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Partition Coefficients for Environmentally Important, Multifunctional Organic Compounds in Hexane + Water

J. Schulte,[†] J. Dürr,[‡] S. Ritter,[†] W. H. Hauthal,[†] K. Quitzsch,[†] and G. Maurer*,[‡]

Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstrasse 3,
D-04103 Leipzig, Germany, and Lehrstuhl für Technische Thermodynamik, Universität Kaiserslautern
Erwin-Schrödinger-Strasse, D-67653 Kaiserslautern, Germany

Experimental results for the partition coefficient of 41 substances (several phenol, indole, biphenyl, and naphthalene derivates, polycyclic aromatic compounds, and polyfunctional haloaromatics) in hexane + water at 298.15 K are reported. Partition coefficients were measured by reversed phase high-performance liquid chromatography and the shake-flask method. The experimental results are compared successfully to predictions by the linear solvation energy relationship method.

Introduction

Partition coefficients describing the distribution of a solute in coexisting organic + aqueous phases are needed in a large variety of applications (Lee and Mackay, 1995; Hansch and Leo, 1995, Karcher and Karabunarliev, 1996). An appropriate method for their measurement is the reversed phase high-performance liquid chromatography (RP-HPLC). For many organic solutes, experimentally determined partition coefficients are available for the system octan-1-ol + water (Leo and Hansch, 1979; Hansch et al., 1995). Octan-1-ol + water partition coefficients are widely used, for example, to quantify structural properties of a solute, such as its hydrophobicity, for the assessment of the environmental fate of pollutants and to approximate the partitioning of pollutants between biological tissues (e.g., membranes and fatty tissues) and water (DeBolt and Kollman, 1995). However, partition coefficients are also required in chemical engineering fields, e.g., in the selection of organic solvents for the extraction of compounds from aqueous phases. In those applications octan-1-ol is only one of a very large number of usual organic solvents. But experimental results for the partition coefficient of organic solutes in other organic solvent + water systems are rarely found in the literature, although a large database is also required to develop and test methods to correlate and predict organic solvent + water partition coefficients using, for example, linear solvation energy relationships (LSER) (Meyer and Maurer, 1993, 1995).

The present work aims to extend the database for partition coefficients by providing experimental data for the partition coefficient of 41 substances (several phenol, indole, biphenyl, and naphthalene derivatives, polycyclic aromatic compounds, and polyfunctional haloaromatics) in hexane + water at 298.15 K.

Partition coefficients reported here have been determined predominantly by liquid−liquid chromatography using different mobile and/or stationary phases. To test the accuracy of that method as well as to confirm some of the experimental HPLC data, some partition coefficients were also measured with the classical shake-flask method. The new experimental results are compared to literature data and to predictions from the LSER method.

Experimental Section

In HPLC experiments for measuring the partition coefficient of a solute between an organic and an aqueous phase, the stationary phase consists of an inert carrier material that is covered with the water-saturated organic phase, while the mobile phase is water, saturated with the organic solvent (Sangster, 1997). Small samples of an unretained substance r and the solute i under investigation are injected into the mobile phase, and the retention times, $t^{(r)}$ and $t^{(i)}$, are measured. When the solubility of substance r in the organic solvent can be neglected ($P_{\mathrm{O/W}}{}^{(r)} = c_{r,\mathrm{org}}/C_{r,\mathrm{w}} \approx 0$), the partition coefficient

$$P_{\mathrm{O/W}}{}^{(i)} = \frac{c_{i,\mathrm{org}}}{c_{i,\mathrm{w}}} \tag{1}$$

is related to the capacity factor

$$k_i = \frac{t^{(i)} - t^{(r)}}{t^{(r)}} \tag{2}$$

by

$$\log P_{\mathrm{O/W}}{}^{(i)} = \log k_i + \log \frac{V_{\mathrm{mob}}}{V_{\mathrm{stat}}} \tag{3}$$

$c_{i,\mathrm{org}}$ and $c_{i,\mathrm{w}}$ are the solute molarities in the organic solvent and in the aqueous phase, respectively. V_{mob} and V_{stat} are the volumes of the mobile and stationary phase, respectively. When experimental results for the capacity factor k_i from HPLC measurements are plotted versus partition coefficients $P_{\mathrm{O/W}}{}^{(i)}$ determined independently (e.g., by the shake-flask method) in a $\log P_{\mathrm{O/W}}{}^{(i)}/\log k_i$ diagram the linear relation of eq 3 generally holds, whereas the slope often deviates considerably from unity. Therefore it is common practice to modify eq 3 for the determination of partition coefficients from direct experimental results for the capacity factor:

$$\log P_{\mathrm{O/W}}{}^{(i)} = a \log k_i + b \tag{4}$$

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* To whom correspondence should be addressed.

