J. Chem. Eng. Data **1997,** *42,* 908−913

Toluene Solubility in Water and Organic Partitioning from Gasoline and Diesel Fuel into Water at Elevated Temperatures and Pressures

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A simple and reliable system for determining the solubility and partitioning behavior of liquid fuel components in liquid water up to 250 °C has been developed. The system shows good agreement with literature values at ambient temperature for the solubility of toluene and for fuel/water partitioning coefficients (K_{fw}). Toluene solubility increased ∼23-fold by raising the temperature from ambient to 200 °C but was not affected at ambient temperature by changing the pressure from 1 to 50 bar. The increases in partitioning of benzene, toluene, ethylbenzene, xylenes, and naphthalene from gasoline into liquid water with increasing temperature ranged from 10-fold for benzene to 60-fold for naphthalene when the temperature was raised from ambient to 200 °C. Similarly, the increases in partitioning of polycyclic aromatic hydrocarbons from diesel fuel into liquid water ranged from ∼130-fold for naphthalene to 470-fold for methylnaphthalene when the temperature was raised from ambient to 250 °C. The effect of temperature on the partitioning of naphthalene into water from gasoline and from diesel fuel was similar, indicating that the fuel composition had little effect on the fuel/water partitioning behavior.

Introduction

Recent studies have demonstrated the ability of hot water (so-called "subcritical water") to selectively extract a wide range of polar and nonpolar organic compounds from a variety of environmental samples such as soils and waste sludges (Hawthorne et al., 1994; Yang et al., 1995; Yang et al., 1997). By a simple raise in the temperature under enough pressure to maintain the liquid state, the polarity of liquid water can be controlled over a very wide range. For example, raising the temperature of water from ambient to 250 °C decreases its dielectric constant (ϵ) from ∼80 to ∼30, which reduces the polarity of water enough that it becomes a very efficient extraction fluid for even nonpolar organics such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) (Hawthorne et al., 1994; Yang et al., 1995; Yang et al., 1997). At lower temperatures, water can be used to extract polar organics, while at higher temperatures water will extract moderately polar and nonpolar organics. Since the polarity of water can be controlled over a wide range, a high degree of selectivity can be achieved. For example, subcritical water extraction of four samples (a soil, a catalyst, and two sludges) demonstrated that at lower temperatures (50 to 150 °C), benzene, toluene, ethylbenzene, xylenes (BTEX), and phenols were quantitatively extracted by liquid water, while PAHs and alkanes were not extracted (Yang et al., 1997). At 250 or 300 °C, liquid water effectively extracted PAHs, but the high molecular weight alkanes (e.g., $>C_{20}$) were still not extracted. The quantitative extraction of the high molecular weight alkanes was achieved only by superheated steam (250 °C and 300 °C at 5 bar) extractions (Yang et al., 1997).

Although supercritical water ($t > 374$ °C, $p > 221$ bar) has received much attention as an extraction solvent (and degradation media) for organic pollutants (Deshpande et al., 1984; Thomason and Modell, 1984; Kershaw, 1989; Hirth and Franck, 1990; Shaw et al., 1991; Krajnc and Levec, 1994; Gloyna and Li, 1995) and the solubility phenomena in supercritical water has been addressed (Shaw et al., 1991), very few reports have described the solubility changes that occur in hot water (Sanders, 1986), despite the fact that very large solubility changes have been observed. For example, the solubility of benzo[*e*]pyrene has been demonstrated to increase from 4 $ng{\cdot}L^{-1}$ to $\sim 1 \times 10^8$ $ng{\cdot}L^{-1}$ by increasing the temperature of liquid water from ambient (Mackay and Shiu, 1977) to 350 °C (Sanders, 1986). Compared to supercritical water, subcritical water is much less corrosive (Shaw et al., 1991). In addition, the potential for selectivity is much greater since the dielectric constant of liquid water can be controlled from 80 (at ambient temperature) to ∼15 (at 350 °C), while the dielectric constant of supercritical water ranges only from ∼2 to ∼15 (Haar et al., 1984).

