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Partition Coefficients of Some Environmentally Important Organic Compounds between 1-Octanol and Water from Reversed-Phase High-Performance Liquid Chromatography

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1-Octanol/water partition coefficients in infinite dilution of several phenol, indole, biphenyl, and naphthalene derivatives, a few polycyclic aromatic compounds, and some polyfunctional haloaromatics determined by using reversed-phase high-performance liquid chromatography (RP-HPLC) are reported. These data may be used for estimating the ecotoxicological impact of those compounds identified in brown coal liquids (e.g., hydroxyaromatic compounds), as well as for the extension of methods to correlate and predict partition coefficients in organic/aqueous liquid phases.

Introduction

For estimating ecotoxicological effects of residues from the former large-scale processing of brown coal to liquid products in the area of Leipzig-Halle-Bitterfeld-Merseburg in the eastern part of Germany, it is important to determine partition coefficients between 1-octanol (or other organic phases) and water. From GC–MS and MS–MS investigations of fractions of coal-derived liquids, the constituent compound classes of those liquid products (e.g., hydroxyaromatic compounds, polycyclic aromatic hydrocarbons) are known (*1*, *2*). Especially, the 1-octanol/water partition coefficients, P_{ow}, of several commercially available phenol, indole, biphenyl, and naphthalene derivatives were determined by using reversed-phase high-performance liquid chromatography (RP-HPLC). Furthermore, for improving the development of linear solvation relationship equations (LSER), partition coefficients were also determined for some polyfunctional haloaromatics.

Experimental Section

The experimental setup (HPLC sytem) consisted of an eluent vacuum degasser, SCM 4000, an isocratic SP 8810 dual piston LC pump, a programmable, variable-wavelength UV–vis absorbance detector, SC 200, with a flow cell, a ChromJet two-channel integrator, SP 4400, connected to a personal computer, a column oven with a Peltier cooling device, and an autosampler, AS 1000, all from Thermo Separation Products GmbH, Darmstadt, Germany, except the column oven, which was from JASCO, Hachioyi, Japan.

Water-satured 1-octanol was used as the stationary phase and 1-octanol-satured water as the mobile phase. Columns and precolumns were packed with Eurospher C-18 (RP-18; 30 mm in length, internal diameter 4 mm, particle size 5 μm, from Knauer, Berlin). The temperature was maintained constant at 25.0 ± 0.5 °C by means of the thermostated column oven. The possibility for coating reversed-phase columns with 1-octanol has been described in the literature (*3–5*). The column and precolumn were coated with water-satured

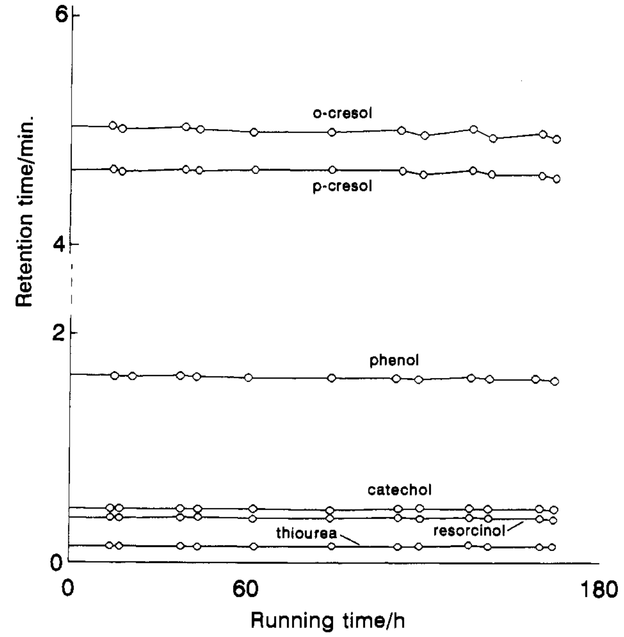

Figure 1.

