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Partitioning of Acidic Solutes between Water and Supercritical Carbon Dioxide. Effect of pH and Ionic Strength

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Partitioning of pentachlorophenol (PCP) between water and CO_2 was investigated to determine the effects of pH and ionic strength on the value of the distribution coefficient, *K*. Decreasing the pH or increasing the ionic strength increased the value of *K*. The distribution coefficient was larger than that predicted by considering the extent of hydrolysis of the solute in the aqueous phase. However, impedance measurements suggest that negligible concentrations of ions exist in the CO_2 phase. Together, these two facts suggest that the aqueous phase hydrolysis equilibrium is shifted toward unhydrolyzed solute as PCP partitions to CO_2. The value of *K* was smaller than the ratio of solubilities of the solute in the two phases, likely due to the effect of solute composition on the solute activity coefficients in each phase. Partitioning isotherms are also reported for the solutes pentachlorophenol, 2,3,4,5-tetrachlorophenol and 2,4-dichlorophenoxyacetic acid at about 40 °C, between about 100 to 270 bar.

Introduction

The techniques currently used for quantifying organic analytes in water usually involve an extraction, either into an immiscible solvent or onto a solid phase. Supercritical fluids have been extensively researched as extractants for solid samples, but there are only a few reports about the direct extraction of analytes from water into a supercritical fluid.[1−5] Researchers have had to tackle problems such as activation of trapping and/or chromatographic phases, the generation of two phases upon sample collection, or restrictor plugging. The use of supercritical carbon dioxide (CO_2) in place of a liquid organic solvent or a solid-phase offers potential advantages for extraction from water in terms of cost, speed, and toxicity of the solvent.

Determination of acidic species in water is often complicated by the tendency of these compounds to partially dissociate in water. Addition of acid to the water phase protonates the analyte, rendering it soluble in the much less polar organic phase. In the case of CO_2, dissolution of CO_2 into the water phases causes the aqueous phase pH to drop to about 3 due to production of carbonic acid.[6] As a consequence, the problem is automatically mitigated so long as the pK_a of the analyte is greater than about 3.0. As well, salt is frequently added to “salt out” the analyte, thus forcing it to partition to the organic phase. The salting-out effect has been observed during the extraction of sulfonylureas from aqueous matrixes with CO_2.[7] The effects of carbonic acid in water in contact with CO_2 may therefore be 2-fold: lowering the pH and increasing the ionic strength. Both of these will have the effect of increasing the partitioning of acidic analytes to the CO_2. The contribution of each to the overall effect is not known.

When water is contacted with CO_2, neither phase is pure as they are mutually soluble. The presence of bicarbonate and carbonate species in the water-rich phase is well documented. However, in the CO_2-rich phase, the effects of dissolved water on the speciation of the carbon containing species are not well understood. Although pure carbon dioxide has a small dielectric constant ($\epsilon_r = 1-1.8$),[8] saturation of CO_2 with water may result in the production of a small number of ions. These in turn may raise the dielectric constant slightly, thereby allowing the partitioning of a small number of polar or ionized species from the water-rich phase into the CO_2-rich phase. Impedance measurements can be used to detect changes in the concentration of ions in this phase.

In a previous paper, we reported on the effects of temperature, pressure, and concentration on the partitioning of pentachlorophenol (PCP) between water and carbon dioxide.[9] In this paper, we report the effects of other variables, namely pH and ionic strength of the aqueous phase. Furthermore, impedance measurements in the CO_2-rich phase are reported. We also present solubility data of PCP in water-saturated CO_2 for comparison with data in pure CO_2, and data of PCP in CO_2-saturated water for comparison with data in pure water.

Experimental Section

The experimental apparatus used for solubility and partitioning experiments was described in detail in a previous publication.[9] A high pressure, stainless steel extraction cell was connected on-line to an HPLC. For this work, the cell was modified by inserting two electrodes in the CO_2 phase for measuring impedance. Each electrode consisted of a 0.5 mm diameter stainless wire insulted in a PEEK tubing sleeve (0.53 mm i.d., Upchurch Scientific). The electrodes were swaged into the cell through 1/16 in. Swagelok to 1/8 in. universal pipe thread unions that were

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drilled out and screwed into threaded openings on one side of the vessel. The electrodes protruded into the cell approximately 1 cm. The cell constant for each pair was calculated using aqueous 0.1 M NaCl.

