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Henry's Law Constant measurements for phenol, *o*-, *m*-, and *p*-cresol as a function of temperature

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Abstract

In this work, a dynamic system based on the water/air equilibrium at the interface within the length of a microporous tube was used to experimentally determine the Henry's Law Constants (HLC) of phenol and cresols. The measurements were conducted over the range 278-298 K in both deionized water and 35 g L⁻¹ ~~o/o~~ solution of NaCl. At 293 K and in pure water, HLC were found to be equal to (in units of M atm⁻¹): phenol, HLC = (1005 ± 270); *o*-cresol, HLC = (690 ± 95); *m*-cresol, HLC = (1324 ± 172); *p*-cresol, HLC = (1742 ± 360). The obtained data were used to derive the following Arrhenius expressions: HLC = (4.1 ± 0.6) × 10⁻⁹ exp((7684 ± 874)/T), HLC = (1.5 ± 0.1) × 10⁻¹⁰ exp((8544 ± 512)/T), HLC = (5.5 ± 0.4) × 10⁻¹¹ exp((9028 ± 508)/T) and HLC = (3.3 ± 0.4) × 10⁻¹¹ exp((9258 ± 818)/T) for phenol, *o*-cresol, *m*-cresol and *p*-cresol, respectively. All of the values for HLC in 35 g L⁻¹ salt solution were 10 to 30% lower than their respective values in deionised water, depending on the compound and the temperature.

These data were then used to estimate the fractions of phenol or of cresols in atmospheric aqueous phase. In order to evaluate the impact of a cloud on the atmospheric chemistry of phenol and cresols, we compare also their atmospheric lifetimes under clear sky (τ_{gas}), and cloudy conditions ($\tau_{\text{multiphase}}$). The calculated multiphase lifetimes (in units of days) are

significantly lower than those in gas phase at a cumulus temperature of 283 K (in parentheses): phenol, 0.26 (0.45); *o*-cresol, 0.17 (0.24); *m*-cresol, 0.13 (0.22); *p*-cresol, 0.11 (0.23).

Keywords: Henry's Law Constant, temperature, salinity, phenol, cresols.

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Introduction

Phenols constitute a class of organic substances of particular environmental interest. Due to their widespread discharge into the environment and their toxicity to many living organisms, phenol and its methyl derivatives (cresols) are presently found on most priority lists of hazardous substances (Mackay, 1991). The major emission sources of phenol and cresol isomers into the troposphere are from automobile exhaust, wood burning and industrial sources. These compounds are released to the environment as fugitive emissions and effluents during coal tar and petroleum refining, metal refining and wood pulping as well as during manufacturing and use of many specialized chemicals (resins, disinfectants, insecticides, fungicides, etc.). Phenol and cresols can also be formed in the atmosphere by gas phase photo-oxidation of alkylbenzenes (Atkinson et al., 1989; Bjergbakke et al., 1996; Klotz et al., 1998; Smith et al., 1998; Berndt et al., 1999; Berndt and Böge, 2001; Volkammer et al., 2002).

Ambient levels of phenol and cresols have been measured in urban atmosphere (Leuenberger et al., 1985). Results of these studies revealed a mean concentration of 320, 71, and 130 ng m⁻³ respectively for phenol, *o*-cresol, and the sum of *m*-cresol and *p*-cresol. Emission data from road traffic indicated that phenol and cresols can reach up to 3% of the overall relative concentrations of the VOCs measured for different locations and engine types (Kurtenbach et al., 1999, 2000; Schmitz et al., 2000).

Phenol and cresol isomers are polar molecules. They have high solubilities in water and are expected to be efficiently scavenged from the gas phase by rain and fog. Values ranging between 0.2 and 9 µg L⁻¹ were measured for phenol at different locations and the concentration of cresols in the rainwater was estimated to be in the range 0.38 – 2 µg L⁻¹ (Kawamura and Kaplan, 1983; Leuenberger et al., 1985; Levsen et al., 1990; Richartz et al., 1990; Grosjean, 1991; Tremp et al., 1993; Allen and Allen, 1997; Lüttke and Levsen, 1997; Lüttke et al., 1997; Belloli et al., 1999; Lüttke et al., 1999; Morville et al., 2001). These concentration levels make them one of the most abundant organic compounds in rainwater.

An additional atmospheric sink for phenol and cresols is the removal by wet and dry depositions. Phenol, cresols and catechols (*o*-dihydroxybenzene) were the most common phenolic compounds identified in seawater sampled in coastal California with typical concentrations ranging from 2.5 to 370 ng L⁻¹ (Boyd, 1994). Biodegradation will generally be

the dominant loss mechanism when cresols are released into water with half-lives of several days in estuarine waters. The half-lives are shorter in fresh water and longer in marine water.

An additional source of phenol and cresols in seawater is the produced water issued from the oil production. Methylphenols are an important group of organic contaminants in produced water with concentrations between 0.6 and 10 mg L⁻¹ in the North Sea (Meier et al., 2003).

The partitioning of phenol and cresol isomers between the aqueous liquid phase and the air has to be investigated in order to shed some light in the understanding of the fate, the transport, and the removal of these pollutants in the troposphere. A key physical characteristic to describe the behaviour of a component in the environment (Rice et al., 1997) is given by the Henry's law constant (HLC) that represents the partitioning between the gas and aqueous phases.

In order to use HLCs in environmental modeling, temperature and salinity effects have also to be investigated. Although several database of HLCs exist for organic compounds (Staudinger and Roberts, 1996; Sander, 1999), a detailed inspection of the literature showed a substantial variation in the previously quoted values for phenol and cresols : the data results may differ by as much as a factor of 3.

In this work, direct HLC determinations have been therefore performed with a dynamic equilibrium system, between 278 and 298 K. The effect on HLCs of a 35 g L⁻¹ ~~0.000/00~~ solution of NaCl, used as a surrogate for an ocean seawater, was also studied over the same temperature range.

Experimental Section

Reagents

Aqueous solutions of phenol and cresols were made using Milli-Q Water (18 mΩ cm). Pure phenol (GC grade, ≥ 99.5%), *o*-cresol (GC grade, ≥ 99.5%), *m*-cresol (GC grade, ≥ 98.0%), and *p*-cresol (GC grade, ≥ 98.0%) were obtained from Fluka Chemical Company and used without further purification. Sodium chloride (≥ 99.8%) was obtained from Riedel-de Haën Chemical Company. The aqueous concentrations used for the experiments were in the range 40-300 mg L⁻¹ for phenol, 80-260 mg L⁻¹ for *o*-cresol, 50-180 mg L⁻¹ for *m*-cresol and 60-310 mg L⁻¹ for *p*-cresol, given that their water solubilities at 298 K are 77500 mg L⁻¹ (Frier, 1976), 25900, 22700, and 21520 mg L⁻¹ respectively (Yalkowsky and Dannenfelser, 1992). To investigate the effects of salinity on HLCs, a water solution of NaCl (35 g L⁻¹) was used.

Dynamic equilibrium system

The measurements of HLC were conducted using a dynamic equilibrium system shown in figure 1 and already used in previous work (Gautier et al., 2003; Katrib et al., 2003; Feigenbrugel et al., 2004).