[†] Universtät Leipzig.

[‡] Universität Kaiserslautern.

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Table 1. Partition Coefficients in Hexane + Water, $P_{H/W}$, at 298.15 K (from Leo and Hansch (1979)) Used for Determining Coefficients *a* and *b* of Eq 4

compound	$\log_{10} P_{H/W}$
Hydrogen Bond Donors	
phenol	−0.96
o-cresol[a]	−0.12
4-ethylphenol	0.23
2,4-dimethylphenol	0.36
3,5-dimethylphenol	0.36
1-naphthol[a]	0.62
Hydrogen Bond Acceptors	
2-methoxyphenol	0.36
benzaldehyde	1.11
4-chlorobenzaldehyde	1.60
benzene[a]	2.06
toluene	2.75

[a] This work; shake-flask method

Parameters *a* and *b* are then determined by correlating partition coefficients (determined by another method) with capacity factors measured by HPLC, keeping in mind that both parameters might also depend on the chemical nature of the partitioning solute, i.e., they might be different for, e.g., nonpolar or hydrogen-bonding substances.

Experiments by Partition Chromatography. The HPLC system was equipped with a programmable, variable wavelength UV/vis detector (model SC 220, Thermo Separation Products GmbH, Darmstadt, Germany), which was operated at 254 nm. The separation columns were similar to those used in previous work (Ritter et al., 1994). The stationary phase support consisted of about 0.7 cm^3 of Lichrospher C-18 end filled RP material. A column oven was used to thermostat the columns at (25 ± 0.5) °C. That temperature fluctuation can cause an absolute uncertainty of about 0.005 in $\log P_{O/W}^{(i)}$ (Leo et al., 1971). The column was flushed for about 45 min with a liquid mixture of methanol and hexane at a flow rate of about 0.5 cm^3/min. Then it was eluted with hexane-saturated water (for several hours) until a stable baseline indicated that the equilibrium between the stationary and the mobile phase was achieved. Experiments were carried out with eluent flow rates from about 0.5 to about 2.0 cm^3/min. The method is not reliable when the retention time becomes very large, i.e., when the partition coefficient is rather large. Therefore the measurements had to be restricted to solutes with $\log P_{O/W} \leq 3.5$. Another experimental difficulty is due to the washing out of the stationary by the mobile phase; therefore the column had to be recoated at regular time intervals. Stock solutions containing about 4 g of an organic solute in 1 L hexane-saturated water were prepared. Samples of the stock solutions (≈0.01 cm^3) were injected into the sample loop of the HPLC equipment. Thiourea was used to determine the "dead time" $t^{(r)}$. More details on the experimental procedure have been given earlier by Ritter et al. (1994).

The components used for calibrating, i.e., for determining the correlation coefficients *a* and *b*, vary considerably in their chemical nature, consisting of nonpolar substances such as toluene and benzene as well as proton donors (e.g., phenol and some of its derivatives) and proton acceptors (like benzaldehyde and chlorobenzaldehyde). Those substances are given in Table 1 together with literature data/sources for the partition coefficient in hexane + water, $P_{H/W}^{(i)}$, used for calibrating. The range of $\log P_{H/W}$ covered by those substances extends from −0.96 (phenol) to 0.62 (1-naphthol) for hydrogen bond donors and from 0.36 (2-methoxyphenol) to 2.75 (toluene) for hydrogen bond acceptors.

