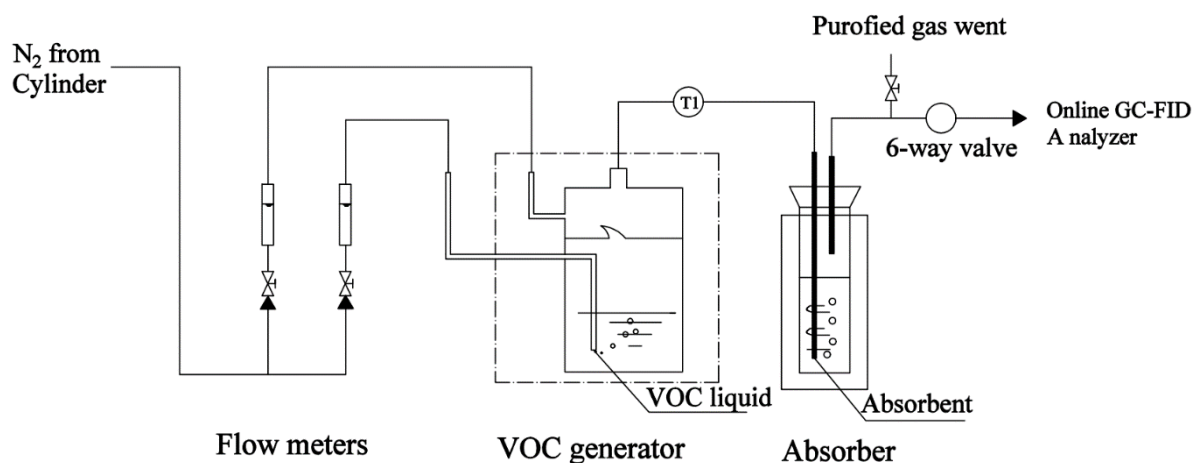


Figure S1. Apparatus for the absorption experiments

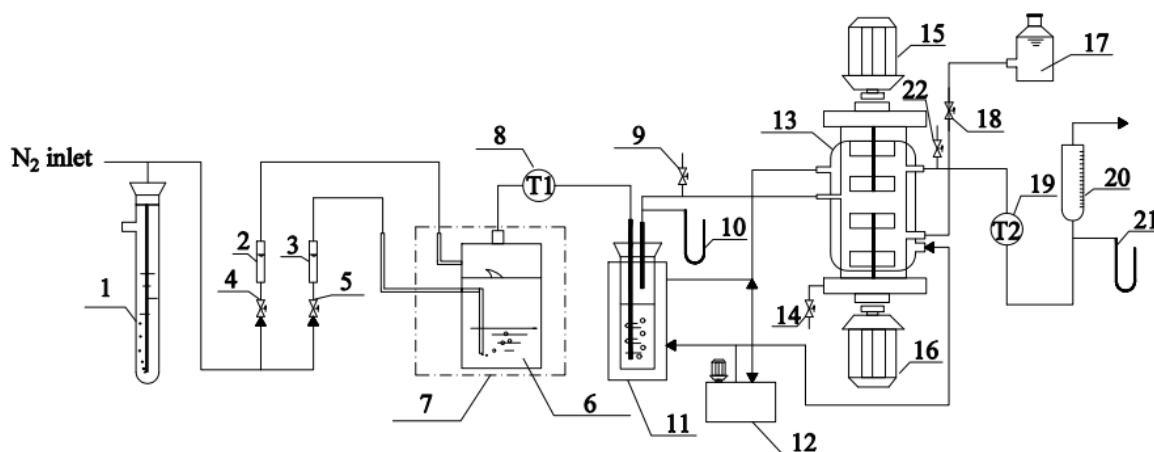


Figure S2. Apparatus for measuring the mass transfer of toluene in CyNMe<sub>2</sub>. 1. Regulator; 2, 3. Gas flow-meters; 4, 5. Gas control valve; 6. Toluene vapor generator; 7, 12. Water bath; 8. Inlet thermometer; 9. Gas sampling point (inlet); 10. Manometer; 11. Water saturator; 13. Stirred cell reactor; 14. Absorbent sampling point; 15, 16. Driving motors; 17. Absorbent bottle; 18. Absorbent control valve; 19. Exit thermometer; 20. Soap film flow-meter; 21. Manometer; 22. Gas sampling point (outlet).