The solubility and partitioning of organic compounds in ambient water has been extensively studied, particularly for environmentally important organic compounds such as fuel components (Coleman et al., 1984; Brookman et al., 1985; Cline et al., 1991; Thomas and Delfino, 1991; Lee et al., 1992). Since very little information is available describing the solubility and partitioning behavior of organic compounds in hot water, the purpose of the present study is to determine the effect of temperature on the solubility and partitioning behavior of organic pollutants from gasoline and diesel fuel in water under enough pressure to maintain the liquid state. A new laboratory device has been built to allow partitioning to be determined over a wide range of pressures (1−50 bar) and temperatures (25−250 °C). The ability of the new method to determine partitioning behavior is demonstrated at ambient temperature by comparison of toluene solubility to literature values, and the partitioning coefficient of fuel components such as BTEX, PAHs, and *n*-alkanes between liquid fuel and water was determined at temperatures ranging from ambient to 250 °C.

Experimental Section

Samples. "Baker Resi-Analyzed" toluene (J. T. Baker Chemical Co., Phillipsburg, NJ) was used to determine the toluene solubility. The gasoline was unleaded API gasoline (API 91-1, American Petroleum Institute). The hydrocarbons range from C_3 to C_{13} with 13.58 mass % of *n*-paraffins,

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S0021-9568(96)00395-0 CCC: $14.00

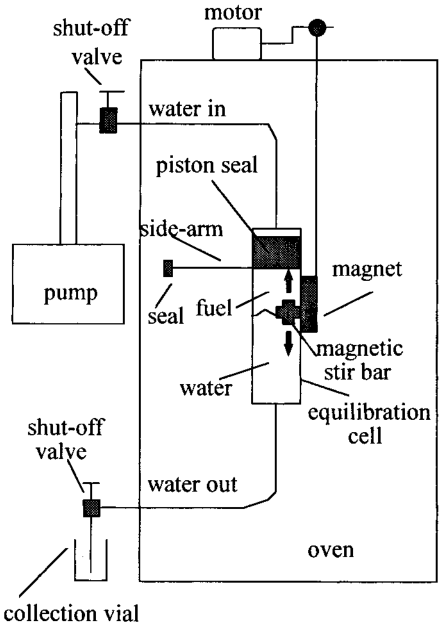

Figure 1. Experimental arrangement for the determination of organic solubility and partitioning in liquid water at elevated temperatures and pressures. Components are described in the text.

27.43 mass % of isoparaffins, 6.84 mass % of naphthenes, 39.05 mass % of aromatics, 11.74 mass % of olefins, and 1.36 mass % of unknowns. The diesel fuel was purchased locally with a hydrocarbon range of $C_{10}-C_{22}$. Since the concentrations of some of the higher molecular weight PAHs were too low in the diesel fuel to determine the fuel/water partitioning coefficients (K_{fw}), selected PAHs including anthracene (0.66 $mg{\cdot}mL^{-1}$ fuel), fluoranthene (0.36 $mg{\cdot}mL^{-1}$), pyrene (0.5 $mg{\cdot}mL^{-1}$), chrysene (0.33 $mg{\cdot}mL^{-1}$), benzo[*b*]fluoranthene (0.56 $mg{\cdot}mL^{-1}$), perylene (0.41 $mg{\cdot}mL^{-1}$), and benzo[*ghi*]perylene (0.34 $mg{\cdot}mL^{-1}$) were spiked into the diesel sample.

Organic (Fuel)−Water Equilibration. A new laboratory device has been built to allow partitioning to be determined over a wide range of pressures and temperatures. Water and liquid fuel (or neat toluene) were loaded into an equilibrium cell inside a gas chromatograph (GC) oven. A movable piston seal was placed on top of the organic phase to isolate the organic phase from the fresh water coming from the pump, which is used to transport the equilibrated water from the cell for collection and analysis. In order to achieve a faster equilibrium, a magnetic stir bar was moved up and down inside the cell by a motor-driven magnet to break the interface between the organic and water phase. Figure 1 shows the experimental setup for the determination of toluene solubility and fuel compound partitioning between bulk fuel and liquid water. System components include the pump, ISCO Model 260D syringe pump (ISCO, Lincoln, NE); water, HPLC-grade water (Fisher Scientific, Fair Lawn, NJ); equilibration cell; Keystone supercritical fluid extraction cell (7 mL, 9.4 mm i.d. × 100 mm length, Keystone Scientific, Bellefonte, PA); side arm, 10 cm long $^{1}/_{16}$ in. stainless steel tubing; piston seal; home-made stainless steel rod (8 mm o.d. × 30 mm length) with spring-loaded o-ring seals on both ends; magnetic stir bar; x-shaped, 10 mm in length; magnet, 18 mm diameter × 10 mm thickness; motor, GT21-18, 1/40 HP motor with variable speed (G. K. Heller Corp., Floral Park, NY); oven, HP Model 5730A GC oven (Hewlett-Packard, Avondale, PA); shut-off valve, HIP Model 15-11AF1 shut-off valve (High Pressure Equipment Co.; Erie, PA); collection vial, 7 mL glass vial (Supelco Inc., Bellefonte, PA). The procedure for the experiment is as follows:

The bottom end of the equilibration cell is sealed first. A cross magnetic stir bar is placed inside the cell (it is very important to make sure that the stir bar is trapped by the magnet attached on the outside wall of the cell). Water (3 mL) and toluene or fuel (1.5 mL) are then loaded into the cell. The piston seal is pushed into the loaded cell from the top. When the lower end of the piston reaches the organic (fuel) surface (no more air running out from the cell through the side arm), the side arm is sealed by a tubing union and cap. The upper end of the cell is then sealed with the cell cap. The loaded and sealed cell is placed inside a GC oven and connected to the water inlet and outlet. The cell is pressurized to the desired pressure by pumping water into the top of the cell while the water outlet (40 cm long $^{1}/_{16}$ in. stainless steel tubing) is closed by the shut-off valve. (Note that this water is used only to pressurize the cell and is isolated from the fuel/water mixture by the piston seals.) For higher temperature experiments, the cell is initially pressurized to ~8 bar. Then the valve between the cell and the pump is closed to avoid the pump running in reverse during the heat-up time. After the oven is heated to the desired temperature, the pump pressure is increased to 50 bar and the valve between the cell and the pump is opened. The oven is purged with ~500 $mL{\cdot}min^{-1}$ of nitrogen during the mixing and equilibration time in order to reduce the hazard of explosion if the equilibration cell leaked (which did not occur during these studies). Please also note that the valve between the cell and the pump remains open all the time (except the heat-up time for the high-temperature experiments) during one experiment to avoid possible high pressure building up inside the cell caused by heating. The temperature of the water inside the equilibration system was measured by a thermocouple placed in a “tee” fitting at the outlet of the equilibration cell and lagged 1 min behind the oven temperature. For example, the water temperature in the outlet of the cell reached 250 °C only 1 min after the oven temperature. The pressure was measured by the water pump. After the desired temperature and pressure are reached, the motor is turned on to drive the magnet attached outside of the cell so that the magnetic stir bar moves up and down inside the cell, thereby breaking the fuel/water interface at a rate of 4 times per second. After the desired mixing time (20 min for toluene−water and 60 min for fuel−water), the motor is turned off. The fuel and water phases are then allowed to separate for 15 min. After the equilibration, the shut-off valve of the water outlet is slowly opened. Then 2 mL of aqueous phase samples were taken at constant pressure by adding fresh water on top of the piston seal. The 2 mL sample is collected in a 7 mL vial that contains 2 mL of methylene chloride. After the collection of the aqueous samples, the pressurization is stopped and the oven is cooled to ambient temperature. The water outlet tubing is disconnected from the cell and rinsed with 3 mL of methylene chloride.

Gas Chromatographic Analysis. Two internal standards (1,3,5-triisopropylbenzene and 1,2,3,4,5,6,7,8-octahydrophenanthrene) were added to the collection vial, as well as to the vial used to collect the transfer line rinsings prior to GC analysis. After the vials were shaken ~100 times by hand, the methylene chloride was removed from the collection and rinsing vials. The PAH analysis was done by gas chromatography/mass spectrometry (GC/MS) (HP Model 5988) using a 25 m × 0.25 mm i.d. (0.17 μm film thickness) HP-5 column (Hewlett Packard). The initial

Table 1. Toluene Solubility (*s*), Partitioning (K_{fw}), and Equilibrium time (*t*) in Water at Ambient and Elevated Temperatures (*t*) and Pressures (*p*) Obtained by Different Methods

method	t/°C	p/bar	t/min	s/μg·mL^{-2}	K_{fw}
literature value (Verschueren, 1977)	20	1		515	
static equilibration	21	1	30	92 (30)[a]	*b*
	21	1	360	346 (10)	*b*
	21	1	960	501 (3)	1600
dynamic mixing	21	1	30	541 (3)	1500
	21	1	960	527 (6)	1600
pressurized cell	21	5	20	538 (10)	1500
	21	50	20	547 (8)	1500
	100	50	20	1590 (3)	530
	150	50	20	4430 (3)	190
	200	50	20	12600 (19)	65

[a] %RSDs based on analyses of triplicate samples. [b] K_{fw} values are not given since the systems did not reach equilibrium.