The solubility of pentachlorophenol was measured in CO_2-saturated water and water-saturated CO_2 by placing 2−3 g pentachlorophenol (Aldrich, 99%+) in the cell with 50 mL distilled, deionized water and filling the void volume with CO_2. Analyte solubility in both the CO_2- and water-rich phases could thus be determined simultaneously. The system was equilibrated for up to 24 h. Pentachlorophenol solubility was also measured in CO_2 bubbled through water prior to contact with the PCP.

Adjustment of the aqueous phase pH, where necessary, was done by addition of hydrochloric acid or sodium bicarbonate to the water prior to pressurizing the cell. The Henderson−Hasselbalch equation was used to calculate the quantity of sodium bicarbonate necessary to buffer the aqueous phase at a pH above that resulting from contact with the CO_2 alone (approximately 3.0). The amount of hydrochloric acid required was also calculated on the assumption that the pH of the water in contact with CO_2 was 3.

The concentration of PCP initially in the water phase during partitioning experiments was between $(1.9−4.3) \times 10^{-6}$ g/g solvent. The initial concentrations of 2,3,4,5-tetrachlorophenol (Supelco, 98%+) and 2,4-dichlorophenoxyacetic acid (Aldrich, 98%) in the water phase were $(2.1 \text{ and } 0.77) \times 10^{-6}$ g/g solvent, respectively.

Results and Discussion

Effects of Water Dissolved in CO_2 and CO_2 Dissolved in Water. In a previous paper we discussed the relationship between solubility of a solute in the pure phases (water and CO_2), and the partitioning of the solute between the two phases in contact with one another.[10] However, all solubility experiments were carried out in the pure phases, whereas during a partitioning experiment there is some mutual solubility of each phase in the other. To determine the effects of water dissolved in the CO_2 rich phase, solubility measurements were made in both pure CO_2 and in CO_2 saturated with water. The results presented in Figure 1 (see also Tables 1 and 2) show that addition of water does not have a significant effect on the solubility of PCP in CO_2. Error bars express the standard deviation of three or more measurements. The majority of the solute−solvent interactions in the CO_2-rich phase are apparently between PCP and CO_2 molecules and do not involve water. It is likely most of the water fraction reacts with CO_2 to form small amounts of carbonic acid, or at least aqueous CO_2, and that little free water exists. Note the solubility of water in CO_2 is small, between 0.1 and 0.3 vol %.[11−13]

The effects of CO_2 dissolved in the water phase were also determined. The data presented in Figure 2 indicate that the solubilities of PCP in water saturated with carbon dioxide are only slightly larger than those in pure water. The volume change upon solution is similar to that in pure water and has a value of 54 $cm^3\ mol^{-1}$, compared with 66 $cm^3\ mol^{-1}$ in pure water. The solubility data are summarized in Tables 3 and 4.