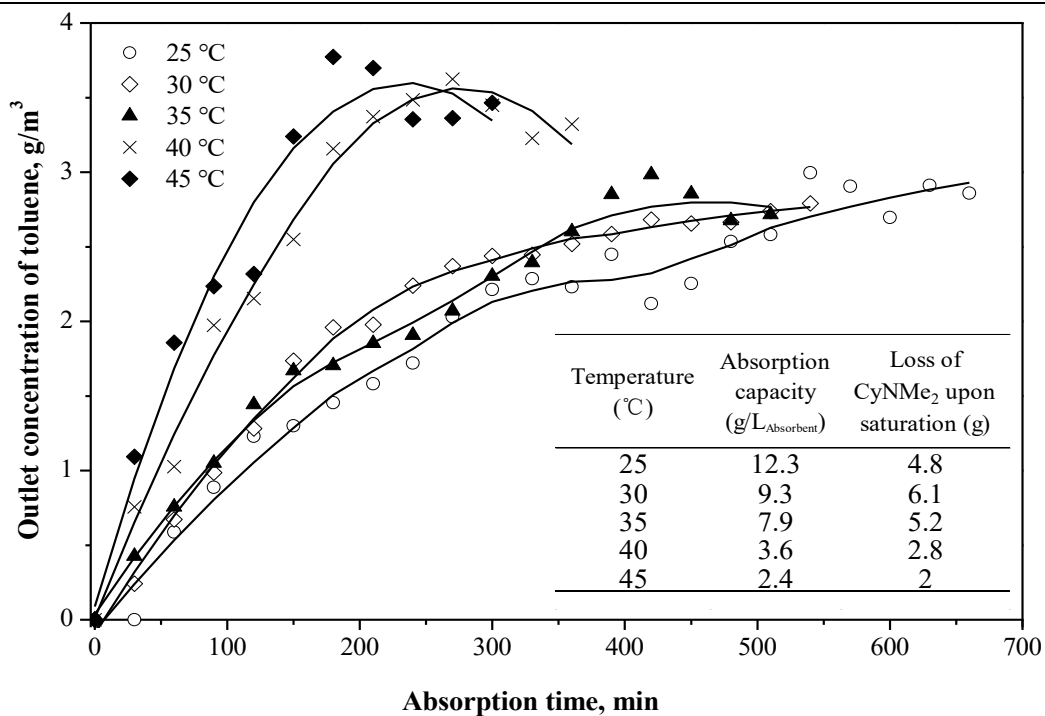


Figure S3. The absorption of toluene in CyNMe<sub>2</sub> at various temperatures. 430 mL/min N<sub>2</sub> carried 2.7 g/m<sup>3</sup> toluene absorbed by 20 mL of CyNMe<sub>2</sub>.

