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Partition Coefficients of Organic Solutes between Supercritical Carbon Dioxide and Water: Experimental Measurements and Empirical Correlations

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CO_2/H_2O partition coefficients ($K^x_{C/W}$) of 18 compounds have been measured at $t = 300$ K and $P = 80$ bar, which is equivalent to a carbon dioxide fluid density of 0.76 g cm^{-3}. This expands the range of compounds for which such data are available to include aldehydes, ketones, esters, and halides. With this contribution, $K^x_{C/W}$ data for 49 compounds are now available. Three correlation methods were tested to estimate partition coefficients based on molecular structure and/or physicochemical properties: (1) comparison to water solubility; (2) comparison to solvent/water partition coefficients; and (3) linear solvation energy relationship (LSER) estimation. Correlations (to within ±0.30 log units) between $K^x_{C/W}$ and either water solubility or octanol/water partition coefficients were found using the first two methods provided that hydrogen-bond donors were excluded from the regression. A correlation (±0.30 log units) was found between $K^x_{C/W}$ and carbon disulfide/water partitioning, with benzyl alcohol as the lone exception. The LSER approach was relatively robust, with good agreement (to within ±0.20 log units) between measurements and predictions for all compounds analyzed. Solute acidity, basicity, and molecular volume were important LSER parameters, reflecting the limited hydrogen bonding opportunities possible in carbon dioxide as compared to water.

Introduction

Although supercritical carbon dioxide ($scCO_2$) is a nontoxic, readily available, benign alternative to traditional organic solvents, its adoption as a solvent for reactions[1] on an industrial scale has been slower than for processes such as extraction.[2] One of the primary reasons for this slow development is that few compounds show appreciable solubility in $scCO_2$ at modest temperatures and pressures. Attempts to increase the solubility of compounds often compromise the environmentally benign nature of $scCO_2$. For instance, though addition of polar organic cosolvents can greatly increase the solubility of many nonvolatile compounds in $scCO_2$,[3,4] the resulting reaction mixture is generally less environmentally innocuous than pure carbon dioxide. Water, which would not significantly impact the green nature of carbon dioxide, is not appreciably soluble in the compressed fluid at moderate conditions[5−8] and cannot be used as a polar cosolvent. The combination of $scCO_2$ and water as a biphasic reaction solvent system, however, is receiving increasing attention.[9−12] Not only do water and $scCO_2$ exhibit complementary solvation powers but the biphasic system presents an ideal way of deploying phase-separable homogeneous catalysts.[11]

Proper analysis of reaction-rate data in water−carbon dioxide systems (and therefore accurate design of biphasic reactors) frequently depends on a knowledge of the partitioning of organic solutes between the two phases. Despite the use of $scCO_2$ as an extraction solvent from highly aqueous media for some time, published data of partition coefficients between water and carbon dioxide are sparse. Although partition coefficients have been reported for 29 compounds at 300 specific state points,[13−24] nearly half of these compounds[22] are substituted phenols. For these compounds, the influence of pressure, density, and temperature on the partition coefficient have been thoroughly characterized, and variables such as water phase ionic strength and pH have been investigated to some degree.[21,24] What is lacking is a broad spectrum of compounds for which partition-coefficient data are available. As a result of the narrow data set, predictive models, which require a larger library of compounds in order to be sufficiently robust, are underdeveloped.

Ideally, a semiempirical model could be developed with the predictive capabilities necessary for engineering purposes. Though many of the studies discussed above presented equations of state (EOSs) for data modeling, such methods are best suited to interpolation of existing temperature−pressure data for a given compound rather than for estimation of partition coefficients of new compounds. By comparison, an empirical approach can be expected to provide estimates of the partition-coefficient solutes based primarily on molecular structure and physicochemical properties. A general predictive method, with sufficient accuracy, would find applications in the design and development of biphasic CO_2-H_2O reaction systems (including reactions occurring in emulsions and microemulsions) and equipment for the extraction of organic species from aqueous streams using a dense CO_2 phase. In addition, such methods would potentially aid the rational design of CO_2−philic ligands for chelation and subsequent extraction of transition metals from water or phase segregation of

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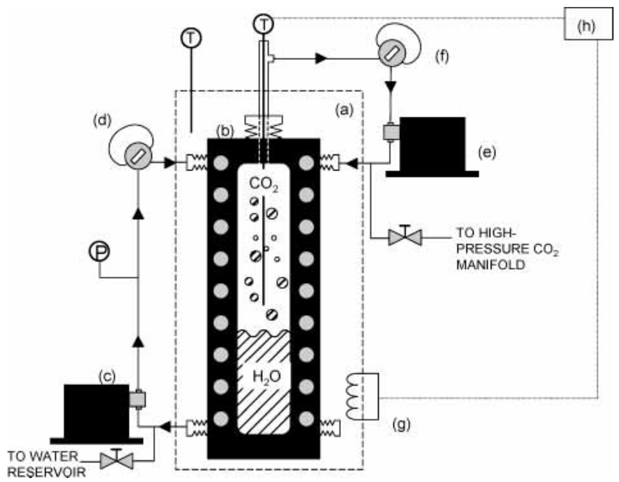

Figure 1. Experimental apparatus used for partition coefficient measurements: a, agitated water bath; b, high-pressure vessel (Jerguson sight gauge); c, water pump; d, water sampling valve; e, carbon dioxide pump; f, carbon dioxide sampling valve; g, water heater/circulator; h, PID controller.

homogeneous catalysis in biphasic (CO_2-H_2O) systems. Robust estimation methods are particularly desirable because measurement of CO_2-H_2O partition coefficients requires specialized, high-pressure equipment.

Given that *a priori* prediction of partition coefficients is such a tantalizing goal, it is not surprising that several researchers have already investigated the possibility. Karásek et al.[22] found no correlation between group-contribution estimates of octanol−water partition coefficients ($K_{O/W}$) and carbon dioxide/water partition coefficients ($K_{C/W}$) for substituted phenols and benzoic acids. Lagalante and Bruno[25] demonstrated the use of linear solvation energy relationships (LSERs) to correlate CO_2-H_2O partition-coefficient data. The investigators reported less than 25% average absolute relative deviation (AARD) between the measured and LSER-predicted values of $K_{C/W}$ for the 6 compounds considered. Both these efforts were limited by the number of compounds analyzed.

In our study, we measured partition coefficients for 18 new compounds at 300 K and 80 bar. These measurements significantly expand the database of partition coefficients to include aldehydes, ketones, esters, and halides. Because previous researchers have sufficiently investigated the effects of temperature and pressure (or density) on $K_{C/W}$ (albeit for a narrow range of compounds), we did not investigate these effects. Our data, combined with the values previously reported in the literature, were then analyzed using three methods: (1) comparison to water solubility, (2) comparison to partitioning in other solvent pairs, and (3) estimation using LSER.

Experimental Section

Apparatus. All measurements were made using a high-pressure cell (Jerguson, 19T-40) with a nominal internal volume of 50 mL. The complete apparatus is shown in Figure 1. There was nearly complete optical access into the high-pressure cell so that 2-phase behavior could be confirmed visually for all experiments. The maximum operating pressure of the cell was rated at 340 bar at 313 K. The high-pressure cell was immersed in a temperature-controlled (Omega, 9001CN) water bath (VWR, 1110). Temperatures in the high-pressure cell were measured to within ±0.5 K (the rated accuracy of the thermocouple as reported by Omega Engineering) using a calibrated T-type thermocouple which was fully immersed in the fluid. Normally, temperature fluctuations during the course of a run were less than 0.2 K. Pressure was measured with a digital (piezo-type) pressure gauge (Omega, DPG5000L-5K) to within ±1 bar (the rated accuracy of the gauge as reported by Omega Engineering). All experiments were performed at 300 K and 80 bar. An EOS[26] accurate for pure CO_2 and recommended by NIST,[27] was used to calculate a fluid density of $0.76 \pm 0.01\ g{\cdot}cm^{-3}$, where the uncertainty is based on the known accuracies of the temperature and pressure measurements. A high-pressure pump (Eldex, BBB-4, rated for $100\ mL{\cdot}min^{-1}$) was used to recirculate the water phase through the CO_2 to provide good interfacial contact for mass transport. The CO_2 phase was recirculated using a second high-pressure pump (Eldex, B-100-S, rated at $5\ mL{\cdot}min^{-1}$) to ensure adequate mixing in the CO_2 phase. The vigorous pumping also limited temperature variations within the fluid to less than approximately 0.2 K.