Compressed air was passed through a microporous PTFE membrane tube (180 cm × 0.8 cm i.d., Sumitomo Corporation) at a highly controlled flow rate (0.1 - 0.5 L min⁻¹). The tube was immersed in about 0.6 L of the diluted aqueous solution containing the phenolic derivative. Phase equilibrium was achieved, for the dissolved compound, at the gas/water interface along the inner surface of the tube. The contact time between the two phases varied between 7 and 36 s depending on the flow rate. At the exit of the reactor, the gas phase which contains the studied compound at equilibrium concentration was then diluted using clean dry air (0.5 L min⁻¹). The compound present in the gas phase was trapped using two cartridges connected in series and filled with a XAD-2 Amberlite resin (Supelco). Before use, this resin was purified by Soxhlet extraction with *n*-hexane/dichloromethane (50/50) for 24 hours and then dried at room temperature (Sanusi et al., 1997; Sauret et al., 2000).

After sampling, the compound was extracted three times by passing 20 mL, 10 mL and 10 mL of methanol through the cartridge. The mass of methanol which stayed in the cartridge was measured after each extraction in order to know the dead volume in the cartridge. The

experiments revealed that for *o*-cresol more than 99% of the compound was trapped in the first cartridge while for phenol, *m*-cresol and *p*-cresol the same percentage ranged respectively between 70 and 100 %, 85 and 100%, and 94 and 100%. 20 minutes to 3 hours were required to concentrate the phenol and cresols in the cartridges. Note that the mass of phenolic derivatives trapped in the cartridges was always negligible compared to their total mass in the aqueous solution so that their aqueous concentration were effectively constant during the course of the experiment.

Analysis

Phenol and cresols were analysed with a GC-MS (CGP 6890N / MSD 5973N, Agilent Technologies) equipped by a 5%- phenylmethylsiloxane capillary column (HP-5MS, 30 m × 0.25 mm i.d. × 2.5 μm film thickness). For this, 1 μL of the solution obtained after extraction was injected in the splitless mode by an automatic sampler (7683, Agilent Technologies). Helium (UHP certified to > 99.9995% from Air Liquid) was used as carrier gas with a flow-rate of 1 mL min⁻¹ and the injector temperature was set at 250°C. For all the solutions, the column temperature was kept at 60°C for 4 min, was then brought to 220°C at a rate of 20°C min⁻¹, and was held at 220°C for 4 min.

In order to increase the sensitivity, phenol and cresols were analysed by applying single ion monitoring mode of the characteristic fragment ions at *m/z* 94, 107, and 108 amu. The gas-phase concentrations of the compounds were quantitatively determined from calibration curves made after each measurement. For this, known concentrations of the compounds were prepared in methanol and 1 μL of the obtained solution was then injected into the GC-MS in order to plot concentration curves versus GC-MS peak areas. The calibration curves were linear in the concentration range used in this study i.e. between 100-4000 μg L⁻¹ for phenol, 200-2000 μg L⁻¹ for *o*-cresol, 200-2000 μg L⁻¹ for *m*-cresol and 160-3300 μg L⁻¹ for *p*-cresol and the correlation coefficients were always greater than 0.99.

Results and discussion

Effect of temperature

The Arrhenius plots of the Henry's Law Constants (in M atm⁻¹) measured for the phenol and cresols in deionized water for a temperature range 278-298 K are presented in figure 2. The HLC values are also listed in tables 1 to 4 where the quoted uncertainties vary between 6 and 18 %. These values correspond to the sum of the uncertainties on the calibration curve

(ranging from 1 and 5 % for phenol and cresols), on the extraction process (determined to be of the order of 5 %), on the flow rates (less than 2.5 % in our conditions) and on the aqueous concentration of the phenol and cresols (less than 0.5 % for the phenol and cresols due to the relatively high aqueous concentrations in the experiments). Within these experimental errors, HLC values of the phenol and cresols are shown to be independent of their aqueous concentration over the ranges stated in the experimental section (see tables 1 to 4) and of the changes in air flow rate ($0.1 - 0.5 \text{ L min}^{-1}$) as shown in figure 3. This confirms that the equilibrium between solution and vapour is indeed achieved at the exit of reactor.

At 293 K, our recommended values of HLC calculated from the Arrhenius expression using a weighted analysis fit (see text below), are the following (in units of M atm^{-1}): $\text{HLC} = 1005 \pm 270$ (phenol); $\text{HLC} = 690 \pm 95$ (*o*-cresol); $\text{HLC} = 1324 \pm 172$ (*m*-cresol); $\text{HLC} = 1742 \pm 360$ (*p*-cresol). The quoted errors correspond to 2σ level and are determined from the standard deviations on both slope and intercept of Arrhenius expression. These data together with those reported in figure 2 show that the position of the methyl groups on the aromatic ring influences largely the HLC values of the cresols. For instance, the HLC of *p*-cresol is approximately 3 times higher than that obtained for *o*-cresol. Moreover, the temperature dependence are very similar for the four studied compounds meaning that their enthalpies of solvation are approximately the same. Based on these observations, it seems that the HLC values of other phenolic derivatives can be predicted at low temperature from a single determination at room temperature.

The following Arrhenius expressions can be derived from our data using a weighted analysis fit: $\text{HLC}(\text{phenol}) = (4.1 \pm 0.6) \times 10^{-9} \exp((7684 \pm 874)/T)$, $\text{HLC}(\textit{o}\text{-cresol}) = (1.5 \pm 0.1) \times 10^{-10} \exp((8544 \pm 512)/T)$, $\text{HLC}(\textit{m}\text{-cresol}) = (5.5 \pm 0.4) \times 10^{-11} \exp((9028 \pm 508)/T)$ and $\text{HLC}(\textit{p}\text{-cresol}) = (3.3 \pm 0.4) \times 10^{-11} \exp((9258 \pm 818)/T)$. The quoted errors are given at the 2σ level from the least-squares analysis. These Arrhenius expressions permit to highlight the strong temperature dependence of HLC values for phenol and cresols. For instance, at 283 K, HLC values are between 2.5 and 3 times higher than those measured at 293 K. This is in quite good agreement with the commonly cited “rule of thumb” (Staudinger and Roberts, 2001) that doubles HLC values per 10°C decrease in temperature.

In Tables 5-8, our values of HLC are compared with those given in the literature. Tables 5-8 also provide previously reported temperature dependence of HLC whenever available.

One note that few measurements, as a function of temperature, are available for *m*- and *p*-cresols and therefore the comparison is rather limited in these cases.

Concerning phenol, our value at 293 K is in quite good agreement with that determined by Tremp et al. (Tremp et al., 1993) using a Stripping Column Technique (see table 5) and with that of Sheikheldin et al., 2001. Our experimental data are also quite consistent with the average value of 9206 M atm^{-1} derived at 278 K from simultaneous measurements of the phenol concentration in gas and aqueous phases (Lüttke and Levsen, 1997). However, our values are between 2 and 5 times lower than the previous ones (Parsons et al., 1971; Abd-El-Bary et al., 1986; Sheikheldin et al., 2001; Harrison et al., 2002) as shown in figure 4. On the contrary, the value reported by Janini and Quaddora (1986) at 296 K is approximately 4 times lower than our own determination.