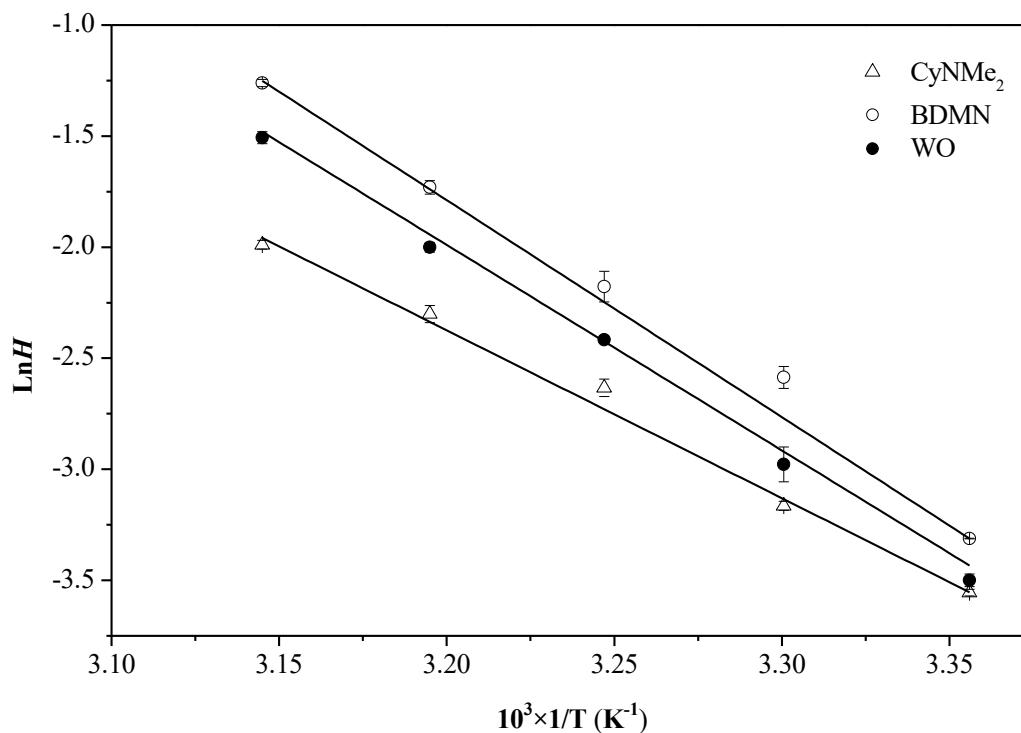


Figure S4. Variation of the natural logarithm of the Henry's law constant with the reciprocal of absolute temperature for toluene in different absorbent.

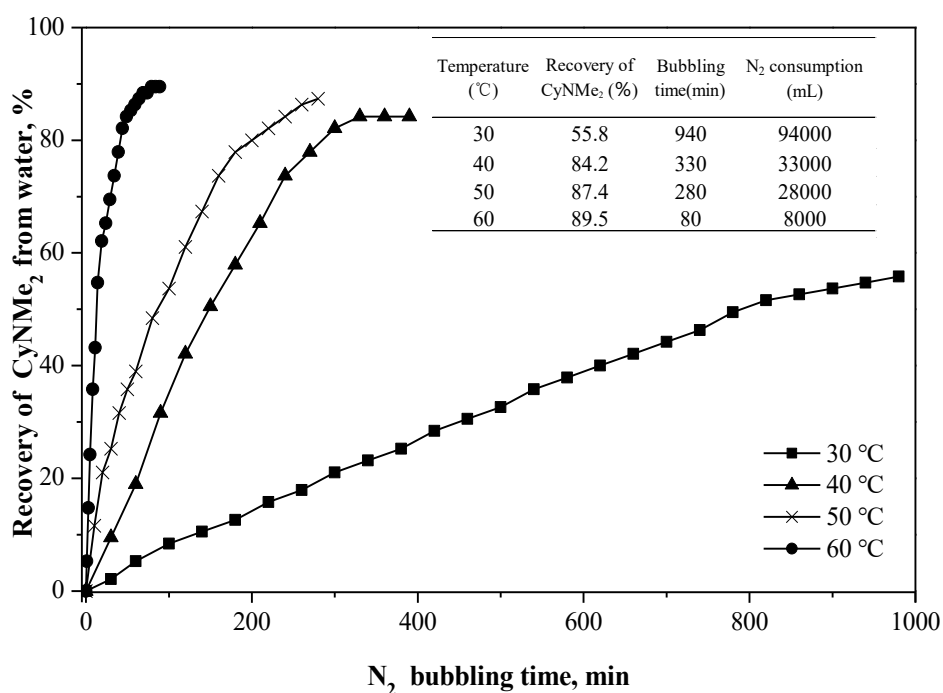


Figure S5. The recovery of CyNMe<sub>2</sub> from carbonated water at various temperatures. 100 mL/min N<sub>2</sub> was bubbled into a single-phase aqueous mixture prepared by mixing CyNMe<sub>2</sub> (10 mL) and UP water (10 mL) and then bubbling CO<sub>2</sub> (30 mL/min) through the mixture at 25 °C. The volume of CyNMe<sub>2</sub> did not reach 100% because of volatile losses.