The recirculating fluids (both water and CO_2) were sampled through high-pressure sampling valves (VICI, UW-type) equipped with sample loops with volumes calibrated to within ±2.5% (VICI). These samples were depressurized by slowly bubbling the expanding gas through a small volume of acetone over several minutes. Samples were then diluted to standard volumes using volumetric flasks (volumes calibrated to within 0.1 to 0.5%, depending on the volume of the flask) prior to further analysis. Both the volume of sample taken from the reactor ($25\ \mu L \le \underline{V}_{S,C}$, $\underline{V}_{S,W} \le 500\ \mu L$) and the volume of acetone used for depressurization and dilution ($5\ mL \le \underline{V}_{D,C}$, $\underline{V}_{D,W} \le 50\ mL$) were varied to confirm that solute collection efficiency was as close to 100% as possible. Chilled (~0 °C) acetone was used for volatile compounds (e.g., hydrocarbons) to minimize evaporative losses.

After dilution, samples were analyzed using gas chromatography (GC, Agilent, 6890) equipped with a flame-ionization detector (FID) and a DB-Wax column (J&W Scientific). The FID was calibrated using standard solutions of defined molar concentrations, and a linear relationship between peak area and molar concentration was observed in all instances. Dilution factors were chosen to ensure final concentrations that were within the bounds of this linear relationship. Taking into account both the errors associated with the sampling procedure and the analytical technique, the concentration of solute in the carbon dioxide phase could be measured to within ±7% and that in the water phase to within ±5% in most cases. For instances in which the concentration of solute in the water phase was on the order of several parts per million (e.g., hexane), the error was estimated as ±15%, reflecting the poor signal-to-noise ratio of such measurements. The uncertainties in experimental determinations of solute concentration in the high-pressure reactor are standard deviations based on chemical analysis of many dozens of samples withdrawn from the reactor under controlled conditions.

Materials. Grade 5.5 carbon dioxide (certified purity greater than 99.999%) was purchased from BOC Gases and used as received. Water was deionized (Barnstead, Nanopure) to a minimum resistivity of 18.0 MΩ·cm and used immediately. All other organic chemicals (including solutes for partitioning and acetone as a solvent) were purchased from Sigma-Aldrich at the highest available purity and used as received.

Methods and Data Analysis. The partition coefficient (denoted, in molar units, as $K^{C}_{C/W}$) of a given solute was calculated from the ratio of its molar concentration in the carbon dioxide phase ($C_i^{(C)}$) to that in the water phase ($C_i^{(W)}$). Molar concentrations of diluted samples were measured by GC (denoted $C_{i,GC}^{(C)}$ and $C_{i,GC}^{(W)}$, respectively) and corrected to the contactor concentrations by the appropriate dilution factors. The partition coefficient can thus be calculated with the following formula

$$K^{C}_{C/W} = \left(\frac{C_i^{(C)}}{C_i^{(W)}}\right) = \left(\frac{C_{i,GC}^{(C)}}{C_{i,GC}^{(W)}}\right)\left(\frac{\underline{V}_{D,C}/\underline{V}_{S,C}}{\underline{V}_{D,W}/\underline{V}_{S,W}}\right) \tag{1}$$

where $\underline{V}_{S,C}$ and $\underline{V}_{S,W}$ are the volumes of the samples taken using the high-pressure sample valve and sample loop, and $\underline{V}_{D,C}$ and $\underline{V}_{D,W}$ are the volumes after dilution with acetone.

The conventional means of presenting data over a range of densities is to use a mole-fraction-based partition coefficient, $K^{x}_{C/W}$. At low concentrations of the solute, the conversion between molar units and mole fraction units is given by

$$K^{x}_{C/W} = K^{C}_{C/W}\frac{\rho_W}{\rho_C}\frac{MW_C}{MW_W} \tag{2}$$

Here, MW_C and MW_W are the molecular weights of carbon dioxide (44.01 g·mol^{-1}) and water (18.01 g·mol^{-1}) and ρ_C and ρ_W are the densities of the respective phases. The density of water[28] was determined to be 1.000 ± 0.002 g·cm^{-3}. For both solvents, the concentration of the solute was assumed to be low enough that pure component densities were accurate.

To allow for equilibration, we waited for at least 3 h between charging the reactor with the solute and taking the first sample. For several runs, we allowed 12 h for equilibration (with continuous recirculation of the two phases) and found that there was no statistical difference between these measurements and those made when 3 h were allowed for equilibration. For each run, between 3 and 6 samples were taken from each phase over a period of 3 h. In a typical run, 5 samples were obtained from each phase. No noticeable drift in GC peak area signal was apparent over the course of the measurements. Initial solute concentration was varied between 4×10^{-3} (wt/wt of CO_2) and 8×10^{-4} (wt/wt of CO_2) with no statistically significant difference in measured values of $K^{x}_{C/W}$. The ratio of the volumes of water and carbon dioxide charged to the reactor was varied from 0.5 to 2.0 with no apparent effect on $K^{x}_{C/W}$.

By use of the procedures described above, between 2 and 6 separate measurements were made of each value for $K^{x}_{C/W}$ reported herein. Reported values of $K^{x}_{C/W}$ are the arithmetic average of these independent measurements. The standard deviation of these replicate measurements was taken to be an estimate of the uncertainty in the reported mean value. To determine the accuracy of a given partition coefficient, the estimated errors in the actual measured variables (i.e., $\underline{V}_{S,C}$, $\underline{V}_{S,W}$, $\underline{V}_{D,C}$, $\underline{V}_{D,W}$, $C_{i,GC}^{(C)}$, $C_{i,GC}^{(W)}$), ρ_C, and ρ_W, were propagated though eqs 1 and 2 using a well-known procedure.[29] In all instances, accuracy was limited by errors in $C_{i,GC}^{(C)}$ and $C_{i,GC}^{(W)}$, and reproducibility was always equal to or better than the estimated accuracy, as should be expected.

Results

Values of $K^{x}_{C/W}$ (at a fixed $scCO_2$ density of 0.76 g·cm^{-3}) for all compounds for which it has been measured are listed in Table 1 (this work) and Table 2 (all other sources). Literature data were interpolated to a $scCO_2$ density of 0.76 g·cm^{-3} in several instances. Interpolation was facilitated by the fact that $K^{x}_{C/W}$ is very nearly a unique function of density for all compounds and conditions for which data are available. No error is given in Table 2 for values interpolated from data in the literature, but on the basis of plots of $K^{x}_{C/W}$ vs ρ, the error due to interpolation is estimated to be less than 20% in most cases. When no data were available at or above a CO_2 density of 0.76 g·cm^{-3}, no attempt to extrapolate existing data to that density was made and the value of $K^{x}_{C/W}$ at the highest density for which data are available is listed instead. The large error reported for the partition coefficient of hexane is due to the low water solubility of this compound. Attempts to measure the partition coefficient of octane were made, but the concentration of octane in the water phase was less than the detection limit of the analytical method (roughly 1 ppm). The detection limit provides a lower-bound estimate of approximately 100 000 for $K^{x}_{C/W}$ of octane.

