Air–Water Partitioning and Aqueous Solubility of Phenols[†]

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Relative volatilities from highly dilute aqueous solutions were measured for phenol, 2-methylphenol, 3-methylphenol, 4-methylphenol, 2,3-dimethylphenol, 2,4-dimethylphenol, 2,5-dimethylphenol, 2,6-dimethylphenol, 3,4-dimethylphenol, and 3,5-dimethylphenol at three temperatures covering the temperature range 75–100 °C with a vapor–liquid equilibrium circulation still. Because of the high dilution of solutions involved, the limiting relative volatility could be determined simply as a ratio of UV absorbances of the equilibrium vapor-phase and liquid-phase samples. In addition, the aqueous solubilities of 2,3-dimethylphenol, 2,5-dimethylphenol, 2,6-dimethylphenol, 3,4-dimethylphenol, and 3,5-dimethylphenol were measured at 20 °C by a conventional batch contacting technique with analysis by UV spectroscopy. The vapor–liquid equilibrium data and solubilities measured in this work and some additional data from the literature were used to obtain limiting activity coefficients γ_1^∞, Henry's law constants H, and air–water partition coefficients K_{aw} covering a range of temperatures from the ambient to the normal boiling point of water. For each phenol, the temperature dependence of γ_1^∞, H, and K_{aw} was used to estimate the limiting partial molar excess enthalpies and enthalpies of hydration. The values of γ_1^∞, H, and K_{aw} for isomeric cresols and xylenols were found to be well correlated with their normal boiling temperatures.

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, its methyl derivates (cresols), and its dimethyl derivates (xylenols) are presently found on most priority pollutants lists *(1)*. 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, pesticides, insecticides, fungicides etc.). Phenols are also emitted to the atmosphere in gasoline and diesel engine exhausts *(2)*.

Air–water partitioning and aqueous solubility of these priority contaminants are the key physicochemical properties needed to estimate their environmental fate and control them as industrial waste water pollutants. An increasing experimental effort has been observed in this direction, recent examples being new measurements of aqueous solubilities of closely related phenolic derivates, chlorophenols and chloroguaiacols, by Mackay et al. *(3, 4)*. However, there is only fragmentary literature for cresols and practically none for xylenols. In addition, some reported data are quite inaccurate or in error, having been obtained by estimation or by unreliable extrapolations from measurements on concentrated solutions.

Relevant information on air–water partitioning of dilute solutions of phenol or *o*-cresol has been reported by Abd-El-Bary *(5)* and Hakuta *(6)*. The relatively high aqueous solubilities of phenol are known quite accurately *(7)* but are beyond the scope of this work, which is focused on highly dilute solutions. A limited number of data on aqueous solubilities of cresols and xylenols were presented by several authors, the most notable being that of Sidgwick et al. in 1915 *(8)*.

The absence of a systematic investigation of air–water partitioning of phenols promoted us to undertake such a study. The objective was to determine air–water partitioning of 10 phenols (phenol, 3 cresols, 6 xylenols) over a broader temperature range and to report aqueous solubilities for those phenols for which data are not available. For this purpose, we measured vapor–liquid equilibria in highly dilute solutions of the 10 phenols in the range 75–100 °C and the aqueous solubilities of 5 solid xylenols at 20 °C. This information supplemented with dilute-solution and pure-component data from the literature enabled us to determine the temperature dependence of limiting activity coefficients, Henry's law constants, or air–water partition coefficients of phenols over the range of temperatures from the ambient to the normal boiling point of water.

Experimental Section

Materials. Phenol and 2,6-xylenol of 99% purity were obtained from Litvínov Chemical Works (Czech Republic). Phenol was fractionally distilled under reduced pressure, and 2,6-xylenol was recrystallized. Samples of the highest commercial purity were purchased for all other phenols and were used without further purification. All three cresols (≥99%) and 3,5-xylenol (99+%) were obtained from Aldrich Chemical Co.; 2,3-xylenol (pure grade, >99%), 2,5-xylenol (pure grade, >98%), and 2,4-xylenol (>97%, major impurity being 2,5-xylenol) were obtained from Fluka; and 3,4-xylenol (pure grade, >98%) was from Loba Chemie (Wien, Austria). Doubly distilled water was used for all measurements.