For *o*-cresol, our experimental determination of HLC at 293 K agrees well, within experimental errors, with the values reported by Tremp et al. (1993) and Sheikheldin et al. (2001), who determined HLC by using a stripping column technique and a single equilibrium static technique, respectively (see table 6). The agreement is also reasonable between our measurement at 298 K and the values reported by Parsons et al. (1972) and Altschuh et al. (1999) while our determination is 2.5 times lower than that determined by Harrison et al. (2002) and 2 times higher than that reported by Janini and Quaddora (1986).

For *m*-cresol, our determination at 293 K is in very good agreement with the previous one reported recently by Sheikheldin et al. (2001) as shown in table 7. Our value at 298 K is also consistent with that determined by Altschuh et al. (1999). However, our value at 293 K is about 2 times higher than the previously reported data by Janini and Quaddora (Janini and Quaddora, 1986) who estimated HLC from experimentally determined activity coefficients and reported vapor pressure data.

For *p*-cresol, our experimental determination of HLC at 293 K in deionized water is consistent with the lower limit estimated by Altschuh et al. and the values obtained by Parsons et al. (1972) and by Tremp et al. (1993) even if these latter are about 30% lower (see table 8). Our value of HLC obtained at 293 K is about more than 3 times higher than the previous one reported by Janini and Quaddora (1986).

For phenol and *o*-cresol, we report respectively the fifth and the fourth temperature dependence of HLC. To our knowledge, we report the second measurement of HLC as a function of temperature for *m*- and *p*-cresol. The previous temperature dependence

recommended by Janini and Quaddora (1986) is probably suspicious because their determination at 293 K are much lower than all the other reported values for the four studied compounds. For phenol and *o*-cresol, our temperature dependence $d(\ln\text{HLC})/d(1/T)$ agrees reasonably with the previous determinations (Parsons et al., 1971; Abd-El-Bary et al., 1986; Harrison et al., 2002).

Effect of salinity

The Arrhenius plots of the Henry's Law Constants, measured for the phenol and cresols in aqueous solutions of NaCl (35 g L⁻¹) simulating seawater for a temperature range 278-298 K, are presented in the figures 4-7. The following Arrhenius expressions can be derived from our data using a weighted analysis fit: $\text{HLC}_s = (1.2 \pm 0.4) \times 10^{-10} \exp((8619 \pm 2240)/T)$, $\text{HLC}_s = (3.4 \pm 0.6) \times 10^{-11} \exp((8905 \pm 1144)/T)$, $\text{HLC}_s = (1.3 \pm 0.4) \times 10^{-10} \exp((8710 \pm 1854)/T)$ and $\text{HLC}_s = (6.8 \pm 1.8) \times 10^{-12} \exp((9651 \pm 1920)/T)$ for phenol, *o*-cresol, *m*-cresol and *p*-cresol, respectively. All of the HLC values for the salt solution were 10 to 30 % lower than their respective values in deionized water (Tables 1-4), depending on the compound and the temperature. For instance, the determined HLC values at 293 K in salt solution obtained from Arrhenius expression given above, can be compared with those measured in pure water (in parentheses): phenol, HLC = 715 ± 430 (1005 ± 270); *o*-cresol, HLC = 532 ± 157 (692 ± 95); *m*-cresol, HLC = 1057 ± 527 (1324 ± 172); *p*-cresol, HLC = 1369 ± 630 (1742 ± 360) (units of M atm⁻¹). This phenomenon is related to the salting-out effect which impacts on the water solubility (reduction in solubility by a factor of 1.25 to 1.40 for the studied compounds).

The effect of salt on the solubility of gases in seawater has been studied theoretically for a variety of small gas molecules (Danckwerts, 1970). The presence of a salt in an aqueous solution changes the water structure in the vicinity of the solute. An empirical relation for the effect of ionic strength on a compound's HLC in an aqueous solution was given by (Setschenow, 1889):

$$\log (\text{HLC} / \text{HLC}_s) = h (\text{NaCl}) \quad (1)$$

where HLC and HLC_s are the Henry's law coefficient of the compound in pure water and in the salt solution, respectively, (NaCl) is the molarity of the NaCl solution and h is the Setschenow salting-out coefficient (L mol⁻¹).

Our results of HLC and HLC_s at 293 K (see tables 5-8) were used to estimate the following Setschenow coefficients: phenol, 0.25; *o*-cresol, 0.19; *m*-cresol, 0.16; *p*-cresol, 0.18. Values of the salting-out coefficients are similar to those of other phenolic derivatives (Xie et al., 1997). Our determinations are also close to those obtained from experiments for phenol by (Morrison, 1944) (0.22 for (NaCl) = 1 M at 298 K) and *m*-cresol by (Carter and Hardy, 1928) (0.17 for (NaCl) = 0.5 M at 298 K).

These data on salting-out are valuable for assessing the solubility of organic substances in seawater from corresponding data for freshwater. The magnitude of the salting-out effect is large enough to have a significant influence on mass transfer rate of phenolic compounds in natural processes. For example, at 293 K and for an ionic strength of 0.6 M, which is representative of seawater, the rate of absorption of the gases into the ocean from the troposphere would be slower than in freshwater of the same temperature.

Atmospheric implications

Once released in the atmosphere, Volatile Organic Compounds (VOCs) can react in the gas phase or can be taken up by water droplets where they can also be oxidized. For most of them, OH radical is the most efficient oxidizing species in both the gas phase (Atkinson, 2000) and the aqueous phase (Ervens et al., 2003). To evaluate the impact of a cloud on the atmospheric chemistry of phenol and cresols, we compare in this section their atmospheric lifetimes under clear sky (τ_{gas}), and cloudy conditions ($\tau_{\text{multiphase}}$).

The lifetime of A in the gas phase ($\tau_{\text{A,gas}}$) taking only into account the reaction of A with OH radicals, is defined as follow:

$$\tau_{\text{A,gas}} = \frac{[\text{A}]_{\text{g}}}{-d[\text{A}]_{\text{g}}/dt} = \frac{1}{k_{\text{OH,g}}[\text{OH}]_{\text{g}}} \quad (3)$$

where $k_{\text{OH,g}}$ is the rate constant of the gas phase reaction of OH radicals with A, $[\text{OH}]_{\text{g}}$ is the mean concentration of OH radicals and $[\text{A}]_{\text{g}}$ is the concentration of A in the troposphere.

If we consider now the cloudy atmosphere as a multiphase reactor where both the gas and aqueous phases coexist, then the multiphase lifetime of A can be defined as (Monod et al., 2003):

$$\tau_{A,multiphase} = \frac{[A]_g + [A]_{aq}}{-d[A]_g/dt - d[A]_{aq}/dt} \quad (4)$$

where $[A]_{aq}$ is the concentrations of A in the aqueous phase. At equilibrium, the fractions of A in the gas ($f_{A,g}$) and aqueous phases ($f_{A,aq}$) are the following:

$$f_{A,aq} = \frac{[A]_{aq}}{[A]_g + [A]_{aq}} = \frac{HLC R L_{wc} T}{1 + HLC R L_{wc} T} \quad (5)$$

$$f_{A,g} = \frac{[A]_g}{[A]_g + [A]_{aq}} = \frac{1}{1 + HLC R L_{wc} T} \quad (6)$$

where R the ideal gas constant (in L atm mol⁻¹ K⁻¹), L_{wc} the dimensionless liquid water content of the cloud (typically 4.2×10^{-7}).