Table 1. Values of $K^{x}_{C/W}$ Measured in This Study[a]

	compound	$K^{x}_{C/W}$
1	acetophenone	48.5 ± 4.6
2	benzaldehyde	39.1 ± 3.7, 39[b]
3	bromobenzene	1 090 ± 100
4	3-buten-2-one	7.8 ± 1
5	chlorobenzene	1 140 ± 110
6	cyclohexane	4 900 ± 600
7	cyclohexene	1 900 ± 300
8	cyclopentene	1 400 ± 180
9	ethylbenzoate	550 ± 100
10	fluorobenzene	770 ± 150
11	hexane	9 000 ± 3 000
12	2-methoxyacetophenone	47.3 ± 4
13	3-methoxyacetophenone	84.0 ± 7
14	methylbenzoate	205 ± 21
15	propiophenone	121 ± 13
16	propylbenzoate	1 050 ± 220
17	tetrahydrofuran	8.5 ± 1.0
18	toluene	1 200 ± 250, 5 083[c]

[a] All data were measured at a fixed CO_2 density of 0.76 g·cm^{-3}. Available literature data for compounds considered in this study are also listed for comparison. [b] Value reported by Wagner et al.[19] [c] Value reported by Yeo and Akgerman,[13] measured at 0.59 g·cm^{-3}.

Some observations can be made regarding the data in Tables 1 and 2. First, the measured partition coefficients span nearly 5 orders of magnitude (from 0.10 to almost 10 000) and include primarily carbon-dioxide-philic compounds (i.e., compounds which prefer CO_2 to water). Salicylic acid, caffeine, and 4-nitrophenol are the only compounds with values of $K^{x}_{C/W}$ that are less than unity. For compounds for which multiple data points are available, there is reasonably good agreement. For example, there are 4 separate estimates of the partition coefficient for phenol,[15,16,18,22] the values of which range from 0.5 to 1.4. Measurements for the partition coefficient of 2,4-dichlorophenol exhibit somewhat better agreement (42[14] to 70[22]). Benzene measurements agreed better still (2 756[13] vs 3 500[16]). Our value for toluene does not agree well with the published value,[13] but there is excellent agreement between our value and the literature value[19] for benzaldehyde. Although variations between research groups may be attributed in part to the density-interpolation technique used here, deviations greater than roughly 40% (±20% for each data point) cannot be attributed to our data-handling procedures.

Curren and Burk[21] may provide insight into the discrepancies in $K^{x}_{C/W}$ reported by different research groups. For the partitioning of pentachlorophenol, Curren and Burk[21]

Table 2. Compilation of All Values for $K^x_{\mathrm{C/W}}$ Reported in the Literature[a]

	compound	$K^x_{\mathrm{C/W}}$	source
1	acetylacetone	3^b	Gervais et al.[24]
2	aniline	2.1	Wagner et al.[19]
3	benzene	$2\,756^c$	Yeo and Akgerman[13]
		3 500	Ghonasgi et al.[16]
4	benzoic acid	1.3	Brudi et al.[18]
5	benzyl alcohol	1.9	Brudi et al.[18]
6	caffeine	0.15	Brudi et al.[18]
7	2-chlorophenol	14	Karásek et al.[22]
8	4-chlorophenol	3	Ghonasgi et al.[16]
9	cyclohexanone	41	Brudi et al.[18]
10	1,2-dichloroethane	154	Sengupta et al.[17]
11	2,4-dichlorophenol	70	Karásek et al.[22]
		30	Akgerman and Carter[14]
12	2,4-dichlorophenoxacetic acid	0.1	Curren and Burk[21]
13	2,4-dimethylphenol	10.7	Karásek et al.[22]
14	hexafluoroacetylacetone	0.7	Gervais et al.[24]
15	2-hexanone	118	Brudi et al.[18]
16	3-methyl-4-chlorophenol	6	Karásek et al.[22]
17	2-methyl-4,6-dinitrophenol	55	Karásek et al.[22]
18	2-methyl-5-hexyloxymethyl-8-quinolinol	500	Ohashi et al.[23]
19	3-methylphenol	4	Ghonasgi et al.[16]
20	naphthalene	347^d	Yeo and Akgerman[13]
21	2-nitrophenol	80	Karásek et al.[22]
22	4-nitrophenol	0.2	Karásek et al.[22]
23	parathion	18.3^d	Yeo and Akgerman[13]
24	pentachlorophenol	80^e	Curren and Burk[20]
		8^f	Curren and Burk[20]
25	phenol	1.0	Brudi et al.[18]
		0.5	Roop et al.[15]
		1.3	Karásek et al.[22]
		1.4	Ghonasgi et al.[16]
26	salicylic acid	0.3	Karásek et al.[22]
27	1,1,2,2-tetrachloroethane	84	Sengupta et al.[17]
28	2,3,4,5-tetrachlorophenol	15	Curren and Burk[21]
29	1,1,2-trichloroethane	28	Sengupta et al.[17]
30	2,4,6-trichlorophenol	150	Karásek et al.[22]
31	vanillin	1.5	Brudi et al.[18]

[a] All data were measured at (or interpolated to) a fixed CO_2 density of 0.76 $g\cdot cm^{-3}$, unless otherwise noted. [b] Data not available at 0.76 $g\cdot cm^{-3}$, value cited measured at 0.85 $g\cdot cm^{-3}$. [c] Data not available at 0.76 $g\cdot cm^{-3}$, value cited measured at 0.50 $g\cdot cm^{-3}$. [d] Data not available at 0.76 $g\cdot cm^{-3}$, value cited measured at 0.59 $g\cdot cm^{-3}$. [e] Reported value measured at a solute concentration of 11.6 $\times 10^{-6}$ mass fraction (total solvent basis). [f] Reported value measured at a solute concentration of 1.27 $\times 10^{-6}$ mass fraction (total solvent basis).

found $K^x_{\mathrm{C/W}}$ to have a strong dependence on the concentration of the solute. When operating under conditions near water saturation, a partition coefficient of approximately 80 was measured, while at 20% of the saturation concentration the partition coefficient was found to be less than 10. Thus, some of the discrepancies between different researchers may be due to differences in the overall solute concentrations that were used in their experiments. Nonetheless, we did not find a strong dependence of solute partitioning on concentration for the combination of compounds and conditions considered in our study.

Partition-coefficient dependence on solute concentration notwithstanding, some generalizations can be made. As a rule, trends in $K^x_{\mathrm{C/W}}$ agree with those predicted based on water solubility. In the series methyl-, ethyl-, propylbenzoate, the partition coefficient increases regularly with the length of the alkyl chain as would be predicted on the basis of decreasing water solubility. Likewise, introduction of cyclization (2-hexanone−cyclohexanone, hexane−cyclohexane) or unsaturation (hexane−hexene) decreases $K^x_{\mathrm{C/W}}$ by increasing water solubility. Increasing the number of carbons in ring structures seems to increase the partition coefficient (cyclopentene−cyclohexene). Addition of the highly water-soluble hydroxyl- functional group decreases the $K^x_{\mathrm{C/W}}$ of benzaldehyde dramatically from 40 to roughly unity (vanillin).

