

Table 1

Henry's law constants (HLC; Matm^{-1}) of the two diastereomers of the nonylphenol isomer 4(3',5'-dimethyl-3'-heptyl)-phenol (NP353(+), NP353(-)), tertiary octylphenol (*t*-OP), and γ -hexachlorocyclohexane (γ -HCH) in artificial seawater with 3.5% NaCl. The reported data are the mean of two different experiments

<i>T</i> (K)	HLC (NP353(+))	HLC (NP353(-))	HLC (<i>t</i> -OP)	HLC (γ -HCH)
278	2151 ± 753	2399 ± 840	2008 ± 703	2906 ± 1017
283	1474 ± 516	1652 ± 578	1277 ± 447	1629 ± 570
288	850 ± 298	966 ± 338	566 ± 198	1176 ± 412
293	593 ± 208	667 ± 233	574 ± 201	1166 ± 408
298	242 ± 85	279 ± 98	195 ± 68	533 ± 189

The air flow rate is at 0.41 min^{-1} .

Table 2

Comparison of experimental Henry's law constants (Matm^{-1}) and derived enthalpies of solvation (ΔH_{soln} , kJ mol^{-1}) for γ -hexachlorocyclohexane (γ -HCH) with previous work

<i>T</i> (K)	HLC (Matm^{-1})	<i>T</i> range (K)	ΔH_{soln} (kJ mol^{-1})	Method ^a	Solution ^b	Reference
293 ^c	876	278–298	−51.3	DES	SW	This work
296 ^c	708				SW	
298 ^c	615				SW	
293	638	278–293		DES	W	Feigenbrugel et al. (2004c)
296	526					
293	665	278–308	−61.4	BS DHS	W	Sahsuvar et al. (2003)
296	513					
293	563	283–313	−57.5	BS	W	Jantunen et al. (2000)
298	195	—	—	WWC	W	Altschuh et al. (1999)
293	390	273.6–318	−45.6	BS	W	Kucklick et al. (1991)
293	362	273.6–296	−51.8	BS	SW	Kucklick et al. (1991)
296	507	—	—	WWC	W	Fendinger and Glotfelty (1988)
293	625	—	—	$P_{\text{sat}}/S_{\text{W}}$	W	Atkins and Eggleton (1971)

^aBS=bubble stripping, DES=dynamic equilibrium system, DHS=dynamic head space, WWC=wetted wall column, VP/ S_{W} =calculated from the vapor pressure and water solubility.

^bSW: artificial seawater, W: pure deionized water.

^cCalculated from the Van't Hoff expression.

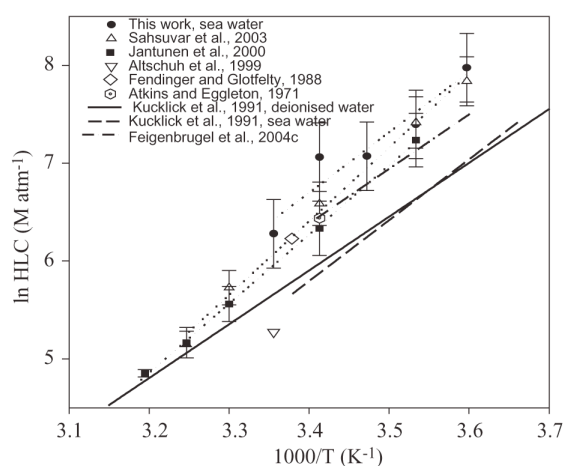


Fig. 4. Plot of HLC versus $1000/T$ for γ -HCH in artificial seawater (3.5% NaCl). Our determinations are compared to the experimental data of the literature. The errors on the HLC are given at 35% level.

(2003); Jantunen et al. (2000); Fendinger and Glotfelty (1988) and Atkins and Eggleton (1971), even if they are slightly higher. On the other hand, our value at room temperature is approximately two times higher than those found by Altschuh et al. (1999) and by Kucklick et al. (1991) as well in pure water as in salted water. As shown in Fig. 4, these authors have highlighted that the salting out effect is negligible for γ -HCH in the temperature range 273.6–296 K which is similar to the temperature range investigated in this work. The results obtained in this work for γ -HCH together with those determined by Feigenbrugel et al. (2004c) indicate that the dynamic equilibrium system could be applied as set-up for the determination of HLCs of semi-volatile organic compounds.

To our knowledge, the HLC values of NP353 diastereomers and *t*-OP presented in this paper are the first based on experimental data. As shown in Figs. 5a and b, a temperature dependence of the HLCs of

