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# Experimentally determined Henry's Law coefficients of phenol, 2-methylphenol and 2-nitrophenol in the temperature range 281–302 K

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## Abstract

The Henry's Law coefficient is a key physical parameter in the partitioning, and hence environmental fate, of a chemical species between air and water. Despite the acknowledged polluting potential of phenol, 2-methylphenol (o-cresol) and 2-nitrophenol, there is extremely poor agreement in the literature of their Henry's law coefficients and, in particular, no apparent systematic measurement of the variation with temperature. Here, a temperature-controlled column-stripping method was employed to determine Henry's Law coefficients for these compounds over the temperature range 281–302 K. Coefficients were derived from regression fits to the observed rates of losses from the liquid phase as a function of column depth in order to explicitly take account of potential non-attainment of equilibrium between liquid and gas phases. Temperature dependent expressions summarising the Henry's Law coefficients of phenol, o-cresol and 2-nitrophenol over the stated temperature range are  $\ln H(\text{Matm}^{-1})=5850/T-11.6$ ,  $\ln H(\text{Matm}^{-1})=6680/T-15.4$  and  $\ln H(\text{Matm}^{-1})=6270/T-16.6$ , respectively (to within 15% of all measured values in this work). A thorough comparison with the previous literature-published values has been undertaken.

Keywords: Partitioning; Temperature dependence; Aqueous solubility

## 1. Introduction

The Henry's Law coefficient,  $H$ , quantifies the extent to which a chemical partitions between air and water. It is a key parameter for modelling the environmental fate of a particular chemical. Such models may be applied, for example, to estimate (1) partitioning of pollutants from the air into rain, cloud or fog-water; (2) volatilisation of pollutants into the atmosphere from contaminated soil or surface water; and (3) absorption of species into the alveoli of the lung.

One particular field of interest is the partitioning of volatile organic compounds (VOC) into the aqueous liquid phase of the atmosphere in order to help understand the fate and transportation of these pollutants in the atmosphere. The relative extent of partitioning and chemistry of VOC between air and liquid also affects the local oxidising capacity of the atmosphere. Phenols, methylphenols (cresols) and nitrated phenols constitute an abundant class of VOC in the air and precipitation waters. These compounds are used as raw materials in the chemical, pharmaceutical, disinfectants,

dyes and herbicides industries, and are also produced in gas-phase oxidation of benzene and toluene (Knispel et al., 1990). Mean phenol, mononitrophenol and cresol concentrations of 320, 24 and 100 ng m<sup>-3</sup>, respectively, have been measured in urban air (Leuenberger et al., 1985), and concentrations in the range 14–70 and 0.8–6.4 ng m<sup>-3</sup> have been measured for phenol and 2-nitrophenol in rural air (Lüttke et al., 1997). Levsen et al. (1990) reported mean rainwater concentrations for phenol, 2-nitrophenol and cresols of 5.6, 0.2 and 2.5 µg l<sup>-1</sup>, respectively. Rainwater concentrations of 4-nitrophenol in the range 0.1–14 µg l<sup>-1</sup> are reported by Schussler and Nitschke (2001). Lüttke et al. (1999) measured concentrations of the order of 5, 0.3 and 0.2 µg l<sup>-1</sup>, respectively, for phenol, 2-nitrophenol and cresols in cloudwater collected at rural upland sites in the UK and Germany, whilst fogwater concentrations in the range 1–90, and 1–10 µg l<sup>-1</sup> were measured by Richartz et al. (1990) for phenol and cresols, respectively. Many of these compounds (particularly nitrophenols) are known to be phytotoxic and, in surface waters, toxic to aquatic organisms. For example, EC (50) values for 2-, 3-, and 4-nitrophenol and 2,4-dinitrophenol on growth of two microalgae, range between 32 and 227 µg ml<sup>-1</sup> (O'Shaughnessy and Sultatos, 1995). The concentrations of nitrophenols have been shown to be higher in leaves of damaged trees than those of healthy specimens (Natangelo et al., 1999). The USEPA guideline for lifetime exposure to phenol in water is 3.5 mg l<sup>-1</sup> (USEPA, 1996), and the drinking-water-quality standard for 2-nitrophenol and 4-nitrophenol is 290 µg l<sup>-1</sup>.

Although major compilations of Henry's Law coefficients exist for many compounds (Staudinger and Roberts, 1996; Sander, 1999), a detailed search of the literature reveals a substantial variation in the previously quoted values for phenol and substituted phenols. In the majority of cases, recommended values presented in the literature are not experimentally determined, but calculated from vapour pressure and solubility data, or via other thermodynamic data, or estimated from a structure–activity relationship. Literature values are frequently merely copied from one source to another. Furthermore, Henry's Law coefficients are often only quoted at one temperature, or with no indication of the temperature. Since effective environmental modelling must take into account the effects of temperature variations, both temporal and spatial, the variation with the temperature of parameters such as H needs to be quantified. The explicit inclusion of the temperature dependence of Henry's Law coefficients is particularly important as values typically increase by the order of a factor of two for a 10 K decrease in temperature. This can have a substantial impact on, for example, the relative importance of gas and aqueous phase to chemical processing in the atmosphere.