Table 1. Results of Calibrations: Reference Compounds and Coefficients *a* and *b* of Eq 2

	log *k'*			log{P_{ow}(eq 3)}	
reference compound	2 $cm^3 \cdot min^{-1}$	4 $cm^3 \cdot min^{-1}$	log P_{ow} (ref)	2 $cm^3 \cdot min^{-1}$	4 $cm^3 \cdot min^{-1}$
1,3-dihydroxybenzene	0.252	0.176	0.80 (*6*)	0.785	0.772
1,2-dihydroxybenzene	0.372	0.301	0.88 (*6*)	0.896	0.890
phenol	1.027	0.948	1.50 (*7*)	1.500	1.502
1-hydroxy-4-methylbenzene	1.508	1.433	1.94 (*7*)	1.943	1.961
1-hydroxy-2-methylbenzene	1.542	1.464	1.98 (*7*)	1.975	1.990
2-isopropyl-5-methylphenol		2.830	3.30 (*7*)		3.282
	$a = 0.922$	$a = 0.946$			
	$b = 0.553$	$b = 0.605$			

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Table 2. Examples for Changes of the Coefficients of Eq 2 with Running Time (Second Recoating, Flow Rate 2 $cm^3 \cdot min^{-1}$)

calibration no.	running time/h	coefficients of eq 2 a	 b	regression coefficient r
1	0	0.9192	0.5543	0.9997
2	14	0.9222	0.5530	0.9998
3	17	0.9238	0.5527	0.9998
4	37.5	0.9262	0.5376	0.9995
5	43.5	0.9308	0.5429	0.9999

Table 3. Substances Used For Calibration

substance	CAS registry no.	synonym	formula	purity/%	supplier
1,2-dihydroxybenzene	120-80-9	catechol	$C_6H_6O_2$	>99 (GC)	J
1,3-dihydroxybenzene	108-46-3	resorcinol	$C_6H_6O_2$	>99	F
1-hydroxy-2-methylbenzene	95-48-7	*o*-cresol	C_7H_8O	>99 fs	S
1-hydroxy-4-methylbenzene	106-44-5	*p*-cresol	C_7H_8O	>99 fs	F
phenol	108-95-2		C_6H_6O	99.5 pa	M
2-isopropyl-5-methylphenol	89-83-8	thymol	$C_{10}H_{14}O$	>99 (GC)	M
thiourea	62-56-6		CH_4N_2S	pa	F