There are some apparent exceptions to the correlation between water solubility and $K^x_{\mathrm{C/W}}$. Reported values for the partition coefficient of toluene bracket those of benzene, though the relative water solubilities of the two compounds would suggest that the partition coefficient of toluene should be greater than that of benzene. As explained previously, for compounds with extremely large values of $K^x_{\mathrm{C/W}}$, the experimental error tends to be rather large, possibly accounting for this surprising trend. Water solubility of benzyl halides decreases regularly in the series fluoro-, chloro-, and bromobenzene. Measured partition coefficients are consistent with water solubility for fluoro- and chlorobenzene but not bromobenzene. Water solubility alone would predict that bromobenzene would partition more favorably into carbon dioxide than does chlorobenzene. As successive chlorines are added to phenol (2-chlorophenol, 2,4-chlorophenol, 2,4,6-trichlorophenol, 2,3,4,5-tetrachlorophenol, and pentachlorophenol), the resulting compounds are generally less water soluble and exhibit higher values of $K^x_{\mathrm{C/W}}$, though 2,3,4,5-tetrachlorophenol does not seem to follow this trend. The fact that 2,3,4,5-tetrachlorophenol does not follow the trend observed for the other chlorophenols may indicate erroneous measurements of one or more of the compounds in the series or it may be indicative of more complicated behavior perhaps related to the effect of solute concentration on the measured partition coefficient.

The position of substituents has a large and irregular effect on $K^x_{\mathrm{C/W}}$; $K^x_{\mathrm{C/W}}$ for 2-nitrophenol is 400 times greater than that for 4-nitrophenol, though $K^x_{\mathrm{C/W}}$ for 2-chlorophenol is only 4 times greater than that for 4-chlorophenol. The strong effect of substituent position was first noted by Karásek et al.[21] and was ascribed to the capacity of the different isomers to form inter- and intramolecular hydrogen bonds. This theory is consistent with intramolecular hydrogen bonding of 2-nitrophenol between the phenolic hydrogen and one of the oxygens in the nitro group. Such intramolecular hydrogen bonding would reduce the capacity of the acidic proton to participate in intermolecular hydrogen bonding and cause the solute to partition more favorably into the carbon dioxide phase than would otherwise be expected. This behavior would be less dramatic in conventional solvent pairs. In these cases, the water phase would likely be buffered at or near neutral pH and 2-nitrophenol is partially ionized at such conditions ($pK_a = 7.21$[30]). In the carbon dioxide−water system at conditions near 300 K and 80 bar, the pH of unbuffered water is roughly 3.0,[31] indicating that 2-nitrophenol is entirely protonated and free to participate in internal hydrogen bonding in both solvents. A much less dramatic effect of substituent location is observed when intramolecular hydrogen bonding is not expected, such as is the case for 2-chlorophenol vs 4-chlorophenol and 2-methoxyacetophenone vs 3-methoxyacetophenone.

Discussion

Three types of empirical methods for correlating data were examined in order to assess their abilities to extend the data set to include new compounds: comparison to water solubility, comparison to other solvent−water pairs, and LSERs. Overall, the water solubility correlation provided relatively good estimates for nonacidic compounds but failed for acidic compounds. The most commonly used solvent pair, octanol/water, also was useful for nonacidic compounds. Carbon disulfide−water partition coefficients correlated well with the carbon dioxide−water data set, though the number of compounds which could be included in the analysis was limited. The LSER approach was relatively robust (±0.20 log units in the best case) for the majority of the available data.

Water Solubility and $K^{x}_{C/W}$. The qualitative trends of $K^{x}_{\mathrm{C/W}}$ seemed to follow those expected from water solubility, encouraging us to investigate a quantitative relationship between these two thermodynamic quantities. We were also motivated by the wealth of data available for the solubility of organic species in water, extension of which to prediction of $K^{x}_{\mathrm{C/W}}$ would be a powerful tool.

A quantitative relationship between the partition coefficient and solubility of a given solute can be derived from thermodynamic considerations. The partition coefficient is described by the inverse ratio of the activity coefficients (γ_i) of the solute i in each of the corresponding phases

$$K^{x}_{\mathrm{C/W}} = \frac{x_i^{(\mathrm{C})}}{x_i^{(\mathrm{W})}} = \frac{\{\hat{f}_i^{(\mathrm{C})}\}/\{(f_i^{(\mathrm{C})}\gamma_i^{(\mathrm{C})})\}}{\{\hat{f}_i^{(\mathrm{W})}\}/\{(f_i^{(\mathrm{W})}\gamma_i^{(\mathrm{W})})\}} = \frac{\gamma_i^{(\mathrm{W})}}{\gamma_i^{(\mathrm{C})}} \tag{3}$$

where $x_i^{(\mathrm{P})}$ and $\hat{f}_i^{(\mathrm{P})}$ refer to the mole fraction concentration and mixture fugacity of the solute i in phase P (either C for carbon dioxide or W for water). The two values, $\hat{f}_i^{(\mathrm{W})}$ and $\hat{f}_i^{(\mathrm{C})}$, must equal each other at thermodynamic equilibrium. Following standard practice,[32] $f_i^{(\mathrm{P})}$, the reference fugacity of solute i in phase P, was taken as the hypothetical state of pure liquid solute at the temperature and pressure of the measurement. We note that many other reference states might also be selected, so care should be taken when interpreting the physical meaning of the activity coefficients in eq 3.

Provided that the saturation solubility of a given solute is small enough for a solution to be considered dilute, eq 3 can be rewritten[32] as

$$\log_{10} K^{x}_{\mathrm{C/W}} = -\log_{10} C_i^{(\mathrm{W}),\mathrm{sat}} - \log_{10} V_{\mathrm{W}} - \log_{10} \gamma_i^{(\mathrm{C}),\mathrm{sat}} \tag{4}$$

In eq 4, $\gamma_i^{(\mathrm{C}),\mathrm{sat}}$ is defined as the activity coefficient of solute i in the carbon dioxide phase, at saturated conditions. V_{W} is the molar volume of water, and $C_i^{(\mathrm{W}),\mathrm{sat}}$ is the saturation solubility of species i in the water phase. To derive eq 4, the activity coefficient for the solute in the water phase was estimated by its solubility mole fraction and the molar volume of water. For solids, a vapor pressure correction is required.[32,33]

If $\gamma_i^{(\mathrm{C}),\mathrm{sat}}$ is a constant, then eq 4 predicts a linear relationship between log $C_i^{(\mathrm{W}),\mathrm{sat}}$ and log $K^{x}_{\mathrm{C/W}}$ with a slope of −1 and an intercept equal to the negative of the sum of log V_{W} and log $\gamma_i^{(\mathrm{C})}$. Figure 2 is a plot of the logarithm of log $K^{x}_{\mathrm{C/W}}$ vs log $C_i^{(\mathrm{W}),\mathrm{sat}}$ for the 30 compounds for which solubility measurements were available.[34] Also shown are lines of equal carbon dioxide phase activity coefficients. For a large subset of the compounds, mainly those that are not hydrogen bond donors (with the exception of benzene[16] which appears to be an outlier), a linear relationship exists between log $C_i^{(\mathrm{W}),\mathrm{sat}}$ and log $K^{x}_{\mathrm{C/W}}$. Benzene may not be an outlier for any physical reason; rather, its reported partition coefficient may be in error due to difficulties in measuring its concentration in water.

The slope of the best-fit line of nonacidic compounds (excluding benzene) is equal to −1.1 ± 0.1. Not surprisingly, both phases are quite nonideal, and the activity coefficients of the dissolved solutes deviate significantly from unity. For non-hydrogen-bond donors, the average value for $\gamma_i^{(\mathrm{C})}$ is roughly 50, while the values of $\gamma_i^{(\mathrm{W})}$ range from 1 to 10 000. As it is derived directly from water solubility data, $\gamma_i^{(\mathrm{W})}$ has a firm basis. There is, however, no fundamental reason to expect $\gamma_i^{(\mathrm{C})}$ to be equal to 50 (or any other value) without further data. For this reason, eq 4 by itself is not particularly valuable as a predictive tool.