Vapor–Liquid Equilibria (VLE). Vapor–liquid partitioning in highly dilute aqueous solutions of phenols was measured using a modified Dvořák–Boublík recirculation still described in detail previously *(9)*. The still is connected to a two-stage, on–off controlled manostating system in which a Texas Instruments quartz pressure gauge (Model 145) served as the measuring device as well as the sensor for the pressure control. The pressure of the system was

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Table 1. Maximum Absorbance Wavelengths λ and Dissociation Constants pK_a of Phenols in Water at 25 °C

compound	λ/nm[a]	pK_a[b]	compound	λ/nm[a]	pK_a[b]
phenol	269	10.02	2,4-xylenol	277	10.60
o-cresol	270	10.32	2,5-xylenol	274	10.41
m-cresol	272	10.09	2,6-xylenol	269	10.63
p-cresol	278	10.27	3,4-xylenol	277	10.36
2,3-xylenol	272	10.54	3,5-xylenol	279	10.19

[a] This work. [b] Reference 10.

maintained to a few pascals and determined with an absolute accuracy better than ∓10 Pa. Since the aqueous solutions were highly dilute ($x_1 < 10^{-5}$), their boiling temperature was practically indistinguishable from that of pure water at the given pressure, and hence no temperature measurement was needed. Phenol mole fractions as low as $x_1 < 10^{-5}$ not only fully guarantee the condition of infinite dilution but suppress the foaming of phenolic solutions which can cause entrainment of liquid into the vapor. Although less than 3 h is generally sufficient to establish steady state conditions in the still, due to the poor boiling characteristics of water, boiling was continued for 4–5 h.

Since there is a strong absorption of UV light exhibited by aromatic compounds, UV spectroscopy was used to analyze the equilibrium phases, specifically with a Carl Zeiss Specord spectrophotometer, Model MT 40. The absorbances were measured at the determined absorption maxima for all of the phenols in the range 269–279 nm as listed in Table 1. The measurement of absorbances was carried out in the differential mode against pure water in cells of 10 mm optical length. While the equilibrium liquid phase samples were used directly for the measurements, most samples of the vapor-phase condensate were measured after appropriate dilution to attain comparable responses and hence better precision. In the limit of high dilution, the ratio of the vapor y_1 and the liquid x_1 equilibrium mole fractions gives the limiting separation factor, i.e. the limiting relative volatility

$$\alpha_{12}^{\infty} = \lim_{x_1 \to 0}(y_1 x_2 / x_1 y_2) = \lim_{x_1 \to 0}(y_1 / x_1) \qquad (1)$$

component 2 being water. Since proportionality relationships were proved to exist between the absorbances and concentrations of the highly dilute solutions studied, there was no need to calibrate the analytical response and the limiting relative volatility α_{12}^{∞} was obtained directly as a ratio of absorbances of the equilibrium vapor- and liquid-phase samples.

All determinations were done at least in triplicate, the individual results agreeing typically within 3%.

Table 2. Experimental Vapor–Liquid Equilibrium Data for Highly Dilute Aqueous Solutions of Phenols: Limiting Relative Volatilities α_{12}^{∞}, Henry's Law Constants *H*, Air–Water Partition Coefficients K_{aw}, and Limiting Activity Coefficients γ_1^{∞}

compound	t/°C	α_{12}^{∞}	H/kPa	$K_{aw}\cdot 10^6$	γ_1^{∞}	ref
phenol	98.5	1.84	177	1075	34.5	[a]
	88.7	1.76	117	729	36.7	[a]
	75.9	1.68	67.1	429	40.9	[a]
	100.0	1.85	188	1140	34.1	6
	80.3	1.74	83.5	528	40.1	6
	27.0	1.12	3.99	28.9	62.5	5
	18.3	0.985	2.07	15.4	66.9	5
	4.0	0.865	0.704	5.50	84.9	5
o-cresol	98.5	4.79	460	2800	115	[a]
	88.7	4.69	313	1940	125	[a]
	75.9	4.52	181	1155	141	[a]
	100.0	4.74	480	2910	112	6
m-cresol	98.5	2.57	246	1500	103	[a]
	88.7	2.40	160	994	110	[a]
	75.9	2.27	90.8	580	128	[a]
p-cresol	98.5	2.65	254	1545	110	[a]
	88.7	2.52	168	1045	120	[a]
	75.9	2.34	93.6	598	138	[a]
	100.0	2.63	267	1620	107	11
2,3-xylenol	98.5	4.79	460	2800	298	[a]
	88.7	4.54	303	1880	323	[a]
	75.9	4.00	160	1020	344	[a]
2,4-xylenol	98.5	6.34	609	3705	332	[a]
	88.7	6.01	401	2490	364	[a]
	75.9	5.85	234	1495	438	[a]
2,5-xylenol	98.5	6.21	596	3625	316	[a]
	88.7	6.00	400	2485	347	[a]
	75.9	5.87	235	1500	407	[a]
2,6-xylenol	98.5	14.0	1340	8170	419	[a]
	88.7	14.3	953	5920	472	[a]
	75.9	13.9	556	3550	529	[a]
3,4-xylenol	98.5	2.56	246	1495	285	[a]
	88.7	2.33	155	965	311	[a]
	75.9	1.91	76.4	488	333	[a]
3,5-xylenol	98.5	3.39	325	1980	311	[a]
	88.7	2.97	198	1230	327	[a]
	75.9	2.63	105	672	377	[a]