Mass accommodation can limit the rate of gas uptake. The accommodation time-scale τ_{accom} can be estimated from the mass accommodation coefficient α as:

$$\tau_{accom} = \frac{1}{\frac{1}{4} \langle c \rangle A_c \alpha} \quad (7)$$

where $\langle c \rangle$ is the mean molecular velocity of the trace gas.

The mass accommodation coefficients α have been measured for the cresol isomers by Louis and coworkers (Leysens et al., 2004) and their values at 293K are respectively equal to 6.6×10^{-4} for *o*-cresol, 1.1×10^{-3} for *m*-cresol, and 2.9×10^{-3} for *p*-cresol. In addition, a value of 8.3×10^{-3} for phenol at 293 K has already been reported by Müller and Heal (Müller and Heal, 2002). From the values of α , the calculated accommodation time scale varies between 0.6 and 8.4 min. In regard to the tropospheric lifetimes of phenol or cresols in the gas phase (see table 9), mass accommodation is indeed a fast process. Therefore, the uptake of these compounds by atmospheric droplets will not be limited by mass transport.

Assuming that equilibrium is effectively rapidly reached, eq. (3) can be written as follows:

$$\tau_{A,multiphase} = \frac{1 + HLC R L_{wc} T}{(k_{OH,g}[OH]_g) + HLC R L_{wc} T \times (k_{OH,aq}[OH]_{aq})} \quad (8)$$

where $k_{\text{OH, aq}}$ is the rate constant of OH reaction with A in aqueous phase, $[\text{OH}]_{\text{aq}}$ is the mean concentration of OH radicals in the tropospheric aqueous phase.

The rate constants of OH reaction with phenol or cresols in both aqueous and gas phases have already been reported (Savel'eva et al., 1972; Feitelson and Hayon, 1973; Field et al., 1982; Semadeni et al., 1995), and are shown in table 9 together with the Henry's law constants determined in this work. By analogy with other cresols, the rate coefficient of OH reaction with *m*-cresol was estimated to $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. These data have then been used to estimate the atmospheric lifetimes of these organic compounds under clear sky (τ_{gas}), and cloudy conditions ($\tau_{\text{multiphase}}$), by using typical concentrations of OH radicals in the gas and in aqueous phases: $[\text{OH}]_{\text{g}} = 1 \times 10^6 \text{ cm}^{-3}$ and $[\text{OH}]_{\text{aq}} = 1 \times 10^{-13} \text{ M}$ (Monod et al., 2003). We assume here that the OH concentration in the gas phase is the same under clear sky and cloudy conditions although it is reduced as soon as clouds are formed, and the magnitude of the decrease strongly depends on the pH value of the droplet (Monod and Carlier, 1999).

At 298 K, the calculated aqueous fraction are the following: phenol, 6.7×10^{-3} ; *o*-cresol, 4.3×10^{-3} ; *m*-cresol, 8.1×10^{-3} ; *p*-cresol, 10.6×10^{-3} . At 298 K which is the temperature where most of experimental rate constants were measured, the atmospheric lifetimes of phenol and cresols are slightly reduced in the cloud as shown in table 9. However, the average temperature of tropospheric clouds is 283 K and therefore, the calculated aqueous fraction of phenol rises from 6.7×10^{-3} to 2.8×10^{-2} when the temperature decreases from 298 K to 283 K, temperature range where the HLC value of phenol increases from 658 to 2815 M atm^{-1} . Assuming that the rate constants of OH reactions with phenol or cresols in the gas and aqueous phases do not vary a lot between 283 and 298 K as it was already observed for many oxygenated VOCs, we can then estimate the multiphase lifetimes of these compounds at 283 K. These calculated lifetimes at 283 K (in units of days) are significantly lower than those at 298 K (in parentheses): phenol, 0.26 (0.38); *o*-cresol, 0.17 (0.22); *m*-cresol, 0.13 (0.19); *p*-cresol, 0.11 (0.18). Considering all the uncertainties associated with the above calculations, one can conclude that the oxidations of phenol and cresols in the gas and aqueous phases are of the same order of magnitude and can really compete. Mechanisms of OH-oxidation in aqueous phase are therefore needed to identify the products that can be deposited to ground by wet deposition and consequently to better estimate the environmental impact of phenol and cresols.

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Figure Captions

Figure 1 : Scheme of the dynamic equilibrium system used to determine Henry's law constants as a function of the temperature.

Figure 2 : Plot of \ln HLC versus $1000/T$ in deionized water for the four compounds studied: phenol, *o*-cresol, *m*-cresol, *p*-cresol, in the temperature range of 278-298 K. Our errors on HLC varied typically between 6 and 18 % and are determined as mentioned in the text.

Figure 3 : Plot of HLC versus the flow rate ranging between 0.1 and 0.5 L min⁻¹ for phenol, *o*-cresol, *m*-cresol, *p*-cresol at 293 K. Our errors on HLC varied typically between 6 and 11 % and are determined as mentioned in the text.

Figure 4 : Plot of \ln HLC versus $1000/T$ for phenol in the temperature range of 278-298 K in deionized and salt water. Our determinations are compared to the experimental data of the literature. Our errors on HLC varied typically between 7 and 9 % and are determined as mentioned in the text. Straight lines represent Arrhenius plots derived by Harrison *et al.* (long dash line), by Abd-El-Bary *et al.* (short dash line), or in this work for deionized water (solid line) and a 35 g L⁻¹ solution of NaCl (dash-dot line).

Figure 5 : Plot of \ln HLC versus $1000/T$ for *o*-cresol in the temperature range of 278-298 K in deionized and salt water. Our determinations are compared to the experimental data of the literature. Our errors on HLC varied typically between 6 and 12 % and are determined as mentioned in the text. Straight lines represent Arrhenius plots derived by Harrison *et al.* (long dash line), or in this work for deionized water (solid line) and a 35 g L⁻¹ solution of NaCl (dash-dot line).

Figure 6 : Plot of \ln HLC versus $1000/T$ for *m*-cresol in the temperature range of 278-298 K in deionized and salt water. Our determinations are compared to the experimental data of the literature. Our errors on HLC varied typically between 8 and 11 % and are determined as mentioned in the text. Solid and dash-dot lines represent Arrhenius plots derived in this work for deionized water and a 35 g L⁻¹ solution of NaCl, respectively.

Figure 7 : Plot of \ln HLC versus $1000/T$ for *p*-cresol in the temperature range of 278-298 K in deionized and salt water. Our determinations are compared to the experimental data of the

literature. Our errors on HLC varied typically between 7 and 18 % and are determined as mentioned in the text. Solid and dash-dot lines represent Arrhenius plots derived in this work for deionized water and a 35 g L⁻¹ ~~0/00~~ ~~0/00~~ solution of NaCl, respectively.