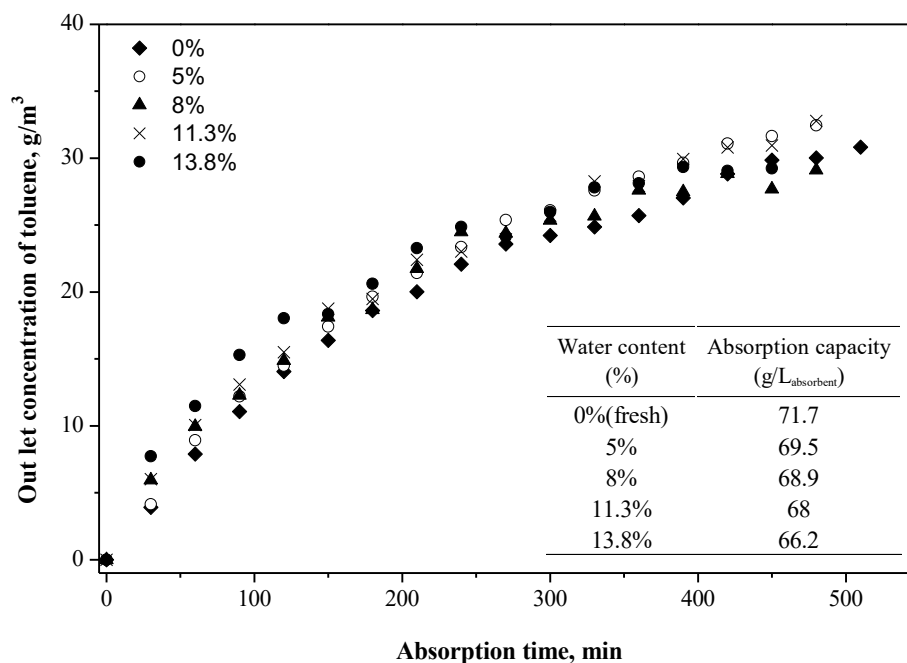


Figure S6. Absorption of toluene in CyNMe<sub>2</sub> containing various amounts of water. 430 mL/min N<sub>2</sub> carried 27 g/m<sup>3</sup> toluene into 20 mL of CyNMe<sub>2</sub> containing various amounts of water.



Table S1. Thermodynamic parameters for the absorption of toluene by switchable-hydrophilicity solvent CyNMe<sub>2</sub>

$T$ (K)	$K_d$ (1/H)×10 <sup>-3</sup>	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol/K)
298	4.72	-20.85		
303	3.23	-20.14		
308	1.90	-19.44	-63.02	-141.50
313	1.34	-18.73		
318	0.99	-18.02		

Table S2. Values of A and B of empirical equation and correlation coefficient

Absorbent	lnH and 1/T			lnE and 1/T		
	$A_H$	$B_H$	$R_H^2$	$A_E$	$B_E$	$R_E^2$
CyNMe <sub>2</sub>	-17.021	-7590	0.993	-22.426	-7736	0.986
BDMA	-23.465	-9414	0.989	-28.356	-9410	0.991
WO	-21.939	-9012	0.997	-28.085	-9409	0.998

## Supplementary Materials

Table S3. Comparison of Henry constant ( $E$ ), activity coefficient ( $\gamma$ ), dynamic viscosity ( $\eta$ ), and absorption capacity of SHSs with other solvents.

Absorbent	$E$ (atm) (25°C)	$\gamma$ (25°C)	$\eta$ (Pa·s) (20°C)	Absorption capacity (g/L) (25°C)	Concentrations $C_{g, \text{toluene}}$ (g/m <sup>3</sup> )
Washing oil (WO)	0.030(this study)	0.78(this study)	0.0041(this study)	14.6(this study)	2.7(this study)
N,N-dimethylbenzylamine (BDMA)(SHS)	0.036(this study)	1.09(this study)	0.0013(this study)	13.3(this study)	2.7(this study)
Di(2-ethylhexyl) adipate (DEHA)	0.02 <sup>3</sup>	0.52 <sup>3</sup>	0.0125 <sup>3</sup>	13.20 <sup>3</sup>	3.7 <sup>3</sup>
N,N-dimethylcyclohexylamine (CyNMe <sub>2</sub> )(SHS)	0.029(this study)	0.75(this study)	0.0011(this study)	12.3(this study)	2.7(this study)
Diisobutyl phthalate (DIBP)	0.034 <sup>3</sup>	0.88 <sup>3</sup>	0.0378 <sup>3</sup>	10.60 <sup>3</sup>	3.7 <sup>3</sup>
Diisooheptyl phthalate (DIHP)	0.028 <sup>3</sup>	0.73 <sup>3</sup>	0.055 <sup>3</sup>	9.06 <sup>3</sup>	3.7 <sup>3</sup>
Diisodecyl phthalate (DIDP)	0.025 <sup>3</sup>	0.65 <sup>3</sup>	0.1188 <sup>3</sup>	8.40 <sup>3</sup>	3.7 <sup>3</sup>
Polyethylene 400 (PEG 400)	0.040 <sup>3</sup>	1.05 <sup>3</sup>	0.1336 <sup>3</sup>	6.80 <sup>3</sup>	3.7 <sup>3</sup>
Silicon oil (PDMS)	0.056 <sup>3</sup>	1.46 <sup>3</sup>	0.0198 <sup>3</sup>	5.31 <sup>3</sup>	3.7 <sup>3</sup>
Polyethylene glycol 300 (PEG 300)	0.082 <sup>3</sup>	2.14 <sup>3</sup>	0.0755 <sup>3</sup>	4.22 <sup>3</sup>	3.7 <sup>3</sup>