Table 4. Substances Investigated

substance	CAS registry no.	synonym	formula	purity/%	supplier
benzo[*b*]furan	271-89-6	coumarone	C_8H_6O	>99 (GC)	F
1-benzothiophene	95-15-8	thionaphthene	C_8H_6S	99	A
biphenyl-2-ol	90-43-7		$C_{12}H_{10}O$	>99 fs	S
biphenyl-4-ol	92-69-3		$C_{12}H_{10}O$	>98 fs	S
2-(1,1-dimethylethyl)phenol	88-18-6		$C_{10}H_{14}O$	>98 fs	S
4-(1,1-dimethylethyl)phenol	98-54-4		$C_{10}H_{14}O$	99	F
1-hydroxy-3-methylbenzene	108-39-4	*m*-cresol	C_7H_8O	>98 fs	S
1,4-naphthalenediol	571-60-8	1,4-dihydroxynaphthalene	$C_{10}H_8O_2$	98	J
1,5-naphthalenediol	83-56-7	1,5-dihydroxynaphthalene	$C_{10}H_8O_2$	99	J
2,3-naphthalenediol	92-44-4	2,3-dihydroxynaphthalene	$C_{10}H_8O_2$	98	J
2,6-naphthalenediol	581-43-1	2,6-dihydroxynaphthalene	$C_{10}H_8O_2$	98	A
1,2-dimethoxybenzene	91-16-7	veratrole	$C_8H_{10}O_2$	99 (GC)	A
2,3-dimethylindole	91-55-4		$C_{10}H_{11}N$	99	J
2-ethylphenol	90-00-6		$C_8H_{10}O$	99	J
5-hydroxyindole	1953-54-4		C_8H_7NO	98	F
9-(hydroxymethyl)fluorene	24324-17-2		$C_{14}H_{12}O$	99	A
indole	120-72-9		C_8H_7N	99 pa	M
2-methylbenzo[*b*]furan	4265-25-2		C_9H_8O	96	A
1,2-dihydroxy-4-methylbenzene	452-86-8	4-methylcatechol	$C_7H_8O_2$	99 (GC)	A
2-methylindole	95-20-5		C_9H_9N	98	F
3-methylindole	83-34-1	skatole	C_9H_9N	>99	F
1-(hydroxymethyl)naphthalene	4780-79-4	1-naphthalenemethanol	$C_{11}H_{10}O$	98	A
2-(hydroxymethyl)naphthalene	1592-38-7	2-naphthalenemethanol	$C_{11}H_{10}O$	99	A
1-hydroxynaphthalene	90-15-3	α-naphthol	$C_{10}H_8O$	>99	F
1-(2-naphthyl)ethanol	40295-80-5		$C_{12}H_{12}O$	>99	F
2-propylphenol	644-35-9		$C_9H_{12}O$	98	J
1,2,3,4-tetrahydro-1-naphthol	529-33-9	tetralol	$C_{10}H_{12}O$	97	A
5,6,7,8-tetrahydro-1-naphthol	529-35-1		$C_{10}H_{12}O$	99	J
5,6,7,8-tetrahydro-2-naphthol	1125-78-6		$C_{10}H_{12}O$	98	J
ω-bromoacetophenone	70-11-1	phenacyl bromide	C_8H_7BrO		Σ
2′-bromoacetophenone	2142-69-0	1-acetyl-2-bromobenzene	C_8H_7BrO	99	F
3′-bromoacetophenone	2142-63-4	1-acetyl-3-bromobenzene	C_8H_7BrO	>98	F
4′-bromoacetophenone	99-90-1	1-acetyl-4-bromobenzene	C_8H_7BrO	>98	F
3′-chloroacetophenone	99-02-5	1-acetyl-3-chlorobenzene	C_8H_7ClO	>97	F
4′-chloroacetophenone	99-91-2	1-acetyl-4-chlorobenzene	C_8H_7ClO	>97	F
2-chlorobenzaldehyde	89-98-5		C_7H_5ClO	>98	F
3-chlorobenzaldehyde	587-04-2		C_7H_5ClO	97	F
4-chlorobenzaldehyde	104-88-1		C_7H_5ClO	>98	F
2,5-difluoro-1-nitrobenzene	364-74-9		$C_6H_3F_2NO_2$		Σ
3,5-difluoro-1-nitrobenzene	2265-94-3		$C_6H_3F_2NO_2$		Σ
1-fluoro-2-nitrobenzene	1493-27-2		$C_6H_4FNO_2$	>98	F
1-fluoro-3-nitrobenzene	402-67-5		$C_6H_4FNO_2$	>97	F
1-fluoro-4-nitrobenzene	350-46-9		$C_6H_4FNO_2$	>98	F