Table 1: Henry's Law Constants of phenol as a function of the temperature determined by using the dynamic equilibrium system.

T (K)	HLC (M atm ⁻¹)
278.15 ^f	4566 ± 355
278.15 ^h	3390 ± 252
278.20 ^f	3618 ± 292
278.25 ^{f,j}	3010 ± 240
283.05 ^e	2983 ± 245
283.15 ^{i,j}	2221 ± 187
283.15	3092 ± 282
283.25 ^g	2369 ± 179
283.25 ^{f,j}	2507 ± 196
288.15 ^h	1716 ± 139
288.15 ^{f,j}	1092 ± 87
288.25 ^g	1809 ± 139
293.15 ^{f,j}	869 ± 68
293.15 ^{f,j}	598 ± 49
293.15 ^e	927 ± 74
293.15 ^c	951 ± 70
293.15 ^h	1055 ± 85
293.25 ^b	946 ± 68
293.25 ^d	1121 ± 80
298.15	501 ± 40
298.15 ^h	737 ± 61

By default, the experiments were carried out in deionized water with a flow rate of 0.2 L min⁻¹ and with an aqueous concentration of phenol of ~ 100 mg L⁻¹ (~ 1.1×10⁻³ M). Experiments carried out with an air flow rate of: ^a 0.1 L min⁻¹; ^b 0.3 L min⁻¹; ^c 0.4 L min⁻¹; ^d 0.5 L min⁻¹. Experiments performed with an aqueous phenol concentration of: ^e ~ 50 mg L⁻¹ (~ 5.3×10⁻⁴ M); ^f ~ 150 mg L⁻¹ (~ 1.6×10⁻³ M); ^g ~ 200 mg L⁻¹ (~ 2.1×10⁻³ M).); ^h ~ 250 mg L⁻¹ (~ 2.7×10⁻³ M). ⁱ ~ 300 mg L⁻¹ (~ 3.2×10⁻³ M) ^j Salt water experiments (35 g L⁻¹ ~~o/oo~~).

Table 2: Henry's Law Constants of *o*-cresol as a function of the temperature determined by using the dynamic equilibrium system.

T (K)	HLC (M atm⁻¹)
278.25	2912 ± 280
278.25 ^h	2858 ± 240
278.35	3548 ± 290
283.15 ^{g, h}	1434 ± 107
283.15 ^e	1824 ± 179
283.25 ^e	1792 ± 212
288.10	1204 ± 103
288.15 ^{f, h}	891 ± 67
288.20	1185 ± 100
293.10 ^e	632 ± 58
293.15 ^{c, e}	623 ± 48
293.15 ^{d, g}	652 ± 42
293.15 ^a	739 ± 76
293.15 ^h	538 ± 45
293.25 ^b	659 ± 49
298.15 ^f	430 ± 33
298.25 ^e	429 ± 40

By default, the experiments were carried out in deionized water with a flow rate of 0.2 L min⁻¹ and with an aqueous concentration of *o*-cresol of ~ 150 mg L⁻¹ (~ 1.4×10⁻³ M). Experiments carried out with an air flow rate of: ^a 0.1 L min⁻¹; ^b 0.3 L min⁻¹; ^c 0.4 L min⁻¹; ^d 0.5 L min⁻¹. Experiments performed with an aqueous *o*-cresol concentration of: ^e ~ 100 mg L⁻¹ (~ 9.3×10⁻⁴ M); ^f ~ 200 mg L⁻¹ (~ 1.9×10⁻³ M).); ^g ~ 250 mg L⁻¹ (~ 2.3×10⁻³ M). ^h Salt water experiments (35 g L⁻¹ ~~o/o~~).

Table 3: Henry's Law Constants of *m*-cresol as a function of the temperature determined by using the dynamic equilibrium system.

T (K)	HLC (M atm ⁻¹)
278.15	6864 ± 568
278.25 ^h	5268 ± 519
283.15	3579 ± 307
283.25 ^{g, h}	2678 ± 241
283.25	3725 ± 336
283.25 ^{g, h}	3464 ± 280
288.15	2281 ± 183
288.25 ^f	2254 ± 203
293.15 ^h	1038 ± 94
293.15 ^{a, f}	1485 ± 169
293.15	1401 ± 112
293.15 ^f	1289 ± 120
293.15 ^e	1314 ± 109
293.15 ^{f, c}	1251 ± 108
293.15 ^h	1038 ± 94
293.25 ^{d, g}	1124 ± 84
293.25 ^{b, f}	1251 ± 98
298.15	776 ± 70
298.15 ^f	809 ± 69

By default, the experiments were carried out in deionized water with a flow rate of 0.2 L min⁻¹ and with an aqueous concentration of *m*-cresol of ~ 150 mg L⁻¹ (~ 1.6×10⁻³ M). Experiments carried out with an air flow rate of: ^a 0.125 L min⁻¹; ^b 0.3 L min⁻¹; ^c 0.4 L min⁻¹, ^d 0.5 L min⁻¹. Experiments performed with an aqueous *m*-cresol concentration of: ^e ~ 50 mg L⁻¹ (~ 5.3×10⁻⁴ M); ^f ~ 100 mg L⁻¹ (~ 1.1×10⁻³ M); ^g ~ 200 mg L⁻¹ (~ 2.1×10⁻³ M). ^h Salt water experiments (35 g L⁻¹^{o/o}).

Table 4: Henry's Law Constants of *p*-cresol as a function of the temperature determined by using the dynamic equilibrium system.

T (K)	HLC (M atm ⁻¹)
278.25 ^e	11090 ± 1998
278.25 ^{h,j}	8829 ± 825
278.35 ^g	11978 ± 1359
283.15 ^j	3873 ± 315
283.15 ^f	4710 ± 382
283.25 ^e	4895 ± 762
288.10 ^I	3138 ± 260
288.15 ^{h,j}	2449 ± 208
288.20 ^g	3297 ± 297
293.10 ^f	1819 ± 187
293.15 ^{g,j}	1400 ± 134
293.15 ^{c,I}	1615 ± 115
293.15 ^d	1671 ± 110
293.15 ^{a,I}	1801 ± 190
293.25 ^b	1682 ± 121
298.15	1074 ± 85
298.25 ^f	1158 ± 117

By default, the experiments were carried out in deionized water with a flow rate of 0.2 L min⁻¹ and with an aqueous concentration of *p*-cresol of ~ 300 mg L⁻¹ (~ 2.8×10⁻³ M). Experiments carried out with an air flow rate of: ^a 0.1 L min⁻¹; ^b 0.3 L min⁻¹; ^c 0.4 L min⁻¹; ^d 0.5 L min⁻¹. Experiments performed with an aqueous *p*-cresol concentration of: ^e ~ 50 mg L⁻¹ (~ 4.6×10⁻⁴ M); ^f ~ 100 mg L⁻¹ (~ 9.3×10⁻⁴ M); ^g ~ 150 mg L⁻¹ (~ 1.4×10⁻³ M); ^h ~ 200 mg L⁻¹ (~ 1.9×10⁻³ M); ⁱ ~ 250 mg L⁻¹ (~ 2.3×10⁻³ M). ^j Salt water experiments (35 g L⁻¹ ~~o/o~~).