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**Nomenclature**

$A$	cross-sectional area of the double-stirred reactor [ $\text{m}^2$ ]
$A_H, A_E, B_H, B_E$	regression coefficients [-]
$C_G$	concentration in gas phase [ $\text{g}/\text{m}^3$ ]
$C_L$	concentration of A in bulk liquid [ $\text{g}/\text{m}^3$ ]
$C_S$	concentration of saturated liquid of toluene and absorbent [ $\text{g}/\text{m}^3$ ]
$E$	Henry constant [atm]
$H$	Henry's constant [-]
$H_C$	Henry constant [ $\text{atm}\cdot\text{m}^3/\text{mol}$ ]
$K_L$	liquid-phase mass transfer coefficient [m/s]
$K_G$	gas-phase mass transfer coefficient [ $\text{mol}/(\text{s}\cdot\text{m}^2\cdot\text{atm})$ ]
$M_S$	gas molecular weight of toluene [ $\text{g}/\text{mol}$ ]
$N_A$	absorption rate [ $\text{mol}/(\text{m}^2\cdot\text{s})$ ]
$P$	total pressure gas phase [KPa]
$P_G$	partial pressure of toluene in the gas phase [KPa]
$P^{\text{sat}}$	saturation pressure of the toluene [KPa]
$Q_G$	gas flow rate [ $\text{m}^3/\text{s}$ ]
$R$	ideal gas constant = $8.314 \text{ [J}/(\text{mol}\cdot\text{K})$ ]
$T$	temperature [K]
$t$	time [s]
$V_G$	volume of the gas phase in reactor [L]
$V_L$	volume of the liquid absorbent [L]
Greek letters	
$\gamma$	activity coefficient [-]
$\eta$	dynamic viscosity [ $\text{Pa}\cdot\text{s}$ ]
$\rho_S$	density of soluble gases under the actual operating temperature [ $\text{kg}/\text{m}^3$ ]
Superscript	
0, t, $\infty$	time
*	equilibrium
Subscripts	
in	inlet of the gas stream
out	outlet of the gas stream

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**References**

- 1 Y. H. Kim and K. H. Kim, A simple method for the accurate determination of the Henry's law constant for highly sorptive, semivolatile organic compounds. *Anal. Bioanal. Chem.*, 2016, **408**, 775-784.
- 2 K. B. Lodge and D. Danso, The measurement of fugacity and the Henry's law constant for volatile organic compounds containing chromophores. *Fluid Phase Equilibria*, 2007, **253**, 74-79.
- 3 F. Heymes, P. Manno-Demoustier, F. Charbit, J. L. Fanlo and P. Moulin, A new efficient absorption liquid to treat exhaust air loaded with toluene. *Chem. Eng. J.*, 2006, **115**, 225-231.
- 4 J. A. Dean, *Lange's Chemistry Handbook, Version 15<sup>th</sup>* World Book Inc, 1999-10.
- 5 J. Wang, P. Lu, Z. Wang, C. Yang and Z. S. Mao, Numerical simulation of unsteady mass transfer by the level set method. *Chem. Eng. Sci.*, 2008, **63**, 3141-3151.
- 6 E. Dumont, G. Darracq, A. Couvert, C. Couriol, A. Amrane, D. Thomas, Y. Andrès and P. Le Cloirec, Volumetric mass transfer coefficients characterising VOC absorption in water/silicone oil mixtures. *Chem. Eng. J.*, 2013, **221**, 308-314.
- 7 E. Dumont, Y. Andrès and P. Le Cloirec, Mass transfer coefficients of styrene and oxygen into silicone oil emulsions in a bubble reactor. *Chem. Eng. Sci.*, 2006, **61**, 5612-5619.
- 8 R. M. Stephenson, Mutual solubilities: water + cyclic amines, water + alkanolamines, and water + polyamines. *J. Chem. Eng. Data*, 1993, **38**, 634-637.