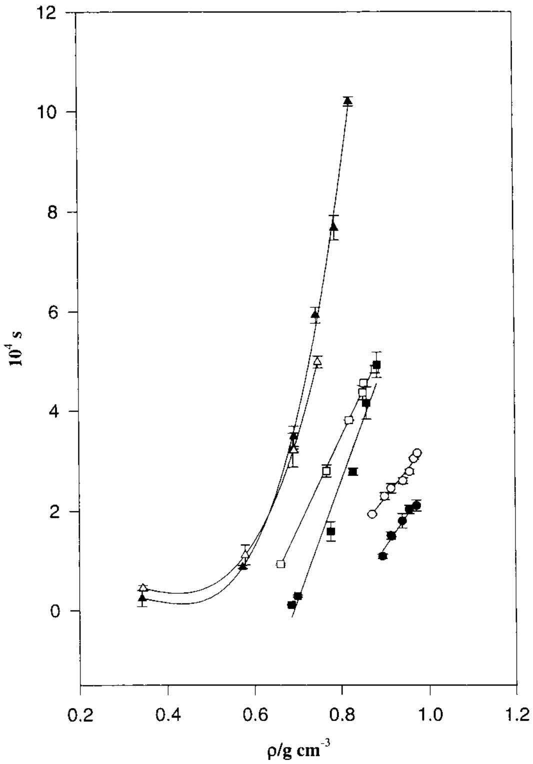

Figure 1. Mole fraction solubility, *s*, of PCP in CO_2 and CO_2 saturated with water as a function of density. CO_2 saturated with water: ●, (19.1 ± 0.3) °C; ■, (39.6 ± 0.3) °C; ▲, (59.6 ± 0.1) °C. Pure CO_2: ○, (20.0 ± 0.5) °C; □, (41.0 ± 0.2) °C; △, (59.5 ± 0.1) °C.

Table 1. Mole Fraction Solubility, *s*, of Pentachlorophenol in Pure Carbon Dioxide

T/°C	*P*/bar	10^4s	*T*/°C	*P*/bar	10^4s
20.0 ± 0.5	97.4	1.93	41.0 ± 0.2	108	0.927
	127	2.29		143	2.80
	153	2.45		177	3.81
	189	2.60		212	4.36
	220	2.78		213	4.55
	252	3.04		246	4.83
	269	3.15	59.5 ± 0.1	107	0.447
				143	1.11
				177	3.22
				178	3.21
				213	4.98

Table 2. Mole Fraction Solubility, *s*, of Pentachlorophenol in Carbon Dioxide Saturated with Water

T/°C	*P*/bar	10^4s	*T*/°C	*P*/bar	10^4s
19.1 ± 0.3	109	1.08	59.6 ± 0.1	107	0.239
	143	1.50		141	0.871
	147	1.49		178	3.49
	175	1.80		210	5.93
	210	2.03		246	7.67
	252	2.11		280	10.2
39.6 ± 0.3	108	0.111			
	111	0.288			
	141	1.59			
	177	2.78			
	212	4.15			
	242	4.92			

To predict *K* for pentachlorophenol, solubility ratios were calculated at ambient temperatures between pure water and pure CO_2, and then between the water- and CO_2-rich phases. The solubility ratios are compared with partitioning data in Figure 3. Best fit lines were determined for each set of solubility data and the solubility ratio as a function of pressure was calculated. *K* for PCP from dilute solution (1.27 ppm) was measured previously as the ratio of its mole fraction in the CO_2-rich phase to its mole fraction in the water-rich phase.[9] The partitioning line was obtained by extrapolating a best fit line through the obtained data. The ratio of PCP solubility between the saturated phases is lower than between the pure phases. This is because the

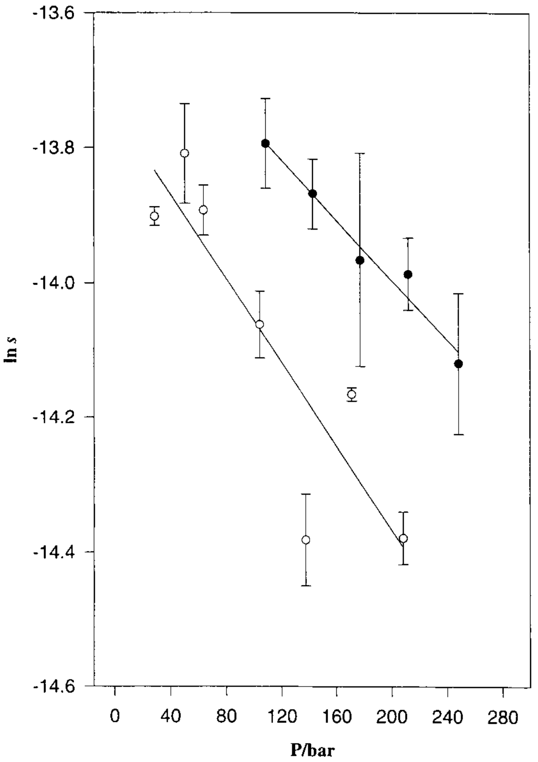

Figure 2. Mole fraction solubility, *s*, as ln *s* of PCP in water and water saturated with CO_2 as a function of pressure: ○, pure water; ●, water saturated with CO_2.