Experiments by the Shake-Flask Method. The classical method for the determination of the partition coefficient is the shake-flask method (OECD Guideline, 1981). In the present work, it was operated with a total volume of 100 cm^3 and ratios of organic phase to aqueous phase volume of about 1:3, 1:1, and 3:1, respectively. The solutes were dissolved in either one of the presaturated phases, and then the other phase was added. The solute concentration in the initial phase was between $\approx 10^{-3}$ and $\approx 10^{-5}$ $mol \cdot L^{-1}$. The flask was shaken for about 6 h in a thermostated water bath. Solute concentration was determined with a two-beam photometer (Uvicon 940, Kontron, Munich, Germany) using thermostated cuvette holders.

Results and Discussion

The shake-flask method was only used for six solutes. For each solute in each phase between 6 and 10 photometric analyses were performed. The experimental results are given as arithmetic averages for the logarithm of the partition coefficient of a component i between hexane and water, $\log P_{H/W}^{(i)}$, in Table 2. The standard deviation σ_i for $x_i \equiv \log P_{H/W}^{(i)}$

$$\sigma_i = \sqrt{\frac{\sum_i^N x_i^2 - \frac{\left(\sum_i^N x_i\right)^2}{N}}{N}} \tag{5}$$

is about 0.1 with a maximum of 0.19 for 1,2-dimethoxybenzene.

Partition chromatography was applied to determine hexane + water partition coefficients for 41 organic substances. Some information on those substances as well as on the substances used for calibration and on the solvents (water, methanol and hexane) is given in Table 4. For each solute between 4 and 14 measurements were carried out. In each measurement the capacity factor was determined. The standard deviation σ_i for $\log k_i$ (and for $\log P_{H/W}^{(i)}$)

$$\sigma_i = \sqrt{\frac{\sum_i^N \log k_i^2 - \frac{\left(\sum_i^N \log k_i\right)^2}{N}}{N}} \tag{6}$$

is about 0.1 with a maximum of 0.30 for 5,6,7,8-tetrahydro-2-naphthol. However, the absolute number for $\log P_{H/W}^{(i)}$ depends on the set of calibration substances used to determine coefficients *a* and *b* of eq 4. Three different sets of calibration substances were studied. Set I (calibration curve I) includes all components given in Table 1; for example, for the calibration curve no distinction is made between hydrogen bond donors and hydrogen bond acceptors. For sets II and III only substances either with hydrogen bond donating properties (calibration curve II) or with hydrogen bond accepting properties (calibration curve III) were considered. For hydrogen bond donating solutes calibration curve II is assumed to be more reliable, whereas for hydrogen bond accepting solutes calibration curve III should be the appropriate choice. However, comparing numbers from the more appropriate calibration curve (either II or III) with those from calibration curve I indicates the uncertainty introduced by the evaluation

Table 2. Partition Coefficients in Hexane + Water, $P_{H/W}$, at 298.15 K

	$\log_{10} P_{H/W}$				
compound	shake-flask method	HPLC cal. curve I	HPLC cal. curve II	HPLC cal. curve III	pred. LSER
p-cresol	−0.34 ± 0.12	−0.36	−0.47		−0.09
2-hydroxybiphenyl	1.30 ± 0.07	1.70	1.37		1.29
1,2-dimethoxybenzene	0.78 ± 0.19	0.91		1.22	1.79
1-fluoro-2-nitrobenzene	0.81 ± 0.15	0.81		1.16	1.45
1-acetyl-2-bromobenzene	1.22 ± 0.12	1.52		1.72	2.03
1-benzothiophene	1.80 ± 0.12	2.35		2.42	2.69

Table 3. Experimental Results for the Partition Coefficient $P_{H/W}{}^{(i)} = c_{i,\mathrm{hexane}}/c_{i,\mathrm{water}}$ of Hydrogen Bond Donors and Acceptors in Hexane + Water at 298.15 K