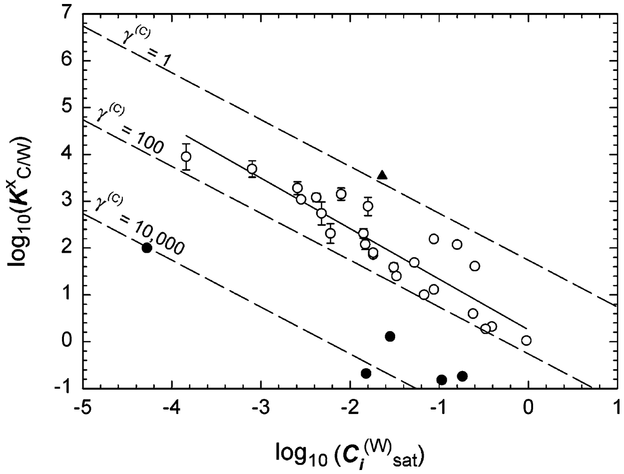

Figure 2. Correlation of measured CO_2/H_2O partition coefficients ($\log_{10} K^{x}_{\mathrm{C/W}}$) to saturation water solubility ($\log_{10} C_i^{(\mathrm{W}),\mathrm{sat}}$): ○, nonacidic solute; ●, acidic solute; ▲, benzene; solid line is the best-fit line; dashed lines denote lines of equal values of $\gamma_i^{(\mathrm{C})}$ ($\gamma_i^{(\mathrm{C})} = 1$, 100, and 10 000, respectively).

Since both the Hildebrand−Scatchard solubility parameter[35,36] and the Hansen solubility indexes[36,37] have been successful in correlating a variety of solvation phenomena, these approaches were also investigated. The single-parameter approach of Hildebrand−Scatchard failed even to predict qualitative trends in $K^{x}_{\mathrm{C/W}}$ (average absolute deviation, AAD ≈ 1.5 log units) when a realistic value of the solubility parameter of carbon dioxide was used.[38−41] Hansen[37] suggests the use of three solubility parameters to describe contributions from dispersive van der Waals, dipole−dipole, and hydrogen-bonding interactions. This approach failed as a 1:1 relationship (AAD ≈ 0.8 log units), though there was a weak correlation between predicted and measured partition coefficients (AAD ≈ 0.5 log units for the best-fit line).

Prediction of $K^{x}_{C/W}$ from Partitioning in Other Solvent Pairs. Our analysis of $K^{x}_{\mathrm{C/W}}$ and water solubility indicated that the behavior of solutes dissolved in the carbon dioxide phase deviates significantly from that expected for an ideal solution, and we decided that solute partitioning between other solvent pairs might be a viable means to capture these nonidealities. Although many solvent pairs are conceivable, perhaps the most ubiquitous is octanol−water. This solvent pair has been used for direct comparison of the partitioning behavior in a number of important systems and has found biological and environmental applications.[42] On the basis of available data, Leo and Hansch[43] have developed a popular group contribution method for predicting octanol−water partition coefficients ($K^{\mathrm{C}}_{\mathrm{O/W}}$) of organic compounds based solely on the identities of the constituent atoms and the molecular geometry. The successes of octanol−water phase partitioning in other research fields[42,43] recommends its use to correlate carbon dioxide/water partitioning coefficients.

Physically, it seems reasonable to expect that partitioning between octanol (a hydrophobic, low dielectric constant solvent) and water would be similar to partitioning between

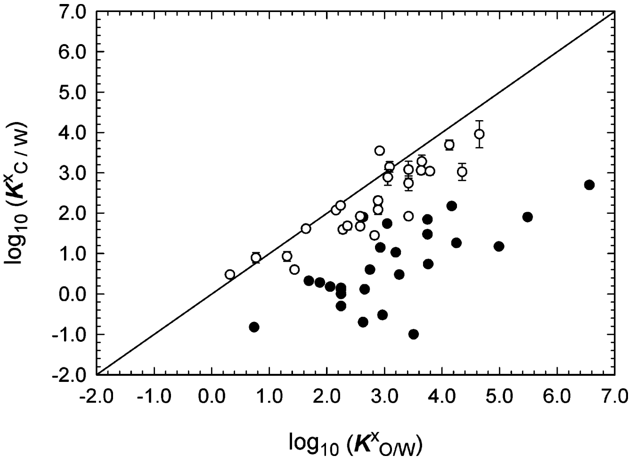

Figure 3. Correlation of $\log_{10} K^x_{C/W}$ (at a fixed CO_2 solvent density of 0.76 $g \cdot cm^{-3}$) to $\log_{10} K^x_{O/W}$ estimated by the methods of Leo and Hansch:[43] ○, nonacidic solute; ●, acidic solute; solid line is the 45° line.

carbon dioxide (also a hydrophobic, low dielectric constant solvent) and water. Some deviation is expected in the case of hydrogen-bonding solutes since octanol[44] probably interacts more strongly via hydrogen bonds than does carbon dioxide.[45−50] Certainly, octanol can act as a hydrogen bond donor, while carbon dioxide clearly cannot. Additionally, $K^x_{O/W}$ might fail to predict the partitioning behavior of fluorinated compounds because this class of compounds is both hydrophobic and oleophobic but is surprisingly soluble in CO_2.[51] These differences notwithstanding, we anticipated that $K^x_{C/W}$ and $K^x_{O/W}$ would be correlated for the hydrocarbon compounds studied here, though there is no reason to expect the two partition coefficients to be exactly equal.

Commercially available software[52] was used to estimate $K^C_{O/W}$ for the 49 solutes presented in Tables 1 and 2. For internal consistency, values of $K^C_{O/W}$ were converted to $K^x_{O/W}$ by assuming a constant octanol density of 0.83 $g \cdot cm^{-3}$. Figure 3 is a plot of $\log_{10} K^x_{C/W}$ vs $\log_{10} K^x_{O/W}$ estimated from group contribution methods. There are several striking features to Figure 3. The first is the overall poor correlation of $K^x_{C/W}$ with $K^x_{O/W}$. Deviation between the two types of partition coefficients ranges from as small as a factor of 1.6 to as large as 4 orders of magnitude. Interestingly, with only 2-buten-3-one as a notable exception, $K^x_{O/W}$ is greater than or equal to $K^x_{C/W}$. A second notable feature in Figure 3 is that there is a much better correlation between $K^x_{O/W}$ and $K^x_{C/W}$ for the subset of compounds which cannot act as hydrogen donors (i.e., compounds with no Brønsted acidity). The correlation for this subset is depicted in Figure 4. Aniline is the only nonacidic compound for which data are available and which does not belong to the highlighted subset. Most likely, aniline is an outlier due to strong Lewis acid−base interactions between amines and carbon dioxide,[45] which in some cases results in chemical reaction to form carbamic acid.[53,54]

For the 26 nonacidic compounds considered, the correlation between $K^x_{O/W}$ and $K^x_{C/W}$ is adequate; the AAD is 0.36 log units. The largest outliers are 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane[17] (absolute deviation = 0.87 log units for both compounds) and benzene[16] (absolute deviation = 1.15 log units). Failure of $K^x_{O/W}$ for the chlorinated ethanes is surprising given that polyhalogenation is included specifically by Leo and Hansch[43] as a structure factor contribution in an effort to capture the decrease in molecular polarity associated with opposing nearby dipoles.