[a] This work.

Solid Solubilities (SLE). Aqueous solubilities of solid xylenols were measured by a conventional batch contacting technique. Excess amounts of xylenols were added to jacketed 50 cm^3 glass equilibrium cells containing double-distilled water and thermostated to 20 ∓ 0.01 °C by a Medingen electronic circulating thermostat U6CP allowing for unattended long-term operation. The mixtures were magnetically stirred for at least 12 h and allowed to settle under the controlled temperature for 48 h. Longer equilibration times were found to yield the same results. Samples of the saturated solutions were withdrawn with 20 cm^3 syringes through glass wool plugs. The first portions of the samples withdrawn were discarded to avoid possible adsorption effects on glass wool. After appropriate dilution, the samples were assayed spectrophotometrically using a computer-interfaced ECOM (Prague, Czech Republic) UV absorbance detector, Model LCD 2082, through which they were pumped by an inert pump MMC (Mikrotechna, Prague, Czech Republic) at a low flow rate. The analyses were carried out at the maximum absorbance wavelengths as given in Table 1. The concentrations were established on the basis of previously obtained absorbance values of standard calibration solutions which were observed to obey Lambert–Beer's law precisely. Two or three independent solubility determinations for each of the solid xylenols were done, and the agreement of the replicates was found to be within 1%.

Solubilities of protolytic solutes such as the phenols studied here are affected by the pH. In our measurements, no buffering was used and the solubilities reported correspond to the natural prevailing pH for the saturated solutions. Under such conditions, the dissociation of the phenolic solutes examined is negligible, as can be inferred from their pK_a values listed in Table 1.

Results

Table 2 lists the results of the VLE measurements for highly dilute aqueous solutions of the phenols (phenol, cresols, xylenols) along with some data previously reported in the literature. Literature data showing serious discrepancies and regarded as doubtful (e.g. Chalov's *(11)* data for *o*-cresol and *m*-cresol and Hakuta's *(6)* data for *m*-cresol) were omitted. Besides the values of limiting relative volatility α_{12}^{∞}, Table 2 gives also the Henry's law constants

Table 3. Experimental Mole Fraction Solubilities x_1 of Cresols and Xylenols in Water and Derived Values of Henry's Law Constants H, Air–Water Partition Coefficients K_{aw}, and Limiting Activity Coefficients γ_1^∞

compound	t/°C	equil	$x_1 \cdot 10^3$	H/kPa	$K_{aw} \cdot 10^6$	γ_1^∞	ref
o-cresol	25.0	LLE	4.46	9.71	70.8	224	12
	30.0	LLE	4.75	13.6	97.4	211	13
	35.3	LLE	5.15	18.8	133	195	8
m-cresol	24.7	LLE	4.01	4.48	32.7	249	8
	25.0	LLE	3.86	4.79	34.9	259	12
p-cresol	25.0	SLE	3.61	4.34	31.6	236[a]	14
	40.2	LLE	3.80	16.3	114	263	8
2,3-xylenol	20.0	SLE	0.579	3.50	25.9	517	[b]
2,4-xylenol	25.0	LLE	1.17	11.0	80.2	856	15
2,5-xylenol	20.0	SLE	0.460	4.83	35.8	616	[b]
2,6-xylenol	20.0	SLE	0.852	16.7	124	652	[b]
3,4-xylenol	20.0	SLE	0.669	1.54	11.4	530	[b]
3,5-xylenol	20.0	SLE	0.652	2.32	17.2	567	[b]
	28.8	SLE	0.919	4.44	32.0	505	16