Various experimental methods for determining Henry's Law coefficients have been proposed, but a commonly used method is that based on a column-stripping technique as described by Mackay et al. (1979). This methodology was chosen as being straightforward to apply for compounds with H values in the range of those under study here. The rate of decline in the concentration of a solution containing the species of interest is measured as it is purged with a flow of gas. As each bubble rises up through the solution in the column, the solute partitions into the gas phase according to its Henry's Law coefficient. Previously, we reported on a method to derive the true value of Henry's Law coefficient when equilibrium of solute with the gas phase is not quite achieved before the bubble reaches the top of the liquid column, using 2-nitrophenol as an example (Müller and Heal, 2001). Here, we report new

primary H data for phenol and 2-methylphenol (o-cresol), and a remeasurement of H for 2-nitrophenol, over a temperature range relevant to environmental processes.

## 2. Experimental

The column-stripping apparatus (height 51 cm, internal diameter 2.4 cm) is described by Müller and Heal (2001). Isothermal conditions were maintained by pumping a coolant from a temperature-controlled recirculation bath through a concentric jacket surrounding the column. A powerful magnetic stirrer ensured thorough mixing of the liquid in the bubble column, confirmed in separate experiments using a dye tracer.

The helium purge gas (BOC 99.99%) entered the base of the column through a sintered glass disk (Pyrex grade 2, 40–100  $\mu\text{m}$ ). To ensure that there was no loss of liquid volume in the column during purging, helium was humidified prior to entering the bubble column by passing it through deionised water (10 M $\Omega$  cm) and a heat exchange system at the same temperature as the bubble column. The volumetric flow rate of He was maintained at 1.00 standard litre per minute (SLPM) for phenol and o-cresol, and 0.30 SLPM for 2-nitrophenol, using mass flow controllers (Tylan FC 280 SA) previously calibrated with a bubble meter. All gas volumetric flow rates were corrected to the experimental temperature ( $T_{\text{exp}}$ ) and pressure, and for the volumetric flow of entrained water vapour. The saturated vapour pressure of water required for the latter correction was obtained from the equation

$$p_{\text{H}_2\text{O}}(\text{Torrr}) = \exp\left(21.1 - \frac{5340}{T_{\text{exp}}(\text{K})}\right).$$

During purging, the concentration of the solute was measured by dual-beam UV absorbance (Schimadzu UV 160A) at the wavelength of maximum absorption (270, 271 and 277 nm, for phenol, o-cresol and 2-nitrophenol, respectively). Initial concentrations of solutes used were  $1.0 \times 10^{-3}$ ,  $4 \times 10^{-4}$  and  $1.5 \times 10^{-4}$  mol dm $^{-3}$  for phenol, o-cresol and 2-nitrophenol, respectively.

## 3. Data analysis

Assuming a well-mixed aqueous phase, equating the rate of loss of solute from the aqueous phase to the rate of increase in the gas phase yields the following first-order decline in concentration,  $c$ , of solute with purging:

$$-\frac{dc}{dt} = \frac{c\phi}{HRTV} + ck_h, \quad (1)$$

where,  $\phi$  is the volumetric gas flow rate,  $V$  is the volume of solution and  $k_h$  is the hydrolysis rate coefficient for the solute. (Here,  $H$  is expressed as a liquid-to-gas ratio, with units). For the phenols under investigation here  $k_h$  is essentially zero. Therefore, the first-order rate coefficient for the decrease in liquid concentration is

$$k' = \frac{\phi}{HRTV} \quad (2)$$

Values for  $k'$  were obtained experimentally from the gradient of plots of  $(\ln c)$  against  $t$ .

In principle, repeating determinations of  $k'$  as a function of  $1/V$  yields  $H$  directly. However, this approach implicitly assumes that equilibrium is reached between the gas and the liquid phases. In some circumstances, the partial pressure,  $p$ , of solute in the gas bubble may not reach equilibrium with the concentration in the liquid at the point of exit of the gas bubble from the top of the liquid. This might occur when using higher flow rates, when operating at low temperatures or when studying the species with a high value of  $H$ . Under these circumstances, the partial pressure of solute in the gas phase after it has passed through the liquid can be written as  $p_{\text{non-equil}}$  ( $p_{\text{non-equil}} < p_{\text{equil}}$ ), with a corresponding, derived, non-equilibrium, Henry's Law coefficient,  $H_{\text{non-equil}}$ , given by

$$p_{\text{non-equil}} = \frac{c}{H_{\text{non-equil}}} \quad (3)$$

Mackay et al. (1979) have previously provided an expression for  $H_{\text{non-equil}}$ , in terms of the true  $H_{\text{equil}}$ , by integrating the equation that equates the rate of increase in solute gas partial pressure to the rate of solute mass transfer across the gas bubble-to-liquid interface

$$p_{\text{non-equil}} = \frac{c}{H_{\text{equil}}} \left( 1 - \exp \left( - \frac{k_{OL} A H_{\text{equil}} RT}{\phi} \right) \right) \quad (4)$$

in Eq. (4),  $A$ , is the total interfacial area between gas bubbles and liquid in the column and  $k_{OL}$  is a mass transfer coefficient whose value is not required. The pressure  $p_{\text{non-equil}}$  signifies the general case of the gas not being in equilibrium with the aqueous concentration  $c$  at the top of the column.