Table 5: Comparison of experimental Henry's law constants for phenol with previous work.

T (K)	H (M atm ⁻¹)	$d \ln H / d(1/T)$ (K ⁻¹)	T range (K)	Technique	Reference
278	9206 ^g	-	-	FE ^a	(Lüttke and Levsen, 1997)
291.5	2709	6375	271-363	DES ^b	(Abd-El-Bary et al., 1986)
293	227	3600	298-308	γ^∞ ^c	(Janini and Quaddora, 1986)
293	1559	-	-	SCT ^d	(Trempe et al., 1993)
293	1858 ± 491	-	-	SEST ^e	(Sheikheldin et al., 2001)
293	3870	5850	284-302	SCT ^d	(Harrison et al., 2002)
298	>421 ^h	-	-	DES ^b	(Altschuh et al., 1999)
298	2900	6800	230-273	Pv ^f	(Parsons et al., 1971)
278	4138 ± 1113	7684 ± 874	278-298	DES ^b	This work, deionized water
291.5	1150 ± 309				
293	1005 ± 270				
298	647 ± 174				
293	715 ± 430	8619 ± 2240	278-293	DES ^b	This work, salt water

^a HLC derived from field experiments; ^b DES: Dynamic Equilibrium System; ^c γ^∞ : Infinite dilution activity in water; ^d SCT: Stripping Column Technique; ^e SEST: Single Equilibrium Static Technique; ^f Pv: Calculated value from the ratio between the vapour pressure, experimentally measured and the solubility; ^g average value; ^h Not used in validation analysis by the author.

Table 6: Comparison of experimental Henry's law constants for *o*-cresol with previous work.

<i>T</i> (K)	<i>H</i> (M atm ⁻¹)	$d \ln H / d(1/T)$ (K ⁻¹)	<i>T</i> range (K)	Technique	Reference
293	338	4600	298-308	γ^∞ ^a	(Janini and Quaddora, 1986)
293	500 ± 116	-	-	SEST ^b	(Sheikheldin et al., 2001)
293	724	-	-	SCT ^c	(Trempe et al., 1993)
293	1560	6680	281-302	SCT ^d	(Harrison et al., 2002)
298	830	-	-	Sol. ^a	(Parsons et al., 1972)
298	638	-	-	DES ^e	(Altschuh et al., 1999)
293	692 ± 95	8544 ± 512	278-298	DES ^e	This work, deionized water
298	424 ± 58				
293	532 ± 157	8905 ± 1144	278-293	DES ^e	This work, salt water

^a γ^∞ : Infinite dilution activity in water; ^b SEST: Single Equilibrium Static Technique; ^c SCT: Stripping Column Technique; ^d Sol.: Calculated value from the ratio between the vapour pressure and the solubility, experimentally measured; ^e DES: Dynamic Equilibrium System.

Table 7: Comparison of experimental Henry's law constants for *m*-cresol with previous work.

<i>T</i> (K)	H (M atm ⁻¹)	d ln <i>H</i> / d(1/ <i>T</i>) (K ⁻¹)	T range (K)	Technique	Reference
293	630	7700	298-308	γ^∞ ^a	(Janini and Quaddora, 1986)
293	1239 ± 199	-	-	SEST ^b	(Sheikheldin et al., 2001)
298	1168	-	-	DES ^c	(Altschuh et al., 1999)
293	1324 ± 172	9028 ± 508	278-298	DES ^c	This work, deionized water
298	798 ± 102				
293	1057 ± 527	8710 ± 1854	278-293	DES ^c	This work, salt water

^a γ^∞ : Infinite dilution activity in water; ^b SEST: Single Equilibrium Static Technique; ^c DES: Dynamic Equilibrium System.

Table 8: Comparison of experimental Henry's law constants for *p*-cresol with previous work.

<i>T</i> (K)	<i>H</i> (M atm ⁻¹)	<i>d ln H / d(1/T)</i> (K ⁻¹)	<i>T</i> range (K)	Technique	Reference
293	530	4600	298-308	γ^∞ ^a	(Janini and Quaddora, 1986)
293	1351	-	-	SCT ^b	(Trempe et al., 1993)
298	1300	-	-	Sol. ^c	(Parsons et al., 1972)
298	> 292 ^e	-	-	DES ^d	(Altschuh et al., 1999)
293	1742 ± 360	9258 ± 818	278-298	DES ^d	This work, deionized water
298	1025 ± 212				
293	1369 ± 630	9651 ± 1920	278-293	DES ^d	This work, salt water

^a γ^∞ : Infinite dilution activity in water; ^b SCT: Stripping Column Technique; ^c Sol.: Calculated value from the ratio between the vapour pressure and the solubility, experimentally measured;

^d DES: Dynamic Equilibrium System; ^e Not used in validation analysis by the author.

Table 9: Rate constants of OH reaction with phenol and cresols in gas and aqueous phases and the corresponding Henry's law constants. The atmospheric lifetimes were calculated

Compound	$k_{\text{OH,g}}^{298\text{ K}}$ ^{a,b}	$k_{\text{OH,aq}}^{298\text{ K}}$ ^c	H ^{298 K} (M atm ⁻¹)	τ_{gas} (days)	$\tau_{\text{multiphase}}$ (days)
Phenol	2.6×10^{-11}	6.7×10^9 ^d	627 g	0.45	0.38
<i>o</i>-cresol	4.9×10^{-11}	1.1×10^{10} ^e	433 g	0.24	0.22
<i>m</i>-cresol	5.2×10^{-11}	-	791 g	0.22	0.19
<i>p</i>-cresol	5.2×10^{-11}	1.2×10^{10} ^f	1101 g	0.23	0.18

^a in cm³ molecule⁻¹ s⁻¹; ^b values reported by Semadeni *et al.* (1995); ^c in M⁻¹ s⁻¹; ^d Field *et al.* (1982); ^e Savel'eva *et al.* (1972); ^f Feitelson and Hayon (1973); ^g our experimental values.