[a] Experimental enthalpy of fusion (12.7 kJ·mol^{-1}) reported in ref 17 was used to calculate γ_1^∞ from the solid solubility. [b] This work.

$$H = \lim_{x_1 \to 0} (f_1/x_1) \tag{2}$$

where f_1 is the solute fugacity in the liquid solution, the air–water partition coefficients

$$K_{aw} = \lim_{c_1^w \to 0} (c_1^a/c_1^w) \tag{3}$$

where c_1^a and c_1^w are the solute molar concentrations in air and water, respectively, and the limiting activity coefficients

$$\gamma_1^\infty = \lim_{x_1 \to 0} \gamma_1 \tag{4}$$

Under the assumption that the vapor phase behaves as an ideal gas, these quantities are related to the limiting relative volatility as

$$H = \alpha_{12}^\infty P_2^s \tag{5}$$

$$K_{aw} = (\alpha_{12}^\infty P_2^s v_2^L)/(RT) \tag{6}$$

$$\gamma_1^\infty = \alpha_{12}^\infty P_2^s/P_1^s \tag{7}$$

where P_1^s and P_2^s are the vapor pressures of pure liquid phenol and water, respectively, and v_2^L is the liquid molar volume of pure water.

Experimental data on aqueous solubilities of cresols and xylenols are summarized in Table 3. This table includes also available literature data on solubilities of cresols and xylenols corresponding to either solid–liquid equilibria (SLE) or liquid–liquid equilibria (LLE). The liquid solubilities taken from the literature refer to the lowest temperatures; the data at higher temperatures as well as data for phenol itself were excluded since such high concentrations are not relevant to the condition of infinite dilution. Henry's law constants, air–water partition coefficients, and limiting activity coefficients derived from the solubilities are also listed in Table 3. Considering that the solubilities are low and assuming that the gas phase is ideal, these quantities were calculated from eqs 8–10 using the mole fraction liquid solubilities x_1^{LLE}. The results obtained from eqs 8–10 should, however, be regarded as estimates, since in accordance with a typical asymmetric behavior of organic–water mixtures, the solubilities of water in phenols (LLE) are quite large *(7)*.

$$H = P_1^s/x_1^{LLE} \tag{8}$$

$$K_{aw} = (P_1^s v_2^L)/(x_1^{LLE} RT) \tag{9}$$

$$\gamma_1^\infty = 1/x_1^{LLE} \tag{10}$$

The calculation from the mole fraction solid solubilities x_1^{SLE} of phenols in water is done using the relations

$$H = P_{1,solid}^s/x_1^{SLE} \tag{11}$$

$$K_{aw} = (P_{1,solid}^s v_2^L)/(x_1^{SLE} RT) \tag{12}$$

$$\gamma_1^\infty = (1/x_1^{SLE}) \exp[(\Delta_{fus}S/R)(1 - T_m/T)] \tag{13}$$

where $P_{1,solid}^s$ is the vapor pressure of solid phenol, $\Delta_{fus}S$ is its entropy of fusion, and T_m is its melting temperature. Equation 13 is approximate, neglecting the temperature dependence of enthalpy of fusion. We used a generalized value of $\Delta_{fus}S$ of 56 J K^{-1} mol^{-1} as recommended for rigid organic molecules by Yalkowsky *(18)*.

Reliable information on vapor pressures of pure liquid and solid phenols and their melting temperatures, which was required for the above-mentioned calculations, was obtained from Andon et al. *(19)*. Unfortunately, except for two phenols with the lowest melting temperatures (*m*-cresol, 2,4-xylenol), Andon's measurements of liquid vapor pressures do not cover the temperature range of interest here. To extend Andon's data to the temperatures of our interest in a reliable manner, we fitted them to the Cox equation *(20)*

$$\ln(P^s/P_0) = (1 - T_0/T) \exp[a + b(T/K) + c(T/K)^2] \tag{14}$$

with $P_0 = 101.325$ kPa and $T_0 = T_{nbp}$, considering the triple point as a constraint in the fitting. We selected the Cox equation for the purpose because of its capability *(21)* of representing correctly vapor pressure data in a broad temperature range. The triple-point coordinates T_t and P_t were approximated well by the normal melting temperature T_m and the corresponding hypothetical sublimation pressure P_{solid}^s (T_m) which we calculated from Andon's solid vapor pressure data. For *m*-cresol and 2,4-xylenol—the two phenols with the lowest melting temperatures—P^s data just above T_m were reported by Andon et al. *(19)*, and therefore we used these data instead of the triple-point information.