(a) Hydrogen Bond Donors

		$\log_{10} P_{H/W}$	
no.	substance *i*	exptl[a]	pred. (LSER)
1	2-ethylphenol	0.42 ± 0.24	0.47
2	2-propylphenol	1.02 ± 0.19[b]	1.03
3	2-*tert*-butylphenol	1.54 ± 0.22[b]	1.78
4	4-*tert*-butylphenol	1.25 ± 0.23[b]	1.78
5	4-methoxyphenol	−0.91 ± 0.19	
6	*m*-cresol	−0.32 ± 0.26	−0.09
7	*p*-cresol	−0.47 ± 0.11	−0.09
8	2,3-dimethylphenol	0.37 ± 0.23	0.48
9	4-methyl-catechol	−0.85 ± 0.18	−1.37
10	1,4-dihydroxynaphthalene	−0.52 ± 0.23	−0.50
11	1,5-dihydroxynaphthalene	−0.79 ± 0.18	−0.63
12	2,3-dihydroxynaphthalene	0.04 ± 0.24	−0.41
13	2,6-dihydroxynaphthalene	−0.86 ± 0.14	−0.63
14	indole	0.20 ± 0.24	
15	2-methylindole	0.74 ± 0.30[b]	
16	3-methylindole	0.87 ± 0.34[b]	
17	1-naphthalene methanol	0.61 ± 0.35	0.80
18	2-naphthalene methanol	0.82 ± 0.21[b]	0.80
19	1-(2-naphthalene)ethanol	1.14 ± 0.23[b]	1.25
20	1,2,3,4-tetrahydro-1-naphthol	0.43 ± 0.25	0.60
21	5,6,7,8-tetrahydro-1-naphthol	0.99 ± 0.36[b]	1.10
22	5,6,7,8-tetrahydro-2-naphthol	0.98 ± 0.30[b]	1.10
23	9-hydroxymethylfluorene	1.28 ± 0.33[b]	
24	2-hydroxybiphenyl	1.37 ± 0.33[b]	1.29
25	4-hydroxybiphenyl	1.21 ± 0.57[b]	1.30

(b) Hydrogen Bond Acceptors

		$\log_{10} P_{H/W}$	
no.	substance *i*	exptl[c]	pred. (LSER)
26	1,2-dimethoxybenzene	1.22 ± 0.31	1.79
27	ethoxybenzene	2.78 ± 0.17[d]	3.40
28	1-fluoro-2-nitrobenzene	1.16 ± 0.35	1.45
29	1-fluoro-3-nitrobenzene	1.47 ± 0.30	1.52
30	1-fluoro-4-nitrobenzene	1.32 ± 0.30	1.61
31	3,5-difluoronitrobenzene	1.69 ± 0.22	1.71
32	2-chlorobenzaldehyde	1.75 ± 0.20	1.38
33	3-chlorobenzaldehyde	1.70 ± 0.24	1.46
34	3′-chloroacetophenone	1.86 ± 0.19	1.67
35	4′-chloroacetophenone	1.83 ± 0.18	1.75
36	2′-bromoacetophenone	1.72 ± 0.20	1.94
37	3′-bromoacetophenone	2.03 ± 0.14	2.03
38	4′-bromoacetophenone	2.01 ± 0.14	1.98
39	phenacyl bromide	1.57 ± 0.21	1.55
40	benzo[*b*]furan	2.39 ± 0.29	2.38
41	benzothiophene	2.42 ± 0.08	2.69

[a] Applying calibration curve II. [b] Results outside of calibration data for calibration curve II. [c] Applying calibration curve III. [d] Results outside of calibration data for calibration curve III.

procedure. The differences in log $P_{H/W}{}^{(i)}$ resulting from applying different calibration curves are about the same as differences between the results from the HPLC and the shake-flask method. Those differences are mostly below 0.3 but might increase for some solutes to about 0.5. The experimental results for the partition coefficients are summarized for hydrogen bond donors and acceptors in parts a and b of Table 3, respectively. All experimental data are within the range covered by calibration curve I; however, some results for hydrogen bond donors as well as one result for a hydrogen acceptor are outside the calibration curves II or III, respectively. Table 3a,b also gives estimates for the experimental uncertainty of log $P_{H/W}$. Those experimental uncertainties are either the standard deviation of the experimental results σ (eqs 5 and 6) or the differences in log $P_{H/W}$ from applying different calibrations curves (hydrogen bond donors: calibration curves I and II, Table 3a; hydrogen bond acceptors: calibration curves I and III, Table 3b), whichever is larger.