Table 3. Mole Fraction Solubility, *s*, of Pentachlorophenol in Water

T/°C	*P*/bar	$10^7 s$
23.6 ± 0.5	1	9.08
	28.5	9.17
	50.3	10.1
	63.8	9.26
	104	7.82
	137	5.68
	171	7.05
20.5 ± 0.4	8.4	5.69

Table 4. Mole Fraction Solubility, *s*, of Pentachlorophenol in Water Saturated with CO_2

T/°C	*P*/bar	$10^7 s$
21.7 ± 1.3	108	10.2
	143	9.50
	177	8.68
	212	8.43
	248	7.42

solubility of PCP in water saturated with CO_2 was slightly higher than in pure water. As well, the solubility of PCP in the CO_2-rich phase was slightly smaller than in pure CO_2.

The distribution coefficient is smaller that the values predicted by both solubility ratios for pentachlorophenol. This result may be explained by considering that *K* is equal to the ratio of activity coefficients for the solute in each phase:

$$K = \frac{\gamma_{\text{solute}}^{H_2O}}{\gamma_{\text{solute}}^{CO_2}} \qquad (1)$$

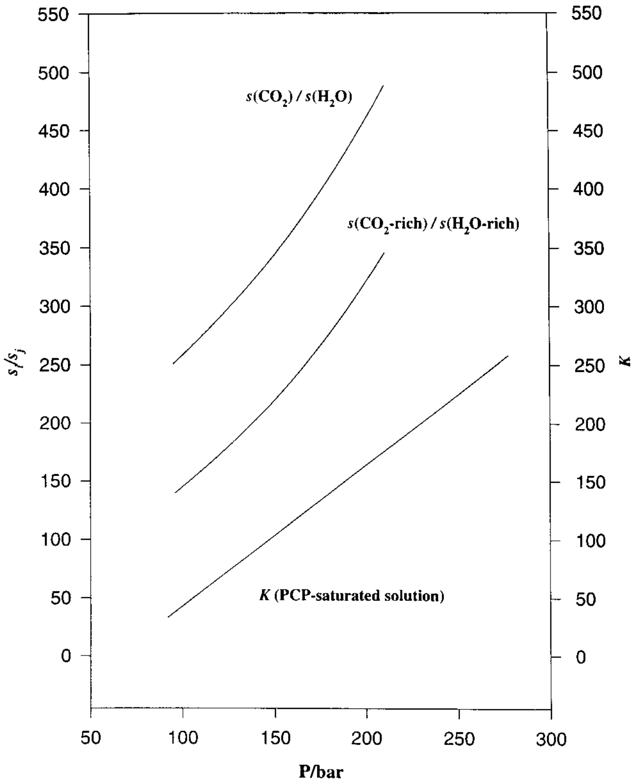

Figure 3. Comparison of the solubility ratios of PCP between CO_2 and water to the distribution coefficient, *K*.

The activity coefficients for PCP have different values (in one or both phases) during partitioning experiments compared with solubility experiments. We have observed previously that solute concentration can have an effect on activity coefficients. In another paper, we showed that *K* becomes smaller if the initial concentration of the solute in the water phase is lowered.[9] During the partitioning experiments performed in this work, the concentrations of PCP in the CO_2- and water-rich phases were about 2 orders of magnitude smaller than during solubility experiments.

Effects of pH. To separate the effects of pH and ionic strength on the partitioning of pentachlorophenol between carbon dioxide and water, the value of *K* was measured as a function of pH, then again as a function of ionic strength at constant pH. The results are presented in Figures 4 (pH) and 5 (ionic strength). Figure 4 shows that the distribution coefficient increases as the pH is decreased. The value of *K* increases from 47 at pH 4.9 to 78 at pH 3.0. At pH 4.9 in water, the percentage of dissociated PCP is 73.8%, which is based on a solute pK_a of 4.74 (measured in our lab). This would suggest that only 26.2% of the PCP is extractable from the water into the CO_2. However, as the undissociated form partitions into the CO_2, the dissociation equilibrium in water shifts toward production of more undissociated PCP, with the result that there is an increase in partitioning to CO_2. The overall effect is that the measured value for *K* is much higher than would be calculated if it is assumed that only the 26.2% undissociated PCP initially present in the water is extracted by CO_2.