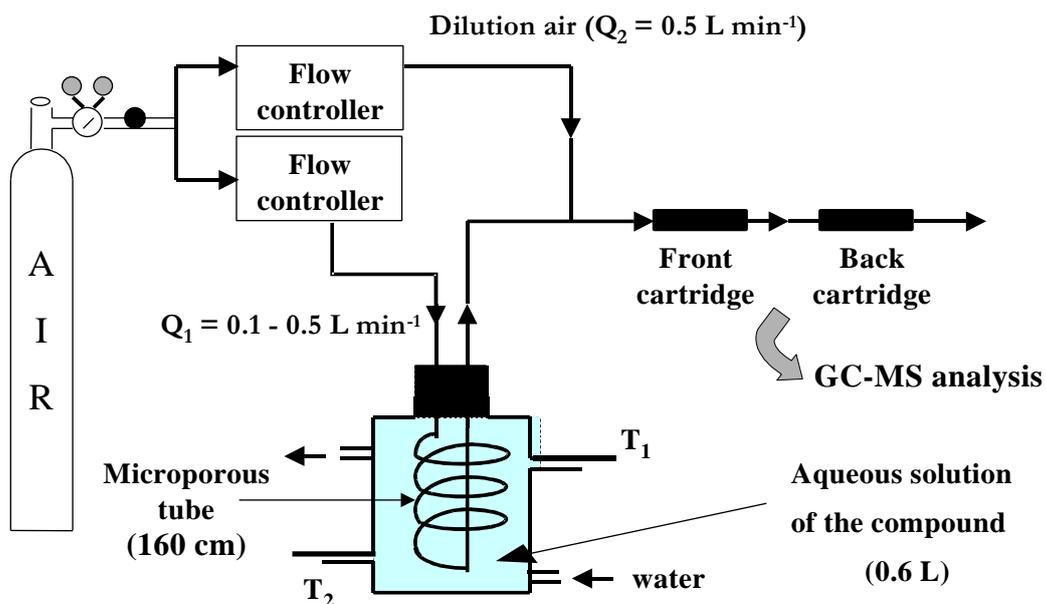


Figure 1

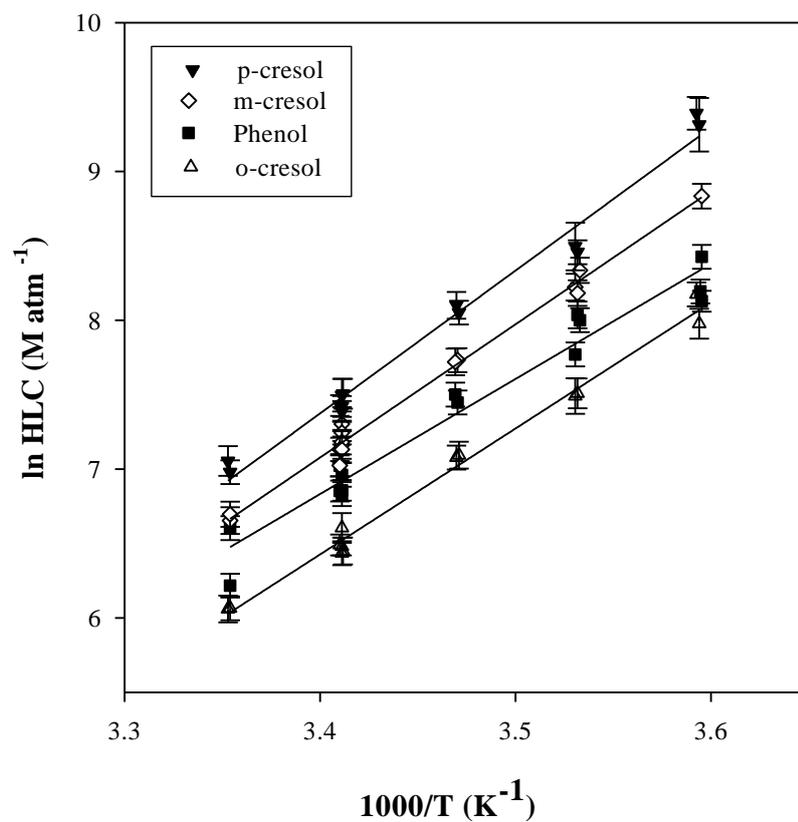


Figure 2

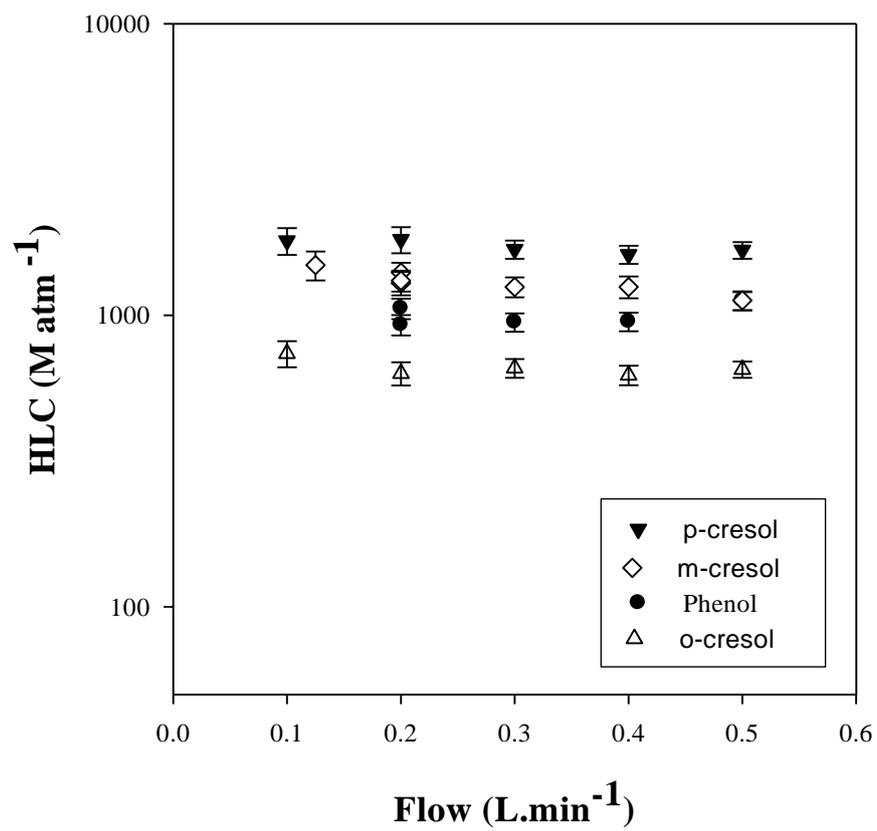


Figure 3

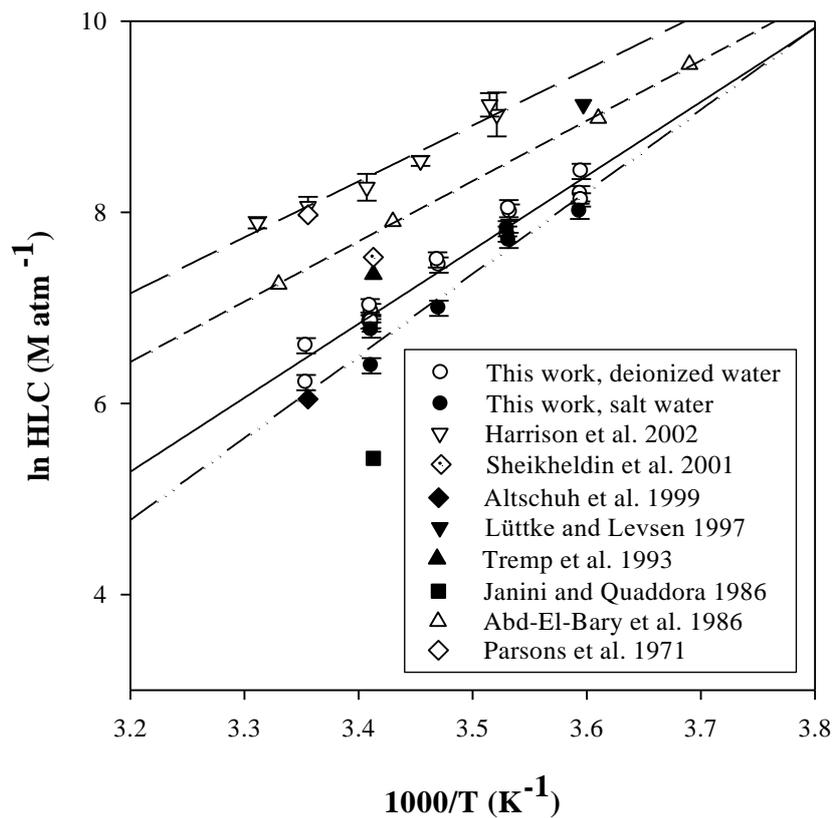