Müller and Heal (2001) extended the analysis in order to derive  $H_{\text{equil}}$  from the measurements of  $H_{\text{non-equil}}$  as a function of column depth,  $z$ . In brief, substitution of Eq. (3) into Eq. (4), and noting that total interfacial area is directly proportional to liquid depth (on the assumption that bubbles do not grow or coalesce), i.e.,  $A=kz$ , where  $kz$  is an unknown constant, yield

$$H_{\text{non-equil}} = \frac{H_{\text{equil}}}{1 - \exp(-(k_{\text{OL}}k_z H_{\text{equil}} RTz)/\phi)} \quad (5)$$

Substitution of Eq. (2), which links Hnon-equil to the experimentally measured first-order purge rate constant  $k'$ , and manipulation yield

$$k' = \frac{\beta}{zH_{\text{equil}}} (1 - \exp(-\alpha H_{\text{equil}} z)), \quad (6)$$

where  $\alpha=k_{\text{OL}}k_z RT/$  and  $\beta=/(sRT)$ , and  $s(=V/z)$  is the internal cross-sectional area of the bubble column. The parameter  $\beta$  consists of constants of known values whereas the parameter  $\alpha$  does not. The value of  $H_{\text{equil}}$  is obtained by fitting Eq. (6) to the set of  $k'$  values measured as a function of  $z$  (at a constant temperature and constant gas flow rate), using  $H_{\text{equil}}$  and  $\alpha$  as adjustable parameters.

#### 4. Results

Henry's Law coefficients for phenol, o-cresol and 2-nitrophenol were derived for temperatures between 281 and 302 K. An example plot of the  $\ln(\text{absorbance})$  versus time, the gradient of which yields  $k'$ , is shown in Fig. 1. The value of  $H_{\text{equil}}$  is obtained by fitting Eq. (6) to pairs of  $k'$  and  $z$  data measured for a given solute at a constant temperature and gas flow rate. An example for 2-nitrophenol at 298 K is shown in Fig. 2. As indicated in Fig. 2, each  $H_{\text{equil}}$  value was obtained from a fit to measurements of  $k'$  at 10 or more column depths. This general approach to determining  $H_{\text{equil}}$  allows for the possibility that equilibrium between gas and aqueous phases may not be established for a given column depth.

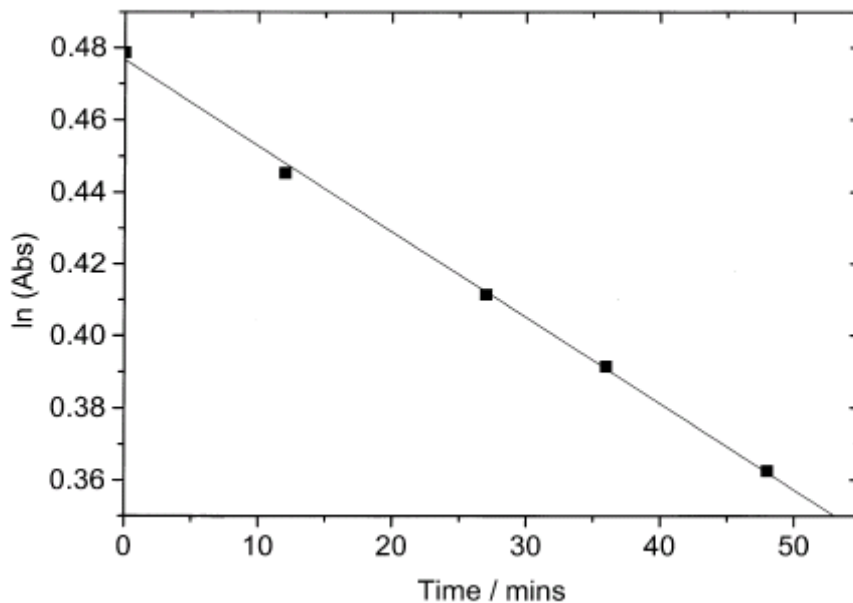


Fig. 1. The observed rate of decline in aqueous phase UV absorption of 2-nitrophenol at 298 K for a purge flow of 0.30 SLPM and column liquid depth  $z=15.7$  cm. The gradient yields a value of  $k'=2.39 \times 10^{-3} \text{ min}^{-1}$ .