Table 2. Effect of Temperature on the Partitioning of Organic Compounds between Gasoline and Liquid Water

	K_{fw} (% RSD)[b]				
	c/g·L^{-1} [a] (% RSD)[b]	21 °C	100 °C	150 °C	200 °C
benzene	16.8 (7)	350 (8)	160 (10)	80 (3)	35 (10)
toluene	75.6 (5)	1100 (6)	390 (9)	150 (5)	60 (7)
ethylbenzene	31.7 (3)	3600 (5)	1200 (3)	420 (2)	120 (7)
m,*p*-xylene	68.8 (3)	3800 (5)	1200 (3)	440 (3)	130 (7)
o-xylene	24.0 (3)	3100 (5)	940 (4)	350 (2)	110 (6)
naphthalene	4.4 (1)	4700 (16)	880 (3)	280 (3)	77 (11)
C_7	10.9 (8)	*c*	*c*	7900 (21)	1500 (21)
C_8	5.9 (4)	*c*	*c*	*c*	4300 (58)

[a] Concentrations are in the original fuel before equilibration with water. [b] %RSDs are based on analyses of triplicate samples. [c] Not detected in the water phase. Detection limit was ~0.7 μg·mL^{-1} water.

Table 3. Comparison of Partitioning Coefficients of Fuel Compounds between Gasoline and Water at Ambient Temperature with Reference Data

	K_{fw} (% RSD)[a]		
	Cline et al., 1991 22 °C, 1 bar	Brookman et al., 1985 13 °C, 1 bar	this work 21 °C, 50 bar
benzene	350 (21)	230	350 (8)
toluene	1300 (14)	980	1100 (6)
ethylbenzene	4500 (13)	3200	3600 (5)
m,*p*-xylene	4400 (12)	3300	3800 (5)
o-xylene	3600 (12)	2300	3100 (5)

[a] % RSDs are based on triplicate or replicate samples.

oven temperature was 80 °C and was ramped to 320 °C at 8 °C per min. The determination of BTEX and alkanes was performed using a HP Model 5890 II GC equipped with a flame ionization detector (FID), using a 60 m DB-1 column with 0.25 mm i.d. and 1 μm film thickness (J&W Scientific; Folsom, CA). The oven temperature was held at 35 °C for 6 min and was then increased to 320 °C at a rate of 6 °C per min. Autosampler injections were performed either in the splitless mode for 0.3 min or in the split mode with a ratio of ~1:30 depending on the analyte concentration for both GC/MS and GC/FID. The individual PAHs, BTEX, and *n*-alkanes were quantitated using standard calibration curves generated from appropriate dilutions of a mixture of target analytes (also compared to the internal standards). The amount detected in the collected water phase was combined with the amount detected in the rinsing to calculate the total amount in the water after equilibration.