Table 4 gives the fitted values of adjustable parameters a, b, and c, the normal melting temperatures T_m, the normal boiling temperatures T_{nbp}, and the triple-point pressures P_t for each phenol. The vapor pressure data for all of the phenols but one were fitted with relative standard deviations significantly lower than 1%, the exception being *m*-cresol ($\sigma_r = 2.8\%$) for which the poorer fit was caused by an excessive scatter in the measurement of very low vapor pressures. The uncertainty (standard deviation) of interpolated P^s values in the temperature range of concern (t_m, 100 °C) as estimated by an error propagation analysis was typically within 3%, rarely exceeding 5% (*m*-cresol, 2,4-xylenol).

The Henry's law constants, air–water partition coefficients, and limiting activity coefficients of phenols evaluated from VLE, LLE, and SLE measurements as given in Tables 2 and 3 were for each phenol plotted in the logarithmic form versus reciprocal absolute temperature. The data involved cover a range of temperatures from the ambient to the normal boiling point of water. As exemplified for several of the phenols studied and for each of the

Table 4. Normal Melting Temperatures[a] T_m, Triple Point Pressures[b] P_t, Normal Boiling Temperatures[a] T_{nbp}, and Parameters a,b, and c of the Cox Vapor Pressure Equation (Eq 14) for Phenols

compound	T_m/K	P_t/Pa	T_{nbp}/K	a	$b \cdot 10^3$	$c \cdot 10^6$	range of data/K
phenol	314.05	184	454.99	3.1368	−2.0745	1.6097	394−455[c]
o-cresol	304.14	70	464.15	3.0862	−1.9642	1.5032	412−465[c]
m-cresol	285.37		475.38	3.2583	−2.6970	2.4639	288−312, 409−477
p-cresol	307.84	40	475.09	3.0743	−1.6234	0.9915	397−476[c]
2,3-xylenol	345.72	384	490.02	2.7810	−0.4447	−0.2932	422−492[c]
2,4-xylenol	297.69		484.08	3.2421	−2.6114	2.2678	298−318, 418−485
2,5-xylenol	348.00	544	484.28	2.7673	−0.3608	−0.4162	417−485[c]
2,6-xylenol	318.77	173	474.18	3.0067	−1.8319	1.4574	418−477[c]
3,4-xylenol	338.26	113	500.10	3.0825	−1.5907	0.9575	445−502[c]
3,5-xylenol	336.42	121	494.84	3.2147	−2.2081	1.6654	428−496[c]

[a] Reference 19. [b] Approximated by the hypothetical sublimation pressure at the normal melting temperature. [c] The triple point coordinates used as a constraint in the data fitting.

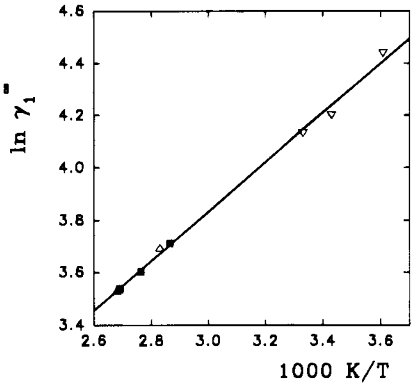

Figure 1. Temperature dependence of limiting activity coefficient γ_1^∞ of phenol (1) in water (2): VLE data of this work (■); Hakuta, ref 6 (△); and Abd-El-Bary, ref 5 (▽).

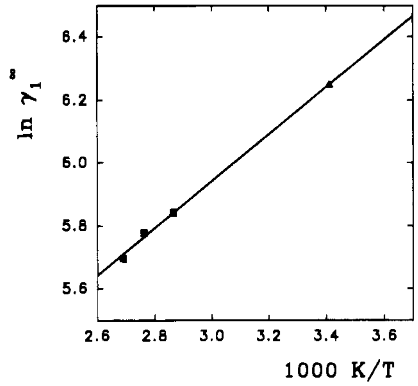

Figure 3. Temperature dependence of limiting activity coefficient γ_1^∞ of 2,3-xylenol (1) + water (2): VLE (■) and SLE (▲) data of this work.