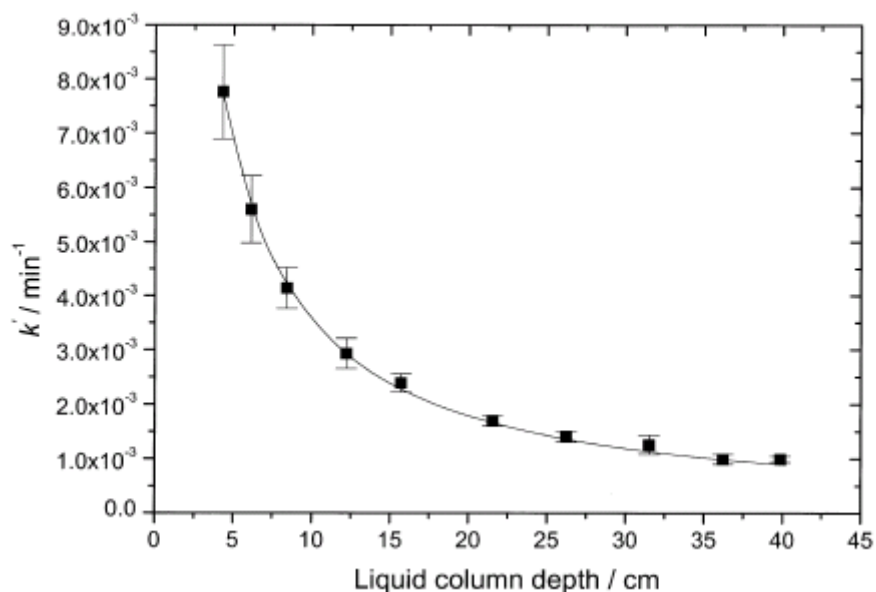


Fig. 2. Plot of  $k'$  and  $z$  (column depth) values for 2-nitrophenol at 298 K. The solid line is the least-squares fit of Eq. (6) to the data, with  $H_{\text{equil}}$  and  $\alpha$  as adjustable parameters, from which the value  $H_{\text{equil}}=86 \text{ M atm}^{-1}$  is obtained. Error bars are 95% confidence intervals of the statistical fits to obtain  $k'$  values.

Throughout the remainder of this paper, the symbol  $H$  is used to refer to the  $H_{\text{equil}}$  values derived using the full analysis as a function of column depth. The values of  $H$  measured in this work are presented in Table 1. Error ranges are the 95% confidence intervals of the statistical fits only. These values of  $H$  may be compared with those given in Table 2, Table 3 and Table 4, which contain together the results of an exhaustive search of the published literature for  $H$  values of phenol, o-cresol and 2-nitrophenol, respectively. Table 2, Table 3 and Table 4 also provide previously reported temperature dependence of  $H$ , wherever available.

Compound	Temperature (K)	$H_{\text{equil}}$ (M atm <sup>-1</sup> )
Phenol	284	8290 ± 1910
	284.5	9180 ± 1130
	289.5	5100 ± 270
	293.5	3870 ± 540
	298	3170 ± 316
	302	2670 ± 159
o-Cresol	281	4520 ± 558
	284.5	3240 ± 185
	289.5	1700 ± 365
	293.5	1560 ± 73
	298	1050 ± 75
	302	870 ± 57
2-Nitrophenol	281	280 ± 20
	284.5	256 ± 14
	289.5	167 ± 6
	293.5	109 ± 5
	298	86 ± 3
	302	65 ± 2

Table 1. Henry's Law coefficients obtained from fitting equation (6) to values of  $k'$  and  $z$ , for phenol, o-cresol and 2-nitrophenol as a function of temperature

The error ranges are 95% confidence intervals in the statistical fits only (calculated as the s.d. of the fitted value multiplied by the appropriate t-statistic).

$T$ (K)	$H$ (M atm <sup>-1</sup> )	$d \ln H /$ $d(1/T)$ (K)	Reference
278	9207 (expt.)		Lüttke and Levsen (1997)
	3858 (calc.)		
283	770		Werner et al. (1987) Dohnal and Fenclova (1995)
	4949		
293	227	3600	Janini and Qaddora (1986)
	1558		Tremp et al. (1993)
	1860		Sheikheldin et al. (2001)
	2188		Sawyer et al. (1994)
	2800	7300	USEPA (1982)
298	> 422		Altschuh et al. (1999)
	490		Hine and Weimar (1965)
	769		Reible (1999)
	1317		Yaws (1999)
	1948		Leuenberger et al. (1985)
	2203		Mabey et al. (1982)
	2455		Schwarzenbach et al. (1993)
	2528		Verschueren (1996)
	2900	6800	Parsons et al. (1971)
	3003		Howard and Meylan (1997)
3007		Staudinger and Roberts (1996)	
5447		Thibodeaux (1996)	

Table 2. Literature values for Henry's Law constant for phenol, and its temperature dependence, wherever available