Comparison with Predictions from the LSER-Method. In the linear solvation energy relationship (LSER) method, the partitioning of a solute to an organic/aqueous two-phase system is described by contributions due to van der Waals forces, free volume effects, interactions due to permanent as well as to induced dipoles, and the tendency to form hydrogen bonds as an electron acceptor (HBA) or an electron donor (HBD) (Meyer and Maurer, 1993). It is assumed that those different effects can be separated, and therefore their contributions to the Gibbs excess energy (and to the logarithm of the partition coefficient) are additive. Each contribution to the logarithm of the partition coefficient is written as a product of two properties: one characterizes the solute, while the other is a property of the organic/aqueous two-phase system:

$$\log P_{O/W}{}^{(i)} = A_{O/W} + v_i \cdot B_{O/W} + \pi_i \cdot C_{O/W} + \delta_i \cdot D_{O/W} + \beta_i \cdot E_{O/W} + \alpha_i \cdot F_{O/W} \quad (7)$$

For hexane + water at 25 °C, the parameters were determined by fitting to a data set of partition coefficients taken from literature, giving $A_{H/W} = 0.404$, $B_{H/W} = 5.382$, $C_{H/W} = -1.786$, $D_{H/W} = 0.856$, $E_{H/W} = -4.644$; and $F_{H/W} = -3.078$ (Dürr, 1997). A solute *i* is characterized by a volume parameter v_i, a polarity parameter π_i, a polarizability parameter δ_i, a HBA parameter β_i, and a HBD parameter α_i. Solute parameters were either taken from Kamlet et al. (1988) or determined by experiment or by estimation (Dürr, 1997). However, no parameters are available for 4-methoxyphenol, indole, 2-methylindole, 3-methylindole, and 9-(hydroxymethyl)fluorene. The solute parameters are given in Table 4.

For 14 (out of 20) HBD compounds, predicted partition coefficients agree with the experimental results within experimental uncertainty (Table 3a). Out of the remaining six solutes, for four solutes the difference between the experimental results and the prediction is less than twice the experimental uncertainty, and for the remaining two solutes the difference is less than the 3-fold of the experimental uncertainty. Such a good agreement is also observed for hydrogen bond accepting solutes (Table 3b). For 12 (out of 16) HBA compounds the predictions from the LSER method agree with the experimental results within experimental uncertainty. For three more solutes that

Table 4. Substances and LSER Parameters (Dürr, 1997)