1-octanol at a flow rate of 0.5 $cm^3 \cdot min^{-1}$ until the detector reported a stable baseline. The column then was flushed with 1-octanol-satured water until a clear eluate was received. Finally, the column was reconnected to the detector, and elution was continued at a flow rate of 0.5–2 $cm^3 \cdot min^{-1}$, until equilibrium (indicated by a stable baseline) was reached. The amount of 1-octanol on the support was determined by gas chromatography on a CP-19 Sil (Chrompack) column after washing with ethanol; it amounts to about 0.7 cm^3 of 1-octanol/g of solid support. Due to a certain displacement of the stationary phase, the prepared column worked correctly for about 100 h only. After this time period, the retention time of the compounds decreased, and the coating of the column had to be renewed. Therefore, the system was flushed with methanol and the column was recoated as described before. The stability behavior of the RP-18, 1-octanol-coated, is demonstrated in Figure 1, where for six organic compounds the retention time is shown as a function of the column running time. Samples of the organic compounds were dissolved in the mobile phase and eluted in an isocratic and isothermal procedure at a flow rate of 2 $cm^3 \cdot min^{-1}$. In order to obtain reasonable retention times, the flow rate had to be increased to 4 $cm^3 \cdot min^{-1}$ in the case of 1-benzothiophene, biphenyl-2-ol, biphenyl-4-ol, 2-(1,1-dimethylethyl)phenol, 4-(1,1-di-

Table 5. Infinite Dilution Partition Coefficients of Some Solutes in 1-Octanol/Water at 25 °C

solute	log P_{ow} (this work)	std dev S^{*a}	log P_{ow} (ref)
5-hydroxyindole	1.11	0.02	
1,2-dihydroxy-4-methylbenzene	1.32	0.01	
1,2-dimethoxybenzene	1.75	0.02	2.21 (*8*)
1-fluoro-2-nitrobenzene	1.84	0.01	
2,5-difluoro-1-nitrobenzene	1.86	0.01	
1-fluoro-4-nitrobenzene	1.89	0.01	
1,4-naphthalenediol	1.90	0.01	
2,6-naphthalenediol	1.90	0.01	
1-hydroxy-3-methylbenzene	1.91	0.01	1.98 (*7*) 1.95 (*8*) 2.01 (*8*) 1.96 (*8*)
1,2,3,4-tetrahydro-1-naphthol	1.98	0.01	
1-fluoro-3-nitrobenzene	2.02	0.01	
3,5-difluoro-1-nitrobenzene	2.03	0.01	
ω-bromoacetophenone	2.19	0.01	
indole	2.19	0.01	2.14 (*7, 8*) 2.25 (*8*) 2.00 (*8*)
1,5-naphthalenediol	2.19	0.02	
4-chlorobenzaldehyde	2.21	0.01	
2,3-naphthalenediol	2.24	0.03	
3-chlorobenzaldehyde	2.26	0.01	
2′-bromoacetophenone	2.28	0.01	
2-chlorobenzaldehyde	2.28	0.01	
1-(hydroxymethyl)naphthalene	2.37	0.01	
4′-chloroacetophenone	2.41	0.01	2.32 (*8*)
1-hydroxynaphthalene	2.43	0.01	2.84 (*7, 8*) 2.98 (*8*) 2.70 (*6*) 2.31 (*8*)
3′-chloroacetophenone	2.43	0.01	
2-(hydroxymethyl)naphthalene	2.45	0.01	
2-ethylphenol	2.46	0.02	2.47 (*7*)
2-methylindole	2.53	0.01	2.53 (*7*)
4′-bromoacetophenone	2.57	0.01	2.43 (*8*)
3′-bromoacetophenone	2.58	0.01	
1-(2-naphthyl)ethanol	2.68	0.01	
benzo[*b*]furan	2.69	0.01	2.67 (*7, 8*)
3-methylindole	2.70	0.01	2.60 (*7, 8*)
9-(hydroxymethyl)fluorene	2.89	0.01	
5,6,7,8-tetrahydro-2-naphthol	2.90	0.01	
2-propylphenol	2.93	0.01	2.93 (*7*)
5,6,7,8-tetrahydro-1-naphthol	2.95	0.01	
2,3-dimethylindole	3.05	0.01	
[biphenyl]-2-ol	3.06	0.02	
4-(1,1-dimethylethyl)phenol	3.16	0.01	3.04 (*7*) 2.94 (*8*) 3.31 (*8*)
1-benzothiophene	3.18	0.01	3.12 (*7*)
2-methylbenzo[*b*]furan	3.22	0.01	
[biphenyl]-4-ol	3.31	0.01	
2-(1,1-dimethylethyl)phenol	3.53	0.01	3.31 (*8*)