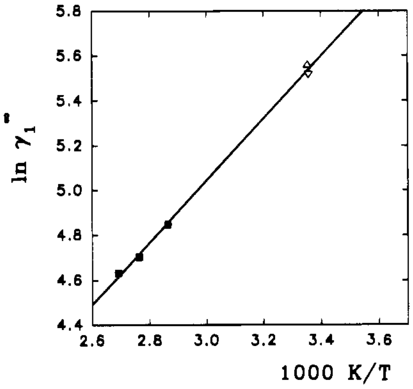

Figure 2. Temperature dependence of limiting activity coefficient γ_1^∞ of *m*-cresol (1) + water (2): VLE data of this work (■); LLE data of Freier, ref 12 (△), and of Sidgwick, ref 8 (▽).

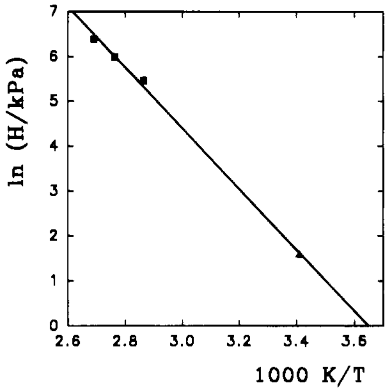

Figure 4. Temperature dependence of Henry's law constant H of 2,5-xylenol in water: VLE (■) and SLE (▲) data of this work.

above quantities in Figures 1−5, there was a good agreement between all of the data (either measured here or obtained from the literature), the van't Hoff plots displaying fairly good linearity. Adjusted parameters of the straight lines, standard deviations of fits, and calculated limiting partial molar excess enthalpies $\overline{H}_1^{E,\infty}$ or enthalpies of hydration H_H and H_K are summarized in Tables 5−7. Also given in these tables are the calculated values of γ_1^∞ at 100 °C, H at 25 °C, and K_{aw} at 25 °C together with their standard deviations estimated according to the error propagation law.

Discussion and Conclusion

As expected, any methyl substitution in the phenol molecule enhances its hydrophobicity and increases the nonideality of aqueous solutions of methylated phenols. Upon each addition of the methyl group the limiting activity coefficient of phenol increases approximately by a factor of 3. Differences in γ_1^∞ of isomeric phenols are relatively small but not negligible. The limiting activity coefficients of isomeric phenols vary slightly but consistently, with their normal boiling temperatures reflecting differences in hydrogen bonding.

A good correlation was also found between the Henry's law constants of isomeric phenols and T_{nbp} of the isomers. Figure 6 shows this correlation at 298 K; similar correlations are observed at other temperatures and for K_{aw}. These relationships suggest not only an overall consistency of the various experimental results but also correct calculational procedures.

A closer inspection of the H and K_{aw} values given in Tables 6 and 7, respectively, reveals that the methylphenols and dimethylphenols with the substitution in the ortho position exhibit generally higher H or K_{aw} values than do the other phenols. The observed behavior appears to be a

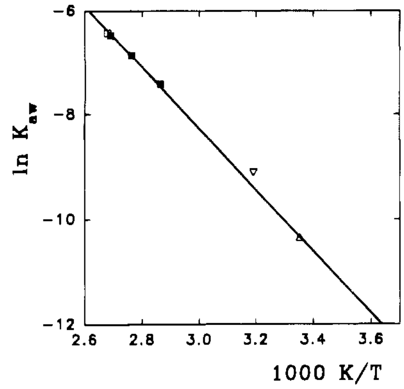

Figure 5. Temperature dependence of air–water partition coefficient K_{aw} of *p*-cresol: VLE data of this work (■) and of Chalov, ref 11 (□); SLE data of Parsons, ref 14 (△); and LLE data of Sidgwick, ref 8 (▽).