Using the measured values of *K*, the composition of the two phases can be determined. Assuming once again that only the undissociated form of PCP partitions into the CO_2, the value of *K* is

$$K = \frac{[\mathrm{PCP}_{CO_2}]}{[\mathrm{PCP}_{(aq)}] + [\mathrm{PCP}^{-}_{(aq)}]} \qquad (2)$$

where $[\mathrm{PCP}_{CO_2}]$ is the concentration of undissociated PCP in the CO_2-rich phase, $[\mathrm{PCP}_{(aq)}]$ is its concentration in the

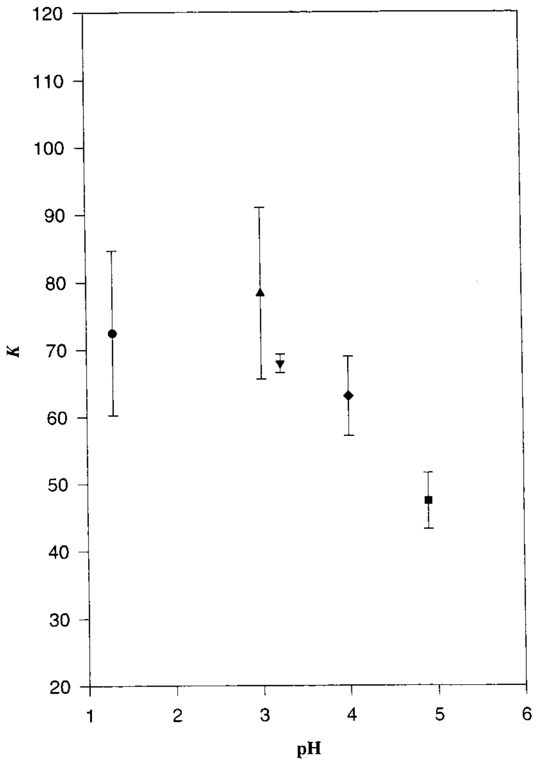

Figure 4. Distribution coefficient, *K*, for PCP as a function of solution pH (0.86 g cm^{-3} CO_2): ●, 40.4 °C; ▲, (40.0 ± 0.9) °C; ▼, (39.1 ± 0.9) °C; ◆, (40.2 ± 0.6) °C; ■, (41.3 ± 0.1) °C.

Table 5. Measured Values of *K* and Calculated Values of % Dissociation As Functions of pH at 40 °C and a CO_2 Density of 0.86 g cm^{-3}

pH	% ionization of PCP in water (calc using eq 3)	measured *K*	actual % PCP^- in system[a]
1.3	0.1	72 ± 12	0.00050
3.0	3.4	78 ± 12	0.023
3.2	5.3	68 ± 1	0.041
4.0	26.2	63 ± 6	0.24
4.9	73.8	47 ± 4	1.25

[a] $[PCP^-_{aq}]/([PCP_{aq}] + [PCP_{CO_2}]) \times 100$.

water-rich phase, and $[PCP^-_{(aq)}]$ is the concentration of pentachlorophenoxide ions in the water-rich phase, resulting from the dissociation of PCP according to

$$PCP_{(aq)} + H_2O_{(l)} \rightleftharpoons PCP^-_{(aq)} + H_3O^+_{(aq)} \tag{3}$$

The concentration of the three species can be calculated knowing the value of *K* and the pH. All species were accounted for, as indicated by mass balances in excess of 90%. The significance of the results in Table 5 is that even at pH values higher than the pK_a of the acidic species being extracted, extraction efficiency is very high. It is not necessary to acidify the aqueous phase since, at pH 3, 99% of the pentachlorophenol can be extracted from a solution with a concentration of 1 ppm with an equal volume of CO_2.