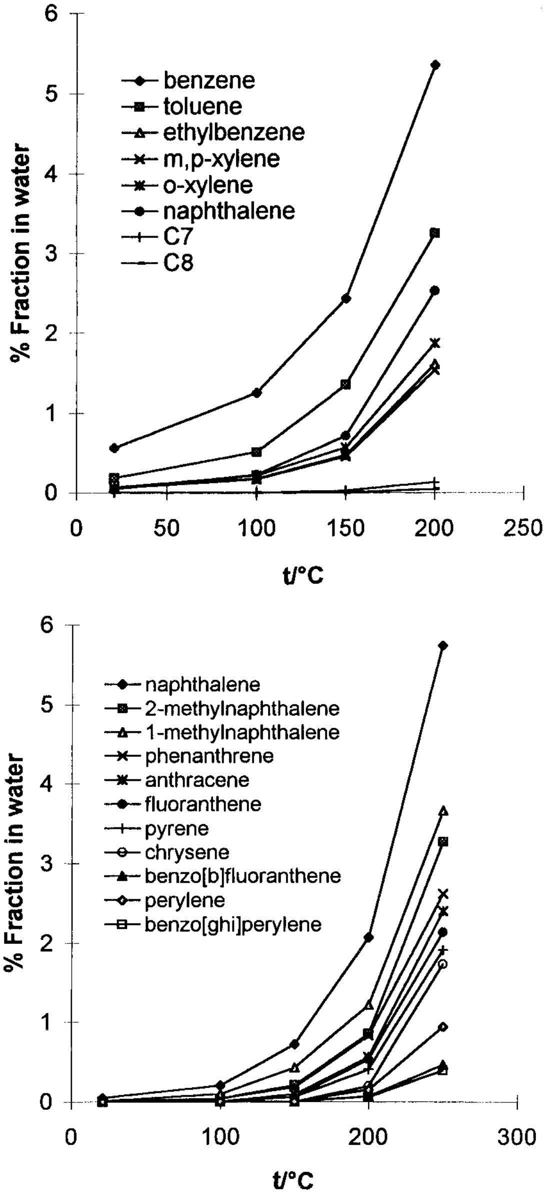

Figure 2. Effect of temperature on the fraction (see text for definition) of each organic in water for gasoline—water (top) and diesel—water (bottom) systems.

Results and Discussion

Toluene Solubility. Initially, 3 mL of water and 1.5 mL of toluene were loaded into a 4.5 mL vial (no head space), and static equilibration was performed for 30 min, 6 h, and 16 h. By using this static equilibration mode, 16 h were required to obtain solubility similar to that reported by Verschueren (1977). When the same water and toluene mixtures (loaded in a 4.5 mL vial as described above) were mixed by a mechanical rotator for 30 min and 16 h, values of 541 and 527 μg·mL^{-1} were obtained for 30 min and 16 h showing that equilibrium was achieved within 30 min using the dynamic mixing mode (Table 1).

Since dynamic mixing yielded much faster equilibration in the vial studies, a magnetic stir bar was used for the pressurized cell method to break the interface of toluene and water in order to achieve a faster equilibration. Using this approach, toluene solubility was first determined at 5 and 50 bar to evaluate the pressure effect on solubility. As shown in Table 1, water pressure did not significantly affect toluene solubility since solubilities at 5 and 50 bar agree within the experimental error. Most importantly, the

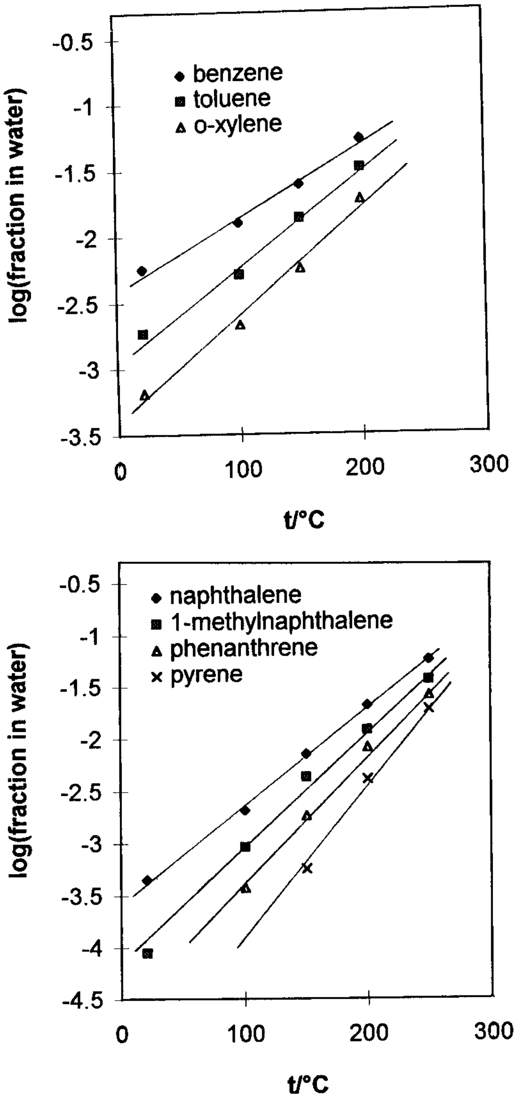

Figure 3. Log (fraction in water) versus temperature for selected organics for gasoline-water (top) and diesel–water (bottom) systems.

solubilities obtained with the pressurized cell are in good agreement with the literature value (Verschueren, 1977) and with the mixed vial values determined in our lab, thus demonstrating the reliability of the pressurized cell method.