[a] $S^* = [[\sum_i^n (x_i - \bar{x})^2]/(n-1)]^{1/2}$ = standard deviation, where x_i = the measured value, $\bar{x}$ = the mean, and n = the number of measurements.

methylethyl)phenol, and 2,3-dimethylindole. The retention time was determined by using a UV–vis detector which was operated at 254 nm for aromatic compounds, and 230 nm for hetero compounds.

Evaluation of Experimental Data

The 1-octanol/water partition coefficient, P_{ow}, is defined as

$$\log P_{ow} = \frac{\text{molarity in solute in 1-octanol phase}}{\text{molarity of solute in aqueous phase}} \qquad (1)$$

It was obtained by linear regression of the experimental results of the capacity factor k'

$$\log P_{ow} = a \log k' + b \qquad (2)$$

The capacity factor, k', was derived from the direct experimental results for dead time t_0 and retention time t_R of the organic solutes according to

$$k' = (t_R - t_0)/t_0 \qquad (3)$$

Thiourea was used for determining the dead time t_0.

Coefficients a and b were determined in calibration procedures, where retention times were measured for organic compounds whose 1-octanol/water partition coefficients were known from the literature. Calibrations were performed in regular intervals of about 10–20 h (*6*). In Table 1 numbers for log k' determined for the reference compounds (first recoating at the beginning of the measurements; flow rates of 2 and 4 $cm^3 \cdot min^{-1}$) in the present work, as well as log P_{ow} taken from the literature and resulting from calibration measurements, are reported. Numbers for log P_{ow} resulting from eq 2 deviate from literature data, taken as reference, by less than 0.03. Additionally, Table 2 gives some examples for the influence of running time on the coefficients a and b of eq 2. Coefficient a increases slowly with increasing running time, while coefficient b decreases. But the resulting differences in log P_{ow} are smaller than 0.01 and therefore well within the experimental uncertainty which is estimated from the comparsion with literature data to ±0.03.

Chemicals

Substances used for calibration are given in Table 3. Besides 1,2-dihydroxybenzene, 1-hydroxy-2-methylbenzene, and 1-hydroxy-4-methylbenzene, thymol was used additionally in the case of phenolic compounds and halogen-containing aromatics (using a flow rate of 4 $cm^3 \cdot min^{-1}$). Thiourea was only used for determining the dead time t_0. log P_{ow} values of the reference compounds were taken from the literature (*6–8*). Table 4 gives the 43 organic compounds for which 1-octanol/water partition coefficients were determined in the present work. In Tables 3 and 4 the abbreviations are the following: fs, for synthesis, pa, for analysis; A, Aldrich-Chemie; F, Fluka; J, Janssen Chimica; M, Merck; S, Schuchard; and Σ, Sigma Chemie.

Results and Discussion

The experimental results for log P_{ow} of 43 polycyclic aromatic compounds, hydroxyaromatic compounds, and polyfunctional haloaromatics are summarized in Table 5 in the order of ascending values of log P_{ow}, together with standard deviations and available literature data. All log P_{ow} numbers are averaged values of at least four experiments, which were evaluated by applying eq 2 with the appropriate running time dependent coefficients a and b. For 14 solutes experimental results are available in the literature. For 3 substances the difference is less than the standard deviation of the new results; for 10 substances the difference exceeds the standard deviation by a factor larger than 2. The largest deviations are observed for 1-hydroxynaphthalene and 1,2-dimethoxybenzene. The influence of molecular structures on the partition coefficient (cf. refs *8* and *9–11*) as well as the meaning of the experimental results with respect to environmental problems of brown coal liquid products is to be discussed later.

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