						LSER parameter				
substance	formula	synonym	CAS no.[b]	supplier	purity %	ν	π	δ	β	α
benzene[c]	C_6H_6		[71-43-2]	Aldrich	99.9+	0.491	0.59	0.68	0.10	0
phenol[c]	C_6H_6O		[108-95-2]	Merck	99.5 pa	0.536	0.72	0.52	0.33	0.61
benzaldehyde[c]	C_6H_7O		[100-52-7]	Fluka	>99	0.606	0.92	1.39	0.44	0
toluene[c]	C_7H_8	methylbenzene	[108-88-3]	PCK	pa	0.592	0.55	1.0	0.11	0
o-cresol	C_7H_8O	2-methylphenol	[95-48-7]	Merck	>99 fs	0.637	0.68	1.0	0.41	0.54
m-cresol	C_7H_8O	3-methylphenol	[108-39-4]	Merck	>98 fs	0.637	0.68	1.0	0.41	0.54
p-cresol	C_7H_8O	4-methylphenol	[106-44-5]	Fluka	>99 fs	0.637	0.68	1.0	0.41	0.54
1,2-dihydroxy-4-methylbenzene	$C_7H_8O_2$	3,4-dihydroxytoluene; 4-methylcatechol	[452-86-8]	Aldrich	>99 (GC)	0.682	0.81	1.0	0.64	0.61
2-methoxyphenol	$C_7H_8O_2$	1-hydroxy-2-methoxybenzene	[90-05-1]	Fluka	>98					
4-methoxyphenol	$C_7H_8O_2$	1-hydroxy-4-methoxybenzene	[150-76-5]	Janssen	>99					
1-benzo[*b*]furan	C_8H_6O	coumarone	[271-89-6]	Janssen	>99	0.641	0.86	1.0	0.17	0
1-benzothiophene	C_8H_6S	thionaphthene	[95-15-8]	Aldrich	99	0.697	0.86	1.0	0.17	0
indole	C_8H_7N		[120-72-9]	Merck	99 pa					
2,3-dimethylphenol	$C_8H_{10}O$		[526-75-0]	Janssen	99	0.738	0.64	1.0	0.42	0.54
2,4-dimethylphenol	$C_8H_{10}O$		[105-67-9]	Fluka	>97 (GC)	0.738	0.64	1.0	0.42	0.54
3,5-dimethylphenol	$C_8H_{10}O$		[103-73-1]	Janssen	98	0.738	0.64	1.0	0.42	0.54
ethoxybenzene	$C_8H_{10}O$		[108-68-9]	Janssen	99 +	0.722	0.72	1.0	0.10	0
2-ethylphenol	$C_8H_{10}O$		[90-00-6]	Janssen	99	0.735	0.66	1.0	0.41	0.54
4-ethylphenol	$C_8H_{10}O$		[123-07-9]	Fluka	>97 (GC)	0.735	0.66	1.0	0.41	0.54
1,2-dimethoxybenzene	$C_8H_{10}O2$	veratrole	[91-16-7]	Aldrich	99 (GC)	0.757	0.84	1.0	0.44	0
2-methylindole	C_9H_9N		[95-20-5]	Fluka	98					
3-methylindole	C_9H_9N	scatole	[83-34-1]	Fluka	>99					
2-*n*-propylphenol	$C_9H_{12}O$		[644-35-9]	Janssen	98	0.833	0.64	1.0	0.41	0.54
1-naphthol	$C_{10}H_8O$	α-naphthol	[90-15-3]	Fluka	>99	0.795	0.97	1.0	0.38	0.54
1,4-dihydroxynaphthalene	$C_{10}H_8O_2$	1,4-naphthalenediol	[571-60-8]	Janssen	98	0.843	1.02	1.0	0.56	0.61
1,5-dihydroxynaphthalene	$C_{10}H_8O_2$	1,5-naphthalenediol	[83-56-7]	Janssen	99	0.843	1.09	1.0	0.56	0.61
2,3-dihydroxynaphthalene	$C_{10}H_8O_2$	2,3-naphthalenediol	[92-44-4]	Janssen	98	0.843	0.97	1.0	0.56	0.61
2,6-dihydroxynaphthalene	$C_{10}H_8O_2$	2,6-naphthalenediol	[581-43-1]	Aldrich	98	0.843	1.09	1.0	0.56	0.61
(±)-1,2,3,4-tetrahydro-1-naphthol	$C_{10}H_{12}O$	(±)-α−tetralol, 1-hydrotetralin	[529-33-9]	Aldrich	97	0.859	0.96	1.0	0.55	0.33
5,6,7,8-tetrahydro-1-naphthol	$C_{10}H_{12}O$		[529-35-1]	Janssen	99	0.854	0.69	1.0	0.40	0.54
5,6,7,8-tetrahydro-2-naphthol	$C_{10}H_{12}O$		[1125-78-6]	Janssen	98	0.854	0.69	1.0	0.40	0.54
2-(1,1-dimethylethyl)phenol	$C_{10}H_{14}O$	2-*tert*-butylphenol	[88-18-6]	Merck	>98 fs	0.928	0.62	1.0	0.34	0.58
4-(1,1-dimethylethyl)phenol	$C_{10}H_{14}O$	4-*tert*-butylphenol	[98-54-4]	Fluka	99	0.928	0.62	1.0	0.34	0.58
1-(hydroxymethyl)naphthalene	$C_{11}H_{10}O$	1-naphthalenemethanol	[4780-79-4]	Aldrich	98	0.895	1.05	1.0	0.50	0.35