$T(K)$	$H$ ( $M atm^{-1}$ )	$d \ln H /$ $d(1/T)/K$	Reference
281	650		Leuenberger et al. (1985)
293	338	4600	Janini and Qaddora (1986)
	459		Sheikheldin et al. (2001)
	800		Tremp et al. (1993)
	3400		Leuenberger et al. (1988)
298	640		Mabey et al. (1982)
	830	7300	Parsons et al. (1972)
Unspecified. Presumed 298	1007		Parker et al. (1994)

Table 3. Literature values for Henry's Law constant for o-cresol, and its temperature dependence, wherever available

$T(K)$	$H$ ( $M atm^{-1}$ )	$d \ln H /$ $d(1/T)/K$	Reference
278	1359 (expt.) 197 (calc.)		Lüttke and Levsen (1997)
281	288		Leuenberger et al. (1985)
293	74		Schwarzenbach et al. (1988)
	80	6200	Tremp et al. (1993)
	130	6290	Müller and Heal (2001)
	132		Mabey et al. (1982)
298	64		Leuenberger et al. (1985)
	70	4600	Staudinger and Roberts (1996)
	80	9600	Rippen et al. (1987)
	106		Howard and Meylan (1997)
	124		Benes and Dohnal (1999)
303	40		Tremp et al. (1993)

Table 4. Literature values for Henry's Law constant for 2-nitrophenol, and its temperature dependence, wherever available

It is clear that the Henry's Law coefficients show a strong temperature dependence over the ambient temperature range of 5–30°C. In thermodynamic terms, Henry's Law coefficient (as defined here) is the equilibrium coefficient corresponding to the hypothetical process of transferring a solute from the pure ideal gas state to a liquid state at infinite dilution in the solvent (water). Thus, using the relationship between an equilibrium coefficient and the standard Gibbs free energy for the forward reaction of the equilibrium,  $\Delta G_0$ , it follows that

$$\ln H = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}, \quad (7)$$

where  $\Delta H^0$  and  $\Delta S^0$  are the standard enthalpy and entropy changes, respectively, of Henry's Law partitioning from gas to liquid. Note that the above expression assumes that  $\Delta H^0$  and  $\Delta S^0$  depend only weakly on  $T$  over a relatively small temperature range.

Plots of  $\ln H$  versus  $1/T$  for the data obtained in this work are shown in Fig. 3, Fig. 4 and Fig. 5 for phenol, o-cresol and 2-nitrophenol, respectively. These figures also include values of  $H$  previously reported in the literature, the vast majority of which are calculated, rather than measured. The legends in Fig. 3, Fig. 4 and Fig. 5 indicate (to the best of our understanding) where the previous literature values are derived from some sort of experimental rather than calculated data.

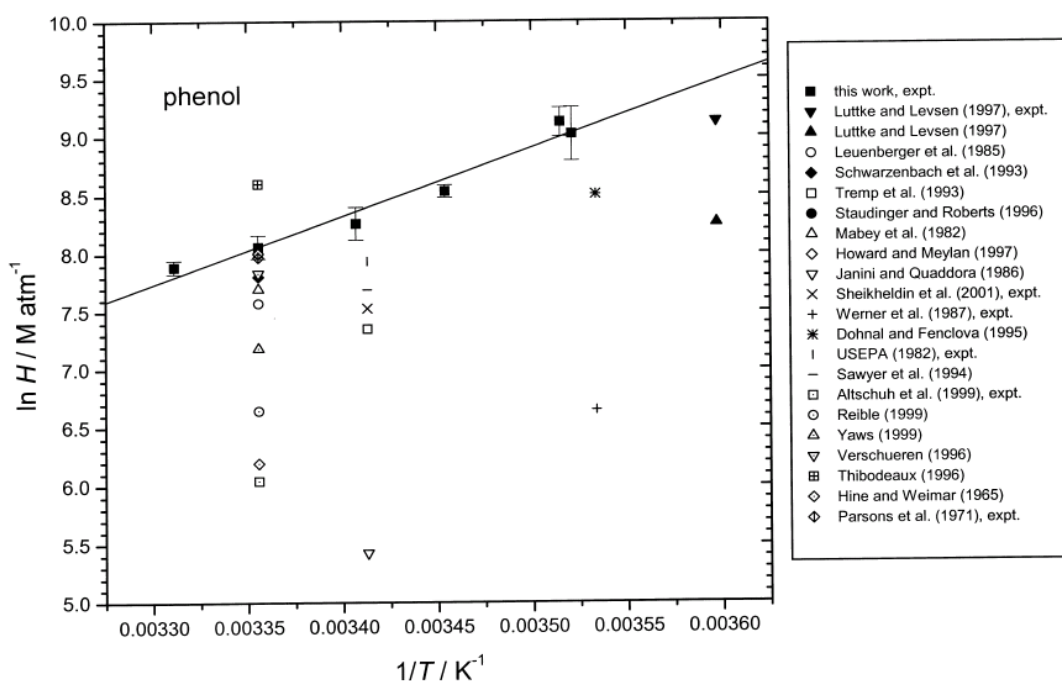


Fig. 3. Plot of  $\ln H_{\text{equil}}$  versus  $1/T$  for phenol. Error bars on data from this work are 95% confidence intervals derived from the statistical fits illustrated in Fig. 2 only. The legend indicates where (to the best of our understanding)  $H$  values were experimentally measured rather than calculated.