Table 5. Temperature Dependence of the Limiting Activity Coefficients of Phenols in Water, ln $\gamma_1^\infty = A_G + B_G/(T/K)$: Fitted Parameters A_G, B_G, Standard Deviation of Fit σ,[a] and Calculated Values of Limiting Partial Molar Excess Enthalpies $\bar{H}_1^{E,\infty}$ and Limiting Activity Coefficients at 100 °C, γ_1^∞(100 °C), along with Their Standard Deviations

compound	A_G	B_G	σ	$\bar{H}_1^{E,\infty} \mp \sigma(\bar{H}_1^{E,\infty})$/ kJ·mol^{-1}	$\gamma_1^\infty \mp \sigma(\gamma_1^\infty)$ (100 °C)
phenol	1.003	943.6	0.02	7.9 ∓ 0.2	34.2 ∓ 0.4
o-cresol	2.095	986.2	0.02	8.2 ∓ 0.2	114 ∓ 1
m-cresol	0.885	1386	0.02	11.5 ∓ 0.3	99.5 ∓ 1.5
p-cresol	1.576	1161	0.02[b]	9.7 ∓ 0.3	109 ∓ 1
2,3-xylenol	3.693	749.7	0.01	6.2 ∓ 0.1	299 ∓ 3
2,4-xylenol	1.965	1429	0.02	11.9 ∓ 0.4	329 ∓ 5
2,5-xylenol	3.385	894.9	0.05	7.4 ∓ 0.7	325 ∓ 11
2,6-xylenol	4.629	548.0	0.07	4.6 ∓ 1.0	445 ∓ 28
3,4-xylenol	3.375	850.2	0.02	7.1 ∓ 0.2	285 ∓ 3
3,5-xylenol	3.589	803.3	0.03	6.7 ∓ 0.4	311 ∓ 7

[a] $\sigma = [\sum_{i=1}^{n}(\ln \gamma_{1,i}^{\infty,\mathrm{exp}} - \ln \gamma_{1,i}^{\infty,\mathrm{calc}})^2/(n - 2)]^{1/2}$. [b] Sidgwick's *(8)* LLE solubility measurement was not considered in the fitting.

Table 6. Temperature Dependence of Henry's Law Constants of Phenols in Water, ln $(H/\mathrm{kPa}) = A_H + B_H/(T/K)$: Fitted Parameters A_H, B_H, Standard Deviation of Fit σ,[a] and Calculated Values of Enthalpies of Hydration H_H[b] and Henry's Law Constants at 25 °C, H(25 °C), along with Their Standard Deviations

compound	A_H	$-B_H$	σ	$-H_H \mp \sigma(H_H)$/ kJ·mol^{-1}	$H \mp \sigma(H)$/ kPa (25 °C)
phenol	21.443	6032	0.04	50.2 ∓ 0.4	3.36 ∓ 0.07
o-cresol	21.832	5827	0.04	48.5 ∓ 0.4	9.8 ∓ 0.2
m-cresol	21.650	5994	0.03	49.8 ∓ 0.5	4.7 ∓ 0.1
p-cresol	22.071	6138	0.04[c]	51.0 ∓ 0.6	4.4 ∓ 0.2
2,3-xylenol	24.600	6839	0.07	56.9 ∓ 1.0	5.3 ∓ 0.3
2,4-xylenol	22.820	6084	0.06	50.6 ∓ 0.9	11.2 ∓ 0.6
2,5-xylenol	24.746	6783	0.13	56.4 ∓ 1.9	7.4 ∓ 0.9
2,6-xylenol	23.920	6179	0.10	51.4 ∓ 1.5	24.4 ∓ 2.2
3,4-xylenol	24.597	7082	0.04	58.9 ∓ 0.5	2.33 ∓ 0.08
3,5-xylenol	24.396	6908	0.04	57.4 ∓ 0.5	3.41 ∓ 0.09

[a] $\sigma = [\sum_{i=1}^{n}(\ln H_i^{\mathrm{exp}} - \ln H_i^{\mathrm{calc}})^2/(n - 2)]^{1/2}$. [b] Enthalpy change corresponding to the isothermal transfer of a mole of the phenolic solute from ideal gas state (P° = 101.325 kPa) to hypothetical infinitely dilute solution having unity solute mole fraction (x_1 = 1). [c] Sidgwick's *(8)* LLE solubility measurement was not considered in the fitting.

consequence of the steric hindrance of the hydroxyl group by the adjacent methyl(s). Clearly, the effect of steric hindrance is most pronounced in 2,6-xylenol, for which the H, K_{aw}, and γ_1^∞ values are by far the largest.