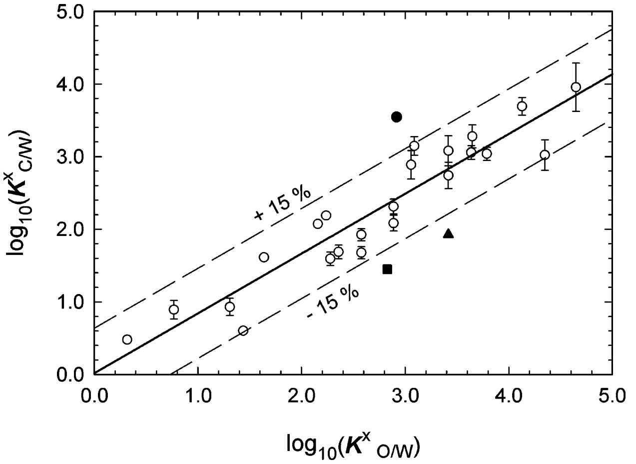

Figure 4. Correlation of $\log_{10} K^x_{C/W}$ (at a fixed CO_2 solvent density of 0.76 $g \cdot cm^{-3}$) to $\log_{10} K^x_{O/W}$ estimated by the methods of Leo and Hansch[43] including only nonacidic solutes: ○, typical nonacidic solutes; ●, benzene; ■, 1,1,2-trichloroethane; ▲, 1,1,2,2-tetrachloroethane; solid line is the best-fit line; dashed lines indicate ±15%.

Table 3. Comparison of Correlations between $K^x_{C/W}$ and Partition Coefficients for Other Solvent/Water Pairs Predicted Using Modified UNIFAC;[57−61] Chlorophenols are Not Included in the Analysis[a]

solvent	AAD (log units)	*N*	exceptions
carbon disulfide	0.29	19	benzyl alcohol
carbon tetrachloride	0.50	22	phenols
ethyl acetate	0.74	31	none
octanol	0.36	26	hydrogen bond donors
perfluorohexane	0.19	7	chlorobenzene[b]
toluene	0.48	29	none

[a] Analysis is restricted to hydrocarbons (e.g., hexane, benzene, etc.) and tetrahydrofuran. [b] Analysis restricted to hydrocarbons (e.g., hexane, benzene, etc.) and tetrahydrofuran.

Benzene is an outlier for both the solubility correlation and the $K^x_{O/W}$ correlation. Inclusion of outliers yields a best-fit slope equal to 0.81 ± 0.09 and an intercept of 0.0 ± 0.3. If the three compounds are neglected, the values of the best-fit slope and intercept are unchanged, though the AAD is reduced to 0.28 log units.

Partitioning between water and several other solvents (toluene, ethyl acetate, carbon tetrachloride, carbon disulfide, and perfluorohexane) was also investigated. The solvents were selected to represent a wide range of properties while maintaining nonpolar character relative to water. Ethyl acetate was selected based partially on the recommendation of a reviewer who suggested that esters might exhibit a hydrogen-bond-accepting capacity similar to that of carbon dioxide.

Partition coefficients were calculated directly from infinite dilution activity coefficients estimated from a modified version of the UNIFAC[55,56] model (UNIQUAC functional-group activity coefficients) developed by J. Gmehling and his colleagues.[57−61] Calculations were performed using commercially available software,[62] and corrections were made to account for the mutual solubilities of the solvent pairs.

Linear correlations were derived to relate $K^x_{C/W}$ to UNIFAC predictions for the solvent/water pairs mentioned above. Table 3 lists the results of these solvent/water correlations in terms of AAD and also provides the number of data points in the regression. UNIFAC estimates of the infinite dilution activity coefficients for chlorinated phenols

Table 4. LSER Solute Descriptors Used in This Study[a]

name	R_2	π_2^H	α_2^H	β_2^H	V_2
acetophenone	0.818	1.01	0.0	0.49	1.0139
aniline	0.955	0.96	0.26	0.41	0.816
benzaldehyde	0.82	1.0	0.0	0.39	0.873
benzene	0.610	0.52	0.00	0.14	0.7164
benzoic acid	0.73	0.9	0.59	0.4	0.932
benzyl alcohol	0.803	0.87	0.33	0.56	0.916
bromobenzene	0.882	0.73	0.00	0.09	0.8914
caffeine	1.5	1.6	0.0	1.35	1.363
chlorobenzene	0.718	0.65	0.00	0.07	0.8388
2-chlorophenol	0.853	0.88	0.32	0.31	0.8975
4-chlorophenol	0.915	1.08	0.67	0.21	0.8975
cyclohexane	0.305	0.1	0.0	0.0	0.8454
cyclohexene	0.395	0.20	0.00	0.10	0.8024
cyclohexanone	0.403	0.86	0.0	0.56	0.861
cyclopentene	0.335	0.2	0.0	0.1	0.6615
1,2-dichloroethane	0.416	0.64	0.10	0.11	0.6352
2,4-dimethylphenol	0.843	0.8	0.53	0.39	1.0569
ethylbenzoate	0.689	0.85	0.0	0.46	1.2135
fluorobenzene	0.477	0.57	0.00	0.10	0.7341
hexane	0.0	0.0	0.0	0.0	0.954
2-hexanone	0.136	0.68	0.0	0.51	0.97
methylbenzoate	0.733	0.85	0.0	0.48	1.0726
3-methyl-4-chlorophenol	0.92	1.02	0.65	0.22	1.038
3-methylphenol	0.822	0.88	0.57	0.34	0.9160
naphthalene	1.340	0.92	0.0	0.20	1.085
2-nitrophenol	1.015	1.05	0.05	0.37	0.949
4-nitrophenol	1.07	1.72	0.82	0.26	0.949
phenol	0.805	0.89	0.6	0.3	0.775
propylbenzoate	0.675	0.8	0.0	0.46	1.354
1,1,2,2-tetrachloroethane	0.595	0.76	0.16	0.12	0.8800
tetrahydrofuran	0.289	0.52	0.00	0.48	0.6223
1,1,2-trichloroethane	0.499	0.68	0.13	0.08	0.7576
toluene	0.601	0.52	0.0	0.15	0.8573

[a] Solute descriptors were based on data from refs 68–70, and appropriate physical descriptions are in the text.

predicted incorrect trends in water solubility, and these solutes were excluded from the partition coefficient analysis. Likewise, UNIFAC estimates of the infinite dilution activity coefficients of phenol compounds in carbon tetrachloride were on the order of 1×10^9, which is not consistent with known solubility behavior. For this reason, phenols were eliminated from the carbon tetrachloride/water analysis. Toluene–water and carbon tetrachloride–water are not strongly correlated with $K^x_{C/W}$ (AAD $\approx$ 0.5, in both cases). Carbon disulfide–water correlates rather well with $K^x_{C/W}$ (AAD $\approx$ 0.3), with the only observed exception being benzyl alcohol. The correlation between $K^x_{C/W}$ and carbon disulfide–water partitioning is consistent with the fact that both carbon dioxide and carbon disulfide are nonpolar solvents with strong quadrupole moments.[63] The correlation between $K^x_{C/W}$ and perfluorohexane–water partitioning is rather striking (AAD $\approx$ 0.2), though the data set is too small to make a conclusive statement. Furthermore, there is no clear physical reason for chlorobenzene to be an outlier, and this is a strong indictment against perfluorohexane–water partitioning as a correlant for $K^x_{C/W}$. It was expected that perfluorohexane and carbon dioxide might exhibit similar solvent strengths given that fluorinated hydrocarbons tend to be highly soluble in $scCO_2$,[51] perhaps due to strong specific interactions between the CF_3 and CF_2 groups and CO_2.[64] Nonetheless, the available data do not substantiate an analogy between carbon dioxide–water partitioning and perfluorohexane–water partitioning.