Effects of Ionic Strength. The effect of increasing the ionic strength was measured by adding $NaCl_{(s)}$ to the aqueous phase and measuring the value of *K* at 40.0 °C and 0.86 g cm^{-3} CO_2. As shown in Figure 3, there was a marked increase in *K* with increasing ionic strength. For analytical purposes, values of *K* above approximately 50 are adequate, since this implies that approximately 98% of the analyte has partitioned into the CO_2 phase. Increasing the ionic strength to 1.0 M causes the value of *K* to increase to 190. This value for *K* is higher than necessary for what is required for a "complete" extraction; however, the effect of ionic strength is illustrated.

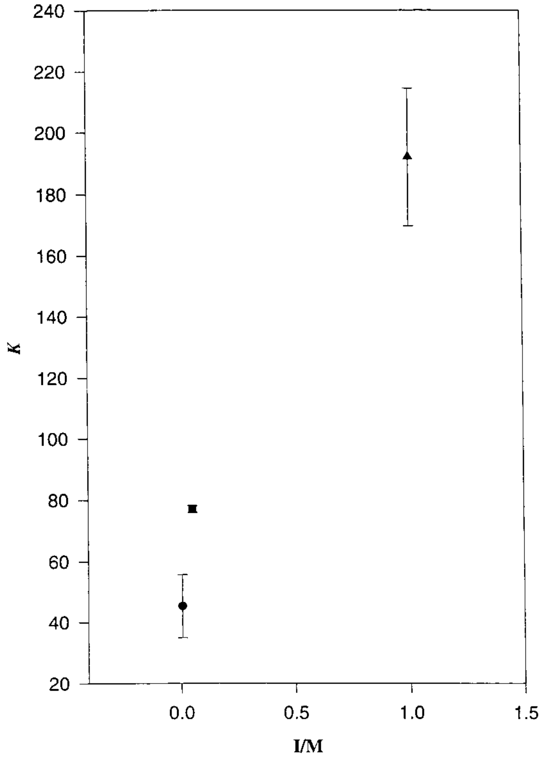

Figure 5. Distribution coefficient, *K*, for PCP as a function of solution ionic strength (0.86 g cm^{-3} CO_2): ●, (39.1 ± 0.9) °C; ■, 40.4 °C; ▲, (39.8 ± 0.1) °C.

Other Solutes. Distribution coefficients for the three solutes pentachlorophenol, 2,3,4,5-tetrachlorophenol (TCP), and 2,4-dichlorophenoxyacetic acid (2,4-D) were determined as functions of density at (42.2, 41.0, and 40.2) °C, respectively. The data are presented in Figure 6. The values of *K* for PCP and TCP are essentially the same, indicating that removing one chlorine atom from PCP (in the ortho position) did not have a significant effect on partitioning as the density of CO_2 was increased. It should be noted, however, that the mass balance of 2,3,4,5-tetrachlorophenol was between 50 and 60%. The mass balance for PCP was greater than 90%.

The values for *K* were lower for 2,4-D than for PCP and TCP. To calculate *K* for 2,4-D, material balance of the solute in the two phases was assumed. At about 0.6 g cm^{-3} CO_2, 95% of the solute was apparently in the water phase at equilibrium. This amount decreased to 16% at a density of 0.9 g cm^{-3}. The distribution coefficient was approximately an order of magnitude smaller for 2,4-D than for PCP. This seems reasonable as it was previously determined that the solubility of 2,4-D in carbon dioxide is also an order of magnitude smaller. As well, water is a good solvent for 2,4-D as it is a stronger acid than PCP and is more readily hydrolyzed.