Figure 4

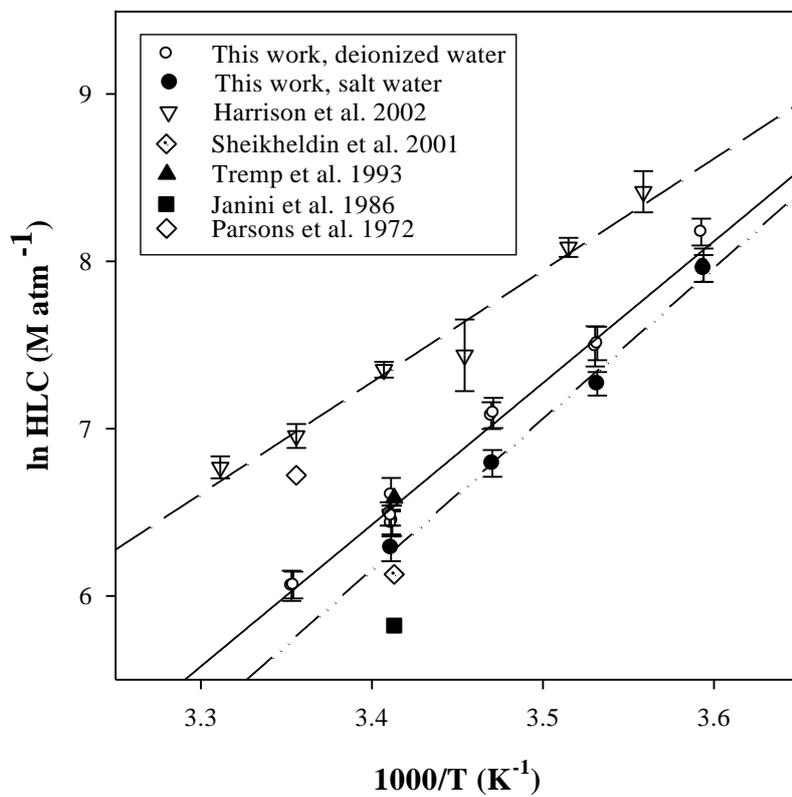


Figure 5

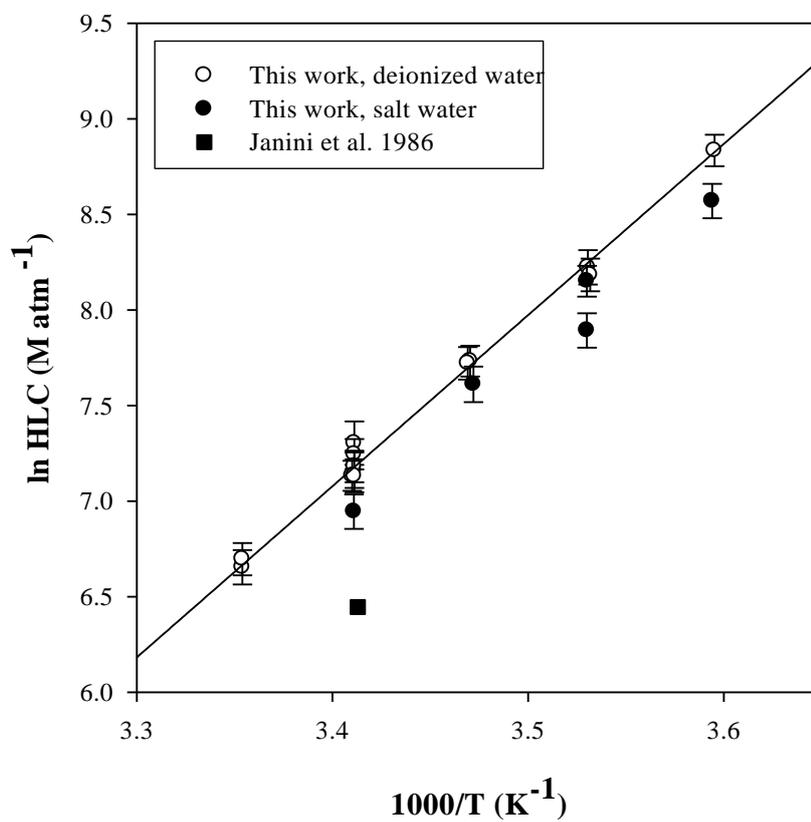


Figure 6

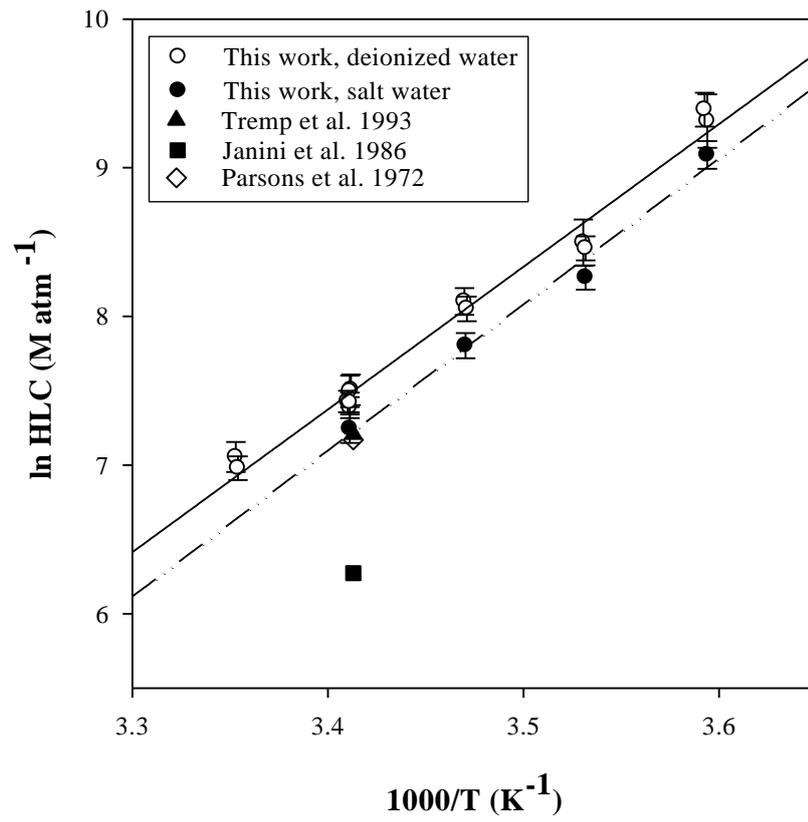


Figure 7