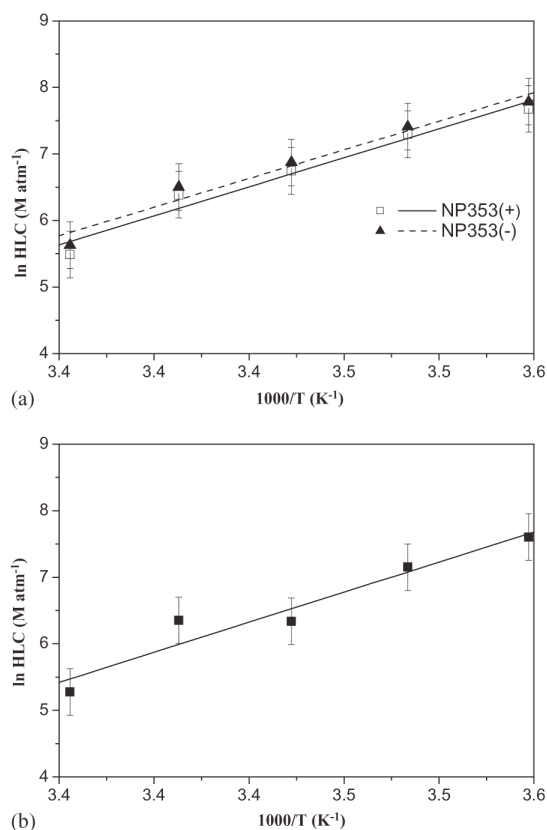


Fig. 5. (a) Plot of HLC versus $1000/T$ for NP353(+) and NP353(-) in artificial seawater (3.5% NaCl) within the temperature range 278–298 K. The errors on the HLC are given at 35% level. (b) Plot of HLC versus $1000/T$ for *t*-OP in artificial seawater (3.5% NaCl) within the temperature ranges 278–298 K. The errors on the HLC are given at 35% level.

NP353(+), NP353(-), as well as *t*-OP is clear over the temperature range from 278 to 298 K.

Therefore, comparison has been done with the previously estimated values for NP. The literature values were recalculated to equal values with the unit M atm^{-1} . The determined HLC values of NP353(+) and NP353(-) (483 and 551 M atm^{-1} , respectively) at 293 K are 37% and 43% of that estimated for 4(3',6'-dimethyl-3'-heptyl)-phenol (NP363, 1281 M atm^{-1}) (Lalah et al., 2001), factor of 5 higher than that estimated for NP (121 M atm^{-1}) (Lalah et al., 2001), and 20 times higher than that used for estimating the air/water exchange of NP (25–33 and 28 M atm^{-1}) in the lower Hudson River Estuary (Dachs et al., 1999; Van Ry et al., 2000). At 293 K, our experimental determinations of HLC for NP353(+), NP353(-) and *t*-OP are consistent with those found for phenolic compounds such as phenol and *p*-cresol in artificial seawater (in units of M atm^{-1}): *t*-OP, $\text{HLC} = 400$; phenol, $\text{HLC} = 715 \pm 430$; *p*-cresol, $\text{HLC} = 1369 \pm 630$ (Feigenbrugel et al., 2004a). This

observation seems to mean that the length of the alkyl chain does not influence so much the HLC value for para-alkyl phenol. The difference of HLCs between NP353 (in artificial seawater) and NP363 (in distilled water) can be a result of the chemical structure, the salting out effect and experimental errors. Since the chemical structure of NP353 and NP363 is very similar, its effect can be neglected in this case. The salting out effect and experimental errors should be the main causes for explaining the HLCs difference between NP353 (in artificial seawater) and NP363 (in distilled water). Lalah et al. (2001) determined the water solubility of NP363 as 53.69 mg l^{-1} , which is a factor of 10 higher than that of technical NP (5.43 mg l^{-1}) determined by Ahel and Giger (1993). It is indicated that the solubility of technical NP was determined by the isomer with the lowest value. However, the vapor pressure of 0.0193 Pa reported for NP363 was very close to the value of 0.0207 Pa for technical NP (Lalah et al., 2001). Consequently, the HLC values are very different when they are estimated with these solubilities and vapor pressures. Obviously, the estimated HLC value has a large influence on the estimation of air/water exchange.

This work presents the first measurements of HLC for NP353(+), NP353(-), and *t*-OP as a function of temperature. This function of temperature can be expressed with a Van't Hoff equation:

$$\text{HLC}(T) = \text{HLC}_{298} \exp\left(-\frac{\Delta H_{\text{solv}}}{R} \left(\frac{1}{T} - \frac{1}{T^0}\right)\right), \quad (4)$$

where HLC is expressed in units of M atm^{-1} , ΔH_{solv} is the solvation enthalpy (kJ mol^{-1}), T is the water temperature (K), T^0 is 298.15 K, and R is the gas constant ($8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$). Assuming that ΔH_{solv} is invariant within a temperature range between 283 and 298 K, the values of ΔH_{solv} were experimentally derived from the plots of $\ln \text{HLC}$ versus reciprocal temperature ($1000/T$) (Figs. 4, 5a and 5b) where the slope of the equation is $-\Delta H_{\text{solv}}/R$. The plots of $\ln \text{HLC}$ for NP353(+), NP353(-), *t*-OP and γ -HCH gave the following regression functions:

$$\ln \text{HLC}_{\text{NP353}(+)} = 8.73(\pm 0.95) \times (1000/T) - 23.61(\pm 3.30), \quad (5)$$

$$\ln \text{HLC}_{\text{NP353}(-)} = 8.61(\pm 0.91) \times (1000/T) - 23.08(\pm 3.18), \quad (6)$$

$$\ln \text{HLC}_{t\text{-OP}} = 9.03(\pm 1.40) \times (1000/T) - 24.83(\pm 4.86), \quad (7)$$

$$\ln \text{HLC}_{\gamma\text{-HCH}} = 6.17(\pm 1.08) \times (1000/T) - 14.28(\pm 3.75), \quad (8)$$

where errors correspond to 1σ level for both slope and intercept of regression functions.