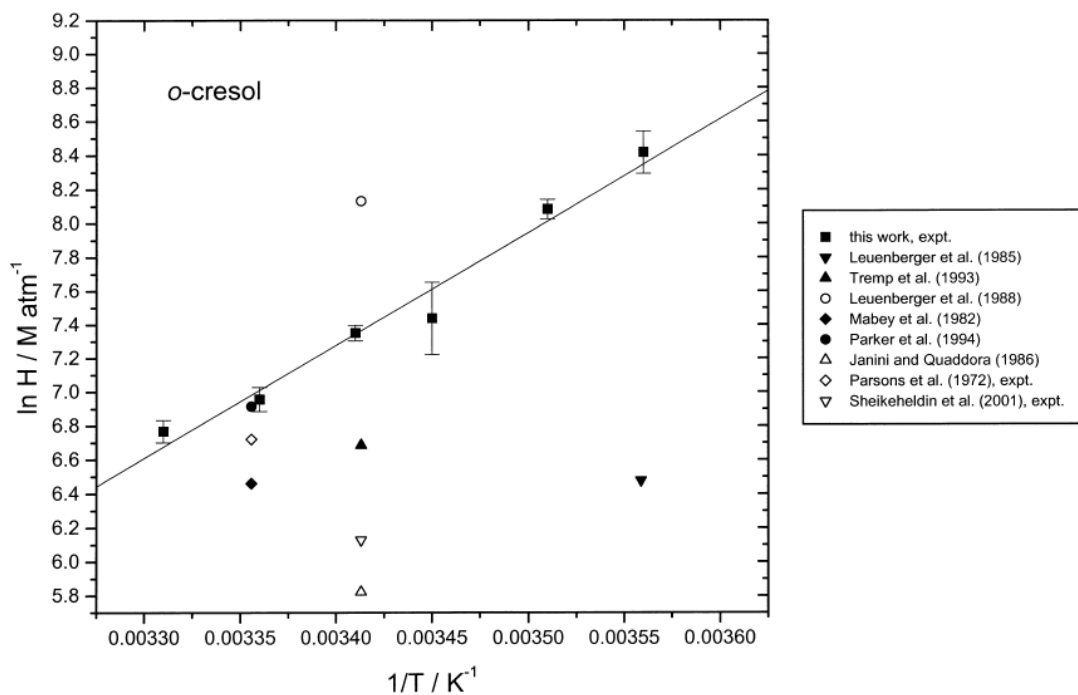


Fig. 4. Plot of  $\ln H_{\text{equil}}$  versus  $1/T$  for o-cresol. Remainder of the caption as for Fig. 3.