Table 7. Temperature Dependence of the Air–Water Partition Coefficients of Phenols in Water, ln $K_{aw} = A_K + B_K/(T/K)$: Fitted Parameters A_K, B_K, Standard Deviation of Fit σ,[a] and Calculated Values of Enthalpies of Hydration H_K[b] and Air–Water Partition Coefficients at 25 °C, K_{aw}(25 °C), along with Their Standard Deviations

compound	A_K	$-B_K$	σ	$-H_K \mp \sigma(H_K)$/ kJ·mol^{-1}	10^6-$[K_{aw} \mp \sigma(K_{aw})]$ (25 °C)
phenol	8.701	5760	0.04	47.9 ∓ 0.4	24.5 ∓ 0.5
o-cresol	9.091	5556	0.04	46.2 ∓ 0.4	71.7 ∓ 1.6
m-cresol	8.909	5722	0.03	47.6 ∓ 0.5	34.2 ∓ 0.7
p-cresol	9.328	5865	0.04[c]	48.8 ∓ 0.6	32.2 ∓ 1.3
2,3-xylenol	11.858	6567	0.07	54.6 ∓ 1.0	38.4 ∓ 2.4
2,4-xylenol	10.077	5811	0.06	48.3 ∓ 0.9	81.6 ∓ 4.5
2,5-xylenol	12.004	6511	0.13	54.1 ∓ 1.9	53.7 ∓ 6.3
2,6-xylenol	11.176	5906	0.10	49.1 ∓ 1.5	178 ∓ 16
3,4-xylenol	11.854	6809	0.04	56.6 ∓ 0.5	17.0 ∓ 0.6
3,5-xylenol	11.654	6636	0.04	55.2 ∓ 0.5	24.8 ∓ 0.7

[a] $\sigma = [\sum_{i=1}^{n}(\ln K_{aw,i}^{\mathrm{exp}} - \ln K_{aw,i}^{\mathrm{calc}})^2/(n - 2)]^{1/2}$. [b] Enthalpy change corresponding to the transfer of a mole of the phenolic solute from ideal gas state c_g = 1 mol/dm^3 to hypothetical infinitely dilute solution having unity solute concentration (c_1 = 1 mol/dm^3). [c] Sidgwick's *(8)* LLE solubility measurement was not considered in the fitting.

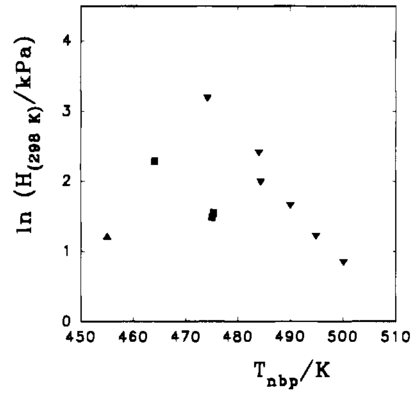

Figure 6. Henry's law constants H of phenols at 298 K plotted against their normal boiling temperatures T_{nbp}: phenol (▲); cresols (■); and xylenols (▼).

In summary, the results presented in this work improve our knowledge about air–water partitioning and aqueous solubility of phenols and provide significantly more accurate information than that offered by current leading estimation methods. For example, the latest version of UNIFAC *(22)*, while yielding fairly acceptable results at 100 °C, fails completely at ambient temperatures, at which it gives 3–6 times lower limiting activity coefficients of phenols in water than those found experimentally, implying a reverse temperature dependence ($\bar{H}_1^{E,\infty} < 0$). It is believed that our data will be of value for estimations of the environmental transport of phenols and for feasibility assessments of their separation from industrial waste water effluents. In this respect, the following general conclusions might be drawn:

(i) When compared to most other priority pollutants, phenols are considerably less hydrophobic, their H and K_{aw} being relatively low. Hence, it implies that volatilization of phenols from water will not be environmentally important, while rain scavenging of phenols from atmosphere will be, on the contrary, an important removal process.

(ii) Limiting separation factors of phenols from water fall with decreasing temperature, which causes the separation of phenols from their dilute aqueous solutions at lower temperatures (e.g. by gas stripping) to become progressively more difficult or even inefficient. For example, for phenol azeotropy occurs at temperatures below 290 K.

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