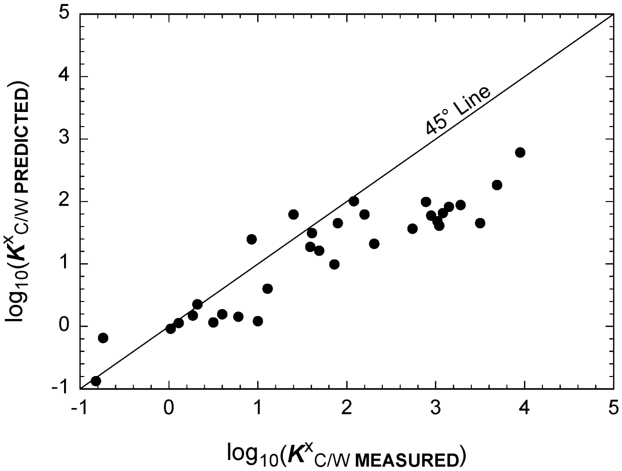

Figure 5. Comparison of partition coefficients measured at a fixed CO_2 density of 0.76 g·cm^{-3} to estimates based on the seven-parameter LSER recommended by Lagalante and Bruno.[25] Parameter values are given in eq 6; the 45° line is shown for comparison.

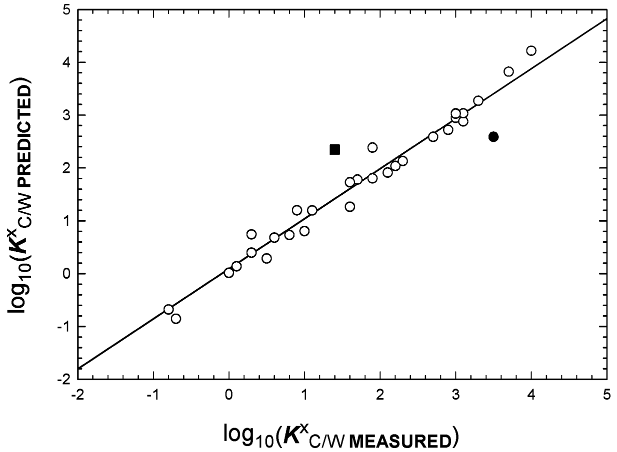

Figure 6. Correlation of partition coefficients measured at a fixed CO_2 density of 0.76 g·cm^{-3} to partition coefficients predicted by a six-parameter LSER (regressed values provided in Table 4, entry 1): ●, benzene; ■, 1,1,2,2-trichloroethane; ○, all other compounds listed in Table 3 (except naphthalene for which only low-density data were available). All 32 available data points were included in the regression.

A comparison of $K^x_{C/W}$ with partition coefficients for other solvent/water pairs provides some insight. Neither hydrogen-bond donating ability (octanol) nor accepting ability (octanol or ethyl acetate) appear to be particularly important for determination of $K^x_{C/W}$. Traditional nonpolar solvents (e.g., toluene and carbon tetrachloride) capture the qualitative behavior of $K^x_{C/W}$ but fail as quantitative predictors. The success of carbon disulfide/water partitioning as a correlant for $K^x_{C/W}$ suggests that the quadrupole moment of carbon dioxide plays an important role in solute partitioning. Solute partitioning between fluorocarbon and water phases may be an interesting area for future research.

Correlation of $K^x_{C/W}$ Using LSERs. LSERs[65] are a third approach to correlating partition coefficients; Lagalante and Bruno[25] have already applied this technique to $K^x_{C/W}$. In general practice, the LSER method[65] assumes that the logarithm of some general thermodynamic or kinetic property (ξ) of a given solute (i) can be related empirically to its physicochemical properties (referred to as solute descriptors) in a linear fashion

$$\log_{10} \xi = \log_{10} \xi_0 + \sum(\text{coefficient})x(\text{solute descriptor}) \tag{5}$$

where ξ_0 is a constant term. For a given property, the

Table 5. Regressed LSER Coefficients for LSERs Describing Partitioning at a Fixed CO_2 Density of 0.76 $g\cdot cm^{-3}$ [a]

			regressed coefficients for respective solute descriptors					
no. terms	r^2	AAD ($\log_{10}$)	ξ_0	R_2	π_2^H	α_2^H	β_2^H	V_2
6	0.95	0.20	1.56 ±0.27	0.000 ±0.380	−0.973 ±0.381	−3.078 ±0.306	−3.319 ±0.374	2.78 ±0.448
5	0.88	0.32	3.300 ±0.314	NA	−0.779 ±0.427	−3.120 ±0.457	−2.472 ±0.513	0.362 ±0.296
4	0.86	0.37	3.100 ±0.307	NA	NA	−3.672 ±0.356	−3.143 ±0.372	0.259 ±0.302
3	0.86	0.38	3.400 ±0.160	NA	NA	−3.667 ±0.354	−3.073 ±0.361	NA

[a] Thirty-two compounds were considered in the regression (all compounds are listed in Table 3 except naphthalene); values for the correlation constant (r^2) and AAD in log units are also Tabulated; definitions for the solute descriptors are located in the text.

Table 6. Regressed Coefficients for LSERs Based on Data Taken over a Range of Carbon Dioxide Densities[a]

			regressed coefficients for respective solute descriptors							
no. terms	r^2	AAD ($\log_{10}$)	ξ_0	R_2	π_2^H	α_2^H	β_2^H	V_2	π_1	$\pi_2^H \times \pi_1$
7	0.89	0.30	3.811 ±0.110	0.0300 ±0.130	−1.260 ±0.200	−3.110 ±0.100	−2.010 ±0.140	0.110 ±0.070	2.450 ±0.240	NA
6	0.88	0.29	3.810 ±0.110	NA	−1.230 ±0.150	−3.110 ±0.100	−2.011 ±0.130	0.110 ±0.070	2.450 ±0.240	NA
5	0.87	0.30	3.150 ±0.080	NA	NA	−3.400 ±0.090	−2.640 ±0.090	0.030 ±0.070	NA	3.130 ±0.270
4	0.87	0.32	3.180 ±0.060	NA	NA	−3.400 ±0.090	−2.630 ±0.090	NA	NA	3.130 ±0.270

[a] Values regressed for the entire data set (33 compounds, 332 data points); values for the correlation constant (r^2) and AAD in log units are also tabulated. Definitions for the solute descriptors are located in the text.

values of the various coefficients (as well as ξ_0) must be determined by regression; however, solute descriptors are typically measured independently by spectroscopic or chromatographic means. On the basis of the LSER approach, the researchers proposed several equations, the most successful of which was

$$\log_{10} K^{x}_{C/W} = 2.175 - 1.578R_2 + 0.6323\pi_2^H - 2.254\alpha_2^H - 1.986\beta_2^H + 0.9221V_2 + 2.343\pi_1 \quad (6)$$

In eq 6, R_2 refers to the excess index of refraction, π_2^H refers to dipolarity or polarizability, α_2^H refers to the hydrogen bond acidity, β_2^H refers to the basicity, and V_2 is a measure of the molar volume as recommended by McGowen.[66] π_1 refers to the solvent dipolarity/polarizability of carbon dioxide and was assumed to be a linear function of reduced density (ρ_r) as suggested by the spectroscopic measurements of Smith and co-workers[67]

$$\pi_1 = 1.15\rho_r - 0.98 \qquad (\rho_r < 0.7) \qquad (7a)$$

$$\pi_1 = 0.173\rho_r - 0.37 \qquad (\rho_r > 0.7) \qquad (7b)$$

When using eq 6 as a correlation for measurements of $K^{x}_{C/W}$, Lagalante and Bruno[25] reported an AARD of 21% (116 data points). Unfortunately, their regression included data for only 6 compounds (phenol, benzyl alcohol, benzoic acid, 2-hexanone, cyclohexanone, and caffeine), thus restricting the general use of eq 6. With measurements of $K^{x}_{C/W}$ for many more compounds now available, we expanded the regression to test eq 6 at a fixed fluid density of CO_2 of 0.76 $g\cdot cm^{-3}$. Solute descriptors for 33 of the compounds were available in the literature[68−70] as listed in Table 4. Figure 5 is a parity plot of the measured values of $\log_{10} K^{x}_{C/W}$ vs values predicted from eq 6 (naphthalene was excluded from the analysis because no $K^{x}_{C/W}$ data were available at a fluid density of 0.76 $g\cdot cm^{-3}$). There is a distinct, though not 1:1, correlation between the measurements and the predictions. All types of compounds (including hydrogen-bond donors) followed the trend line reasonably well, and there were no clear outliers.