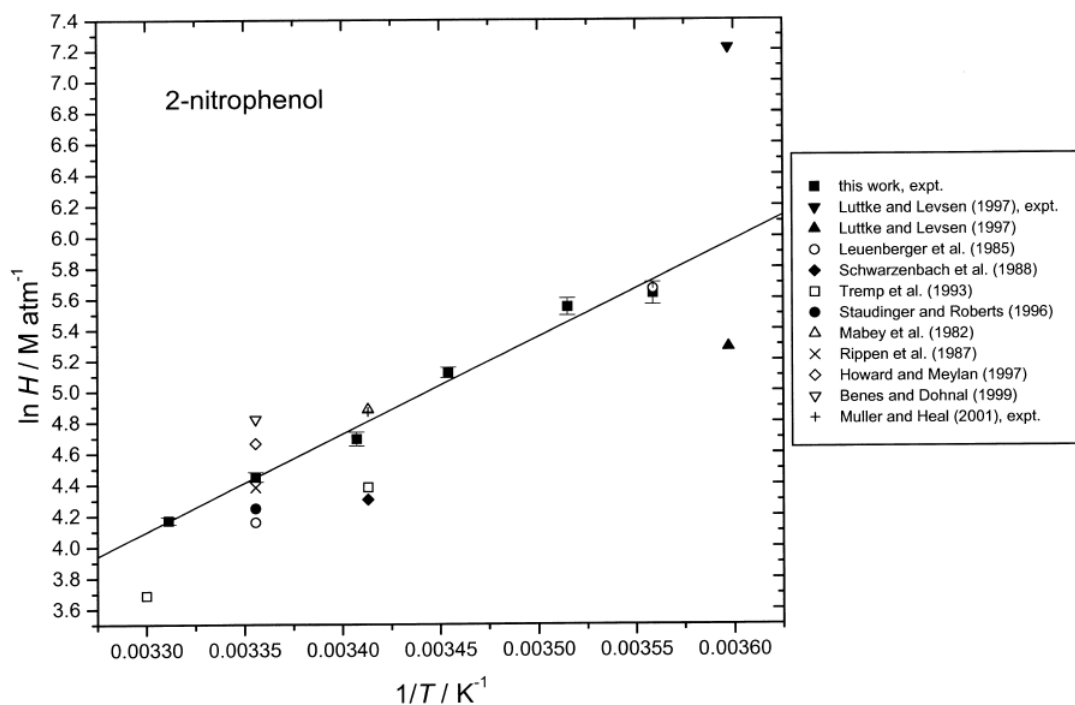


Fig. 5. Plot of  $\ln H_{\text{equil}}$  versus  $1/T$  for 2-nitrophenol. Remainder of the caption as for Fig. 3.

The solid line in Fig. 3, Fig. 4 and Fig. 5 is the linear fit of Eq. (7) to our data only, and provides the following temperature-dependent expressions for summarising Henry's Law coefficients over the temperature range covered in this work (within 15% of measured values at any individual temperature):

$$\text{phenol : } \ln H(\text{M atm}^{-1}) = \frac{5850}{T} - 11.6,$$

$$o\text{-cresol : } \ln H(\text{M atm}^{-1}) = \frac{6680}{T} - 15.4,$$

$$2\text{-nitrophenol : } \ln H(\text{M atm}^{-1}) = \frac{6270}{T} - 16.6.$$

The slope coefficient of these lines,  $d \ln H/d(1/T)$ , may be compared in Table 2, Table 3 and Table 4 with those few values reported previously for the temperature dependence in  $H$ . The gradient and intercept of each line in Fig. 3, Fig. 4 and Fig. 5 are equal to  $-\Delta H^0/R$  and  $\Delta S^0/R$ , respectively. The derived thermodynamic parameters are summarised in Table 5.

Compound	$\Delta H^0$ (kJ mol <sup>-1</sup> )	$\Delta S^0$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Phenol	$-48.6 \pm 13.0$	$-96.2 \pm 44.4$
<i>o</i> -Cresol	$-55.5 \pm 13.1$	$-128 \pm 45$
2-Nitrophenol	$-52.1 \pm 8.9$	$-138 \pm 31$

Table 5. Standard enthalpy and entropy changes for the Henry's Law solubility of phenol, *o*-cresol and 2-nitrophenol

Quoted error ranges are 95% confidence intervals from the linear fits to the measured data shown in Fig. 3, Fig. 4 and Fig. 5.

## 5. Discussion

Values of  $H$  below a few hundred  $\text{M atm}^{-1}$  determined using Eq. (2) or Eq. (6) are not significantly different, based on 95% confidence intervals of the statistical fits. For situations in which Henry's Law coefficients are higher, Eq. (2) is not uniquely defined (since it is a function of column depth) and  $H$  values determined using Eq. (2) are systematically smaller than those obtained from fitting Eq. (6) to  $k'$  values as a function of depth. The experimental method is limited to the determination of  $H$  values  $<104 \text{ M atm}^{-1}$  because the slow rate of partitioning from aqueous to gaseous phases at these higher solubilities requires purging on day, rather than, hour time-scales.

The overall uncertainty in the measured values may be larger than that quoted in Table 1 because of other sources of measurement error. Three fundamental assumptions in column stripping experiments, namely: (1) the liquid is completely mixed; (2) the system remains isothermal throughout; and (3) the liquid volume remains constant throughout the experiment, were validated as described in the

experimental section. The temperature-dependent expressions quoted above (and plotted in Fig. 3, Fig. 4 and Fig. 5) should encompass random variations in the above conditions. Systematic error in volumetric flow rate was eliminated by external calibration of the flow.

Despite the importance of the chemicals investigated, Fig. 3, Fig. 4 and Fig. 5 and Table 2, Table 3 and Table 4 show that there has been no previous consensus on their Henry's Law coefficients and, in particular, little previous systematic measurement of the dependence on temperature. In some instances, there are difficulties in determining the temperature at which the reported value applies. This is of particular concern given the obvious strong variation in H values even over a 20 K temperature range.

The H values reported previously for phenol have been extraordinarily variable, as is evident from Fig. 3 and Table 2. For example, at 298 K reported H values vary between  $>422 \text{ M atm}^{-1}$  (Altschuh et al., 1999) and  $5447 \text{ M atm}^{-1}$  (Thibodeaux, 1996). The linear fit to  $\ln H$  versus  $1/T$  data obtained from this work yields H values for phenol ranging from  $2450 \text{ M atm}^{-1}$  at 302 K to  $8370 \text{ M atm}^{-1}$  at 284 K ( $3180 \text{ M atm}^{-1}$  at 298 K). To our knowledge, our work represents one of the very few systematically measured temperature dependent H data for phenol. The  $d \ln H/d(1/T)$  gradient of the temperature dependence of our data is 5850 K. The data of Parsons et al. (1971) very closely match our results, both for absolute value of H and for the temperature dependence. The other two reported temperature dependence coefficients of 3600 (Janini and Qaddora, 1986) and 7300 K (USEPA, 1982) (Table 2) are somewhat different from our value. The data of Janini and Quaddora (1986) appear particularly suspect; they report absolute H values in excess of an order of magnitude lower than that obtained by the vast majority of other workers.