Impedance Measurements. Based on the high *K* values obtained for PCP, and on the presence of dissolved water in the CO_2 phase, it might be argued that some of the hydrolyzed form of PCP had partitioned to the CO_2 phase. To determine whether this was the case, the impedance of the CO_2 phase was measured. Pure CO_2, CO_2 saturated with water, and CO_2 during a PCP partitioning experiment from water all had impedances greater than 20 MΩ. This was the largest impedance that could be measured. The

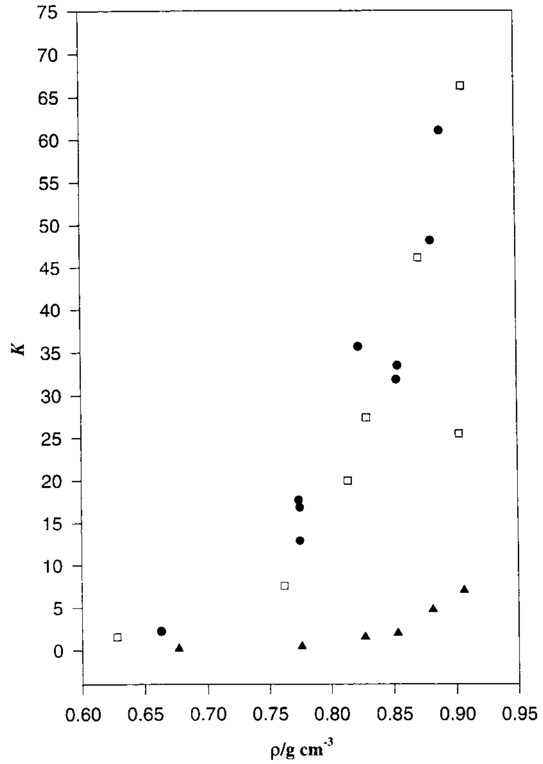

Figure 6. Distribution coefficient, *K*, as a function of density: ●, TCP at (41.0 ± 1.0) °C; □, PCP at (42.2 ± 1.1) °C; ▲, 2,4-D at (40.2 ± 1.0) °C.

minimum number of ions in CO_2 was estimated assuming the impedance of CO_2 was at least 20 MΩ and the conductivity of a hypothetical solution 1 M in $H_3O^+_{(aq)}$ and 1M in $HCO_3^-{}_{(aq)}$ was 390 Ω^{-1} cm^2 mol^{-1}. The concentration of ions in the CO_2-rich phase was calculated to be less than 10^{-12} mol L^{-1}. However, in one liter of carbon dioxide in equilibrium with water there is approximately 0.1 mol of water, that is, no higher than 0.1 mol of carbonic acid. In a water solution containing this concentration of H_2CO_3, the concentration of ions is of the order of 10^{-8} mol L^{-1}. The data therefore indicate that the hydrolysis of carbonic acid in the CO_2-rich phase is negligible. Since this also indicates there is very little free water in the CO_2 phase, then there is none to cause the hydrolysis of the PCP. The existence of pentachlorophenoxide ions in the CO_2 phase is therefore unlikely. The reason for the large partitioning of PCP to CO_2 must be the shifting of the PCP dissociation equilibrium as unhydrolyzed PCP partitions into the CO_2 phase, as explained before.

Conclusions

The partitioning of acidic solutes from water to CO_2 is governed partly by their solubilities in the two phases. The magnitude of the distribution coefficient is only slightly dependent on solute hydrolysis as the concentration of hydrolyzed solute remaining in the water phase is small. Hydrolysis of the solute in the aqueous phase is compensated for by a shift in the hydrolysis equilibrium as the unhydrolyzed form of the solute partitions into the CO_2 phase. Lower distribution coefficients for the more acidic 2,4-D (compared with PCP) are due to its higher solubility in water and lower solubility in CO_2, as opposed to the hydrolysis of 2,4-D in water.

The ratio of solubilities of a solute in the two pure phases cannot always be used as a good estimate of the distribution coefficient because the solubilities in the phases in contact with one another are different from those in the pure phases. In particular, the distribution coefficient of PCP is smaller than the ratio of its solubilities in the two pure phases.

Increasing the ionic strength increased the partitioning of PCP from water to CO_2. This indicates that the increase of partitioning at low pH likely is due to the dual effect of decreasing the hydrolysis and of increasing the ionic strength.

Impedance measurements indicate negligible concentrations of ions in the CO_2 phase. It is therefore unlikely there is partitioning of hydrolyzed PCP into CO_2. These results support the conclusion that the hydrolysis equilibrium shifts toward more unhydrolyzed PCP as the PCP partitions into the CO_2 phase.

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