2-(hydroxymethyl)naphthalene	$C_{11}H_{10}O$	2-naphthalenemethanol	[1592-38-7]	Aldrich	99	0.895	1.05	1.0	0.50	0.35
2-hydroxybiphenyl	$C_{12}H_{10}O$|	biphenyl-2-ol	[90-43-7]	Merck	99 fs	0.961	1.02	1.50	0.45	0.54
4-hydroxybiphenyl	$C_{12}H_{10}O$	biphenyl-4-ol	[92-69-3]	Merck	98 fs	0.961	1.02	1.50	0.45	0.54
(±)-2-(1-hydroxyethyl)-naphththalene	$C_{12}H_{12}O$	(±)-methyl-2-naphthylcarbinol	[40295-80-5]	Fluka	>99	0.993	1.05	1.0	0.53	0.33
9-(hydroxymethyl)fluorene	$C_{14}H_{12}O$	9-(hydroxymethyl)fluorene	[24324-17-2]	Aldrich	99					
3,5-difluoronitrobenzene	$C_6H_3F_2NO_2$		[2265-94-3]	Sigma	99	0.676	1.11	1.0	0.26	0
1-fluoro-2-nitrobenzene	$C_6H_4FNO_2$	2-fluoronitrobenzene	[1493-27-2]	Fluka	>98	0.651	1.11	1.0	0.28	0
1-fluoro-3-nitrobenzene	$C_6H_4FNO_2$	3-fluoronitrobenzene	[402-67-5]	Fluka	>97	0.651	1.06	1.0	0.28	0
1-fluoro-4-nitrobenzene	$C_6H_4FNO_2$	4-fluoronitrobenzene	[350-46-9]	Fluka	>98	0.651	1.01	1.0	0.28	0
2-chlorobenzaldehyde	C_7H_5ClO		[89-98-5]	Fluka	>98	0.698	1.02	1.39	0.40	0
3-chlorobenzaldehyde	C_7H_5ClO		[587-04-2]	Fluka	97	0.698	0.97	1.39	0.40	0
4-chlorbenzaldehyde	C_7H_5ClO		[104-88-1]	Fluka	>98	0.698	0.92	1.39	0.40	0
ω-bromoacetophenone	C_8H_7BrO	phenacyl bromide	[70-11-1]	Sigma		0.818	1.00	1.0	0.50	0
1-acetyl-2-bromobenzene	C_8H_7BrO	2′-bromacetophenone	[2142-69-0]	Fluka	99	0.821	1.00	1.0	0.45	0
1-acetyl-3-bromobenzene	C_8H_7BrO	3′-bromacetophenone	[2142-63-4]	Fluka	>98	0.821	0.95	1.0	0.45	0
1-acetyl-4-bromobenzene	C_8H_7BrO	4′-bromoacetophenone	[99-90-1]	Fluka	>98	0.821	0.90	1.0	0.45	0
1-acetyl-3-chlorobenzene	$C_8H_7C_{10}$	3′-chloroacetophenone	[99-02-5]	Fluka	>97	0.796	0.95	1.12	0.45	0
1-acetyl-4-chlorobenzene	$C_8H_7C_{10}$	4′-chloroacetophenone	[99-91-2]	Fluka	>97	0.796	0.90	1.12	0.45	0
water	H_2O		[7732-18-3]	Merck	HPLC					
hexane	C_6H_{14}		[110-54-3]	Fluka	HPLC					
methanol	CH_3OH		[67-56-1]	Merck	HPLC					

[a] Abbreviations: PCK, Petrochemisches Kombinat, Schwedt (Germany); GC, purity determined by gas chromatography; pa, for analysis; fs, for synthesis; HPLC, for HPLC. [b] Supplied by the author. [c] LSER parameter from Kamlet et al. (1988).

difference is smaller than twice the experimental uncertainty. Only for ethoxybenzene (pred. 3.40; exptl 2.78 ± 0.17) and for benzothiopene (pred. 2.69; exptl 2.42 ± 0.08) the difference is more than twice the experimental uncertainty.

These comparisons thus confirm that the LSER method provides reliable estimates for partition coefficients in liquid two-phase systems of hexane + water near ambient temperature.

Summary

Partition coefficients in hexane + water were determined for 41 solutes (25 proton donors and 16 proton acceptors) at 298.15 K by means of the reverse-phase high-performance liquid chromatography (RP-HPLC) method. For those substances such experimental data has not been available in the literature before. Most experimental results agree within experimental uncertainty with predictions from the linear solvation energy relationship (LSER) method.

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