Previous Henry's Law data for o-cresol are considerably more sparse, and are again variable (Fig. 4 and Table 3). Measurements in this work are within the scatter of the data previously reported. Two temperature-dependence coefficients have been previously reported for o-cresol (Table 3). The  $d \ln H/d(1/T)$  coefficient of 7300 K reported by Parsons et al. (1972) is within 10% of our value of 6680 K. However, as for phenol, the data reported by Janini and Qaddora (1986) are quite significantly lower and cannot be recommended for serious comparison.

The most consistent previous data are for 2-nitrophenol (Fig. 5 and Table 4) although, even for this species, reported values of H vary by a factor of 2 at 298 and 293 K and almost by a factor of 7 at 278 K. Our results, for temperatures between 281 and 303 K, bisect the extremities of previously measured or estimated values. Our extrapolated value of  $H=390 \text{ M atm}^{-1}$  at 278 K indicates that the experimental value of  $1359 \text{ M atm}^{-1}$  reported by Lüttke and Levsen (1997) at this temperature is considerably high. The fit to our temperature-dependent data for 2-nitrophenol yields a  $d \ln H/d(1/T)$  coefficient of 6270 K. The three coefficients reported previously are 4600 (Staudinger and Roberts, 1996), 6200 (Trempe et al., 1993) and 9600 K (Rippen et al., 1987) (Table 4). The  $\Delta H^0$  and  $\Delta S^0$  values for gas-to-liquid equilibrium partitioning of 2-nitrophenol (Table 5) agree extremely well with the values of  $\Delta H^0=-52.3 \pm 8.1 \text{ kJ mol}^{-1}$  and  $\Delta S^0=-138 \pm 28 \text{ J mol}^{-1} \text{ K}^{-1}$  from the preliminary work by Müller and Heal (2001), using the same technique.

The effect of dissociation of the dissolved phenol has not been considered in the above analysis. Both phenol and o-cresol have an acid dissociation constant ( $pK_a$ )  $>10$  at 298 K, and are effectively not dissociated in pure water. However, 2-nitrophenol has a  $pK_a$  of 7.2, and is appreciably dissociated in pure water. In this experiment, where pure He was used as the purge gas, the aqueous concentrations used were ca.  $1.5 \times 10^{-4}$  M, which would be in equilibrium with gas-phase concentrations of  $1.7 \times 10^{-6}$  atm. At these concentrations, the solution would be slightly acidic (pH 5.5), but only a small fraction (ca. 2%) of the dissolved 2-nitrophenol would be dissociated. If the experiment had been conducted at lower concentrations, a much greater fraction of the dissolved compound would have been dissociated, with the effective Henry's Law constant (relative to 'totally dissolved 2-nitrophenol') increasing from 86 to 139  $M \text{ atm}^{-1}$  at infinite dilution, at 298 K. In the real atmosphere, in the presence of  $\text{CO}_2$  and possibly other acidic gases, the buffering of atmospheric water at a pH of 5.6 or less ensures that the effective Henry's Law constant (i.e. relative to 'totally dissolved 2-nitrophenol') is  $<89 M \text{ atm}^{-1}$  at 298 K, or well within the experimental uncertainty. However, in the presence of gaseous ammonia or alkaline dust, where cloud and rain pH could be  $>7$ , the effective Henry's Law coefficient will increase above that for the undissociated compound.

In terms of their fate in the atmosphere, compounds with Henry's law coefficients in the approximate range  $10^2$ – $10^4 M \text{ atm}^{-1}$  are very sensitive to the particular conditions of the condensed aqueous phase. For example, for a compound with  $H=10^2 M \text{ atm}^{-1}$ , the fraction partitioning into the aqueous phase (at equilibrium) rises from  $<0.1\%$  to 2% as the liquid volume fraction increases from  $10^{-7}$  to  $10^{-5}$ , whereas for a compound with  $H=10^4 M \text{ atm}^{-1}$ , the fraction partitioning into the aqueous phase rises from 2% to 70% for the same change in liquid volume fraction. These figures illustrate the importance that the changes in ambient temperature (through its effect on  $H$ ) have on the partitioning. However, compounds like phenol, o-cresol and 2-nitrophenol are reactive species, so their atmospheric lifetime is not determined solely by equilibrium partitioning but by the relative kinetic rates of gas phase production and loss, rates of gas/liquid interfacial transfer, and rates of reaction within the aqueous phase. These coupled processes must be modelled in order to meaningfully compare lifetimes of different removal processes in the atmosphere wherein Henry's law coefficient is an important parameter in these models.

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