Although these initial results were encouraging, eq 6 clearly is not reliable as a predictive tool. Therefore, the coefficients of several LSERs of the form suggested by eq 6 were regressed using the new data. Two approaches were taken: (1) correlation using only data at a fixed CO_2 solvent density of 0.76 $g\cdot cm^{-3}$ and (2) correlation using all available data.

The performance of four equations with the general form of eq 6 was evaluated for a CO_2 solvent density of 0.76 $g\cdot cm^{-3}$. At a fixed density, the number of adjustable parameters in eq 6 is reduced to 6 since the CO_2 polarizability term (π_1) and the constant term are redundant. The number of parameters was further reduced based on statistical significance. Our primary objective was to reduce the number of adjustable parameters needed for a satisfactory correlation.

Figure 6 compares predicted and measured values of $K^{x}_{C/W}$ on a log scale at a fixed CO_2 density of 0.76 $g\cdot cm^{-3}$. Although the overall fit is reasonable ($r^2 \approx 0.88$, AAD = 0.20 log units, maximum deviation = 0.96 log units), there are two outliers: benzene[16] and 1,1,2,2-tetrachloroethane.[17] Benzene is an outlier in all three analyses (water solubility, solvent pairs, and LSER), and 1,1,2,2-tetrachloroethane is an outlier in both the $K_{O/W}$ and LSER analyses (solubility data were not available for this compound). The values and the errors of the regressed parameters of the 4 LSER correlations are listed in Table 5. The values in Table 5 reflect the contributions of both benzene and 1,1,2,2-tetrachloroethane. The three most important parameters are found to be α_2^H, β_2^H, and V_2. In their studies of partitioning between water and the nonpolar refrigerants R143a[71] and R134a[72] Lagalante, Bruno, and their co-workers found that the same parameters dominated. Quantitatively, the LSER parameter values presented here agree more closely with those reported for partitioning between water and hydrocarbon solvents.[68] The importance

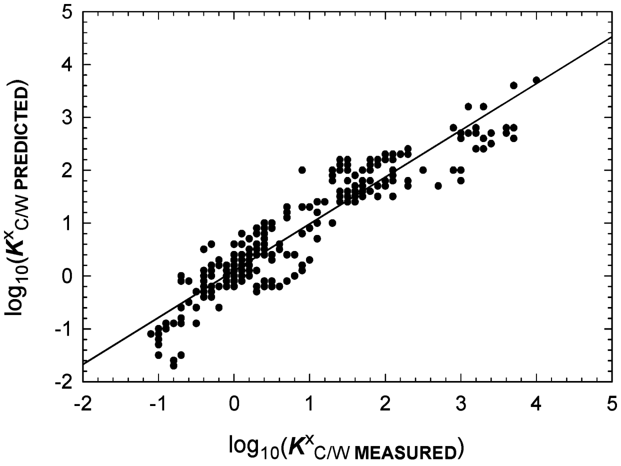

Figure 7. Correlation of measured partition coefficients to partition coefficients predicted by a seven-parameter LSER; all available data over a range of CO_2 densities from 0.2 to 0.9 g·cm^{-3} were considered (332 data points, 33 compounds). Regressed parameters for the LSER are listed in Table 5 (entry 1).

of solute acidity and basicity should not be taken as an indicator of the hydrogen-bond capacity of carbon dioxide. Instead, the large values of α_2^{H} and β_2^{H} are probably related to the hydrogen-bonding capacities of water relative to carbon dioxide.

All available data for a set of 33 compounds (as in Table 4) were analyzed using the technique described above; 332 data points, covering a range of CO_2 densities from 0.2 to 0.9 g·cm^{-3}, were utilized. Four separate forms of the LSER were tested, and the results are listed in Table 6. In two trials, we considered the addition of the cross term corresponding to the product $\pi_1 \times \pi_2^{\mathrm{H}}$ as suggested by Lagalante and Bruno.[25] Including all 7 parameters in the regression yielded acceptable correlations ($r^2 \approx 0.89$, AAD $= 0.30$ log units, maximum deviation $= 1.20$ log units). Figure 7 is a comparison between measured and LSER-predicted values (using the form suggested by eq 6 and the coefficient values listed as entry 1 in Table 6) of log $K_{\mathrm{C/W}}^{x}$ for the entire data set. Although there is considerable scatter, there are no clear outliers. In this particular LSER model, the most important parameters were α_2^{H}, β_2^{H}, V_2 (as before), and π_1 (which accounts for the dependence of $K_{\mathrm{C/W}}^{x}$ on CO_2 density). Consideration of all available density data leads to regressed LSER coefficients which agree rather closely with those reported by Lagalante and Bruno[71,72] to describe partitioning between water and the near-critical, nonpolar refrigerants, R143a and R134a.

A library of 33 compounds (and 332 separate data points) is a good start for establishing a predictive method adequate for screening purposes or predictions in trends. For compounds which are similar to those considered in this study, the LSER approach should provide estimates to within roughly ±0.30 log units of log $K_{\mathrm{C/W}}^{x}$. Although this error may seem large, values of $K_{\mathrm{C/W}}^{x}$ measured for a given compound at identical conditions vary by as much as 50% between research groups. For the most reliable estimates of $K_{\mathrm{C/W}}^{x}$ for compounds for which no partitioning data are available, we recommend using the three methods in conjunction. If the three methods agree to within their uncertainty, the estimated value can be used with reasonable confidence. More work is needed to improve our understanding of the behavior of acidic compounds in biphasic CO_2/H_2O mixtures.

Conclusions

Values of $K_{\mathrm{C/W}}^{x}$ for 18 new compounds have been measured at 300 K and 80 bar carbon dioxide fluid density of 0.76 g·cm^{-3}. This study expanded the database while focusing on aromatics, alkanes, and alkenes, with one exception: heterocyclic tetrahydrofuran. $K_{\mathrm{C/W}}^{x}$ correlated fairly well with solute solubility in water except for the case of acidic compounds (Brønsted acidity). Use of $K_{\mathrm{O/W}}^{x}$ (estimated by a group contribution method) as a correlant for $K_{\mathrm{C/W}}^{x}$ gave mixed results. A good correlation is found for non-hydrogen-bond donors, but the overall correlation for the entire data set is extremely poor. Although only 19 solutes could be included in the analysis, carbon disulfide−water phase partitioning correlated well with carbon dioxide−water phase partitioning, with only one exception: benzyl alcohol. There was a good correlation between LSER predictions and experimental measurements with no restrictions on the solutes. Important LSER parameters were solute acidity and basicity. For nonacidic solutes, the three approaches (correlation to water solubility, solvent−water partitioning, and LSERs) are complementary and could be used in conjunction to obtain estimates of $K_{\mathrm{C/W}}^{x}$ for which no prior data are available.

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