Previous work shows that water temperature has more influence than pressure on the water extraction efficiencies of nonpolar organics (Hawthorne et al., 1994; Yang et al., 1995; Yang et al., 1997). Therefore, toluene solubility was determined at different temperatures (at 50 bar). As expected, toluene solubility significantly increased by raising the temperature. For example, toluene solubility increased from 547 μg·mL^{-1} at ambient temperature to 12 600 μg·mL^{-1} at 200 °C, an increase of 23-fold (Table 1).

Partitioning of Fuel Components from Gasoline into Water. The organic partitioning coefficient between fuel and water is normally defined as the following equation (Brookman et al., 1985; Cline et al., 1991):

$$K_{fw} = C_f/C_w$$

where K_{fw} is the fuel–water partitioning coefficient, C_f is the concentration of component in fuel after the fuel–water equilibration (calculated by subtracting the loss in the organic phase from the initial concentration), and C_w is the concentration of component in water after the fuel–water equilibration.

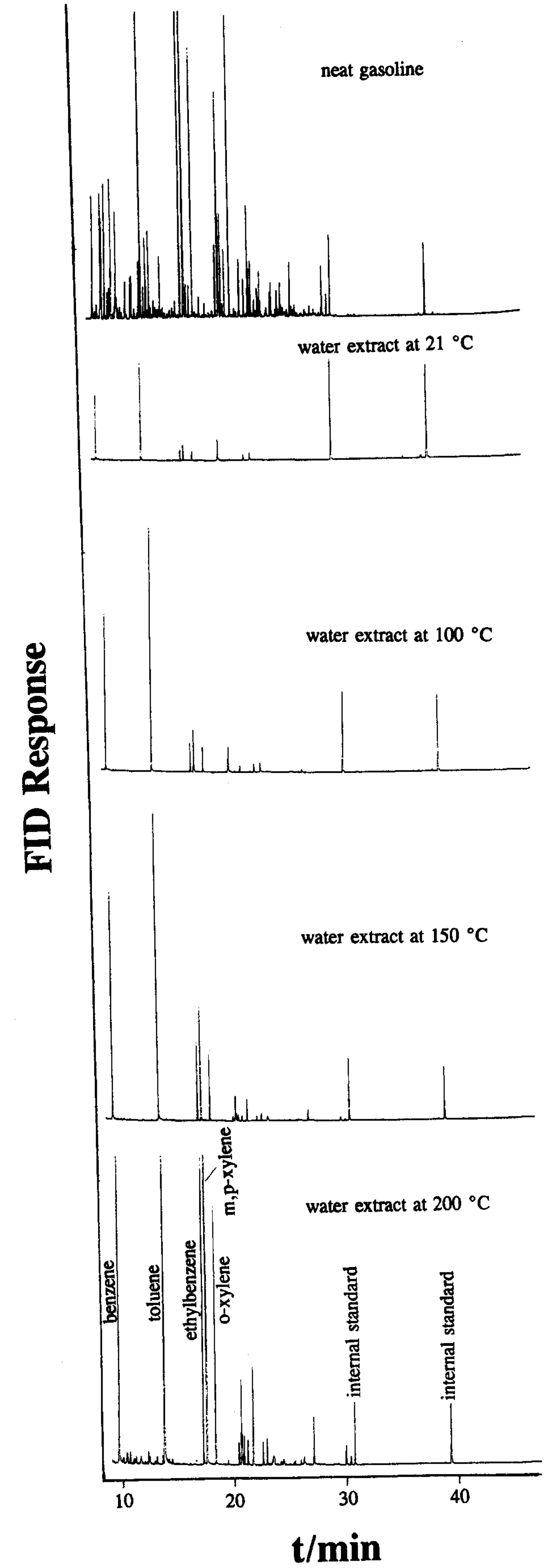

Figure 4. Chromatograms of neat gasoline and the aqueous extracts (after gasoline-water equilibration) at different temperatures.

The partitioning coefficient (K_{fw}) of fuel components in the gasoline–water system was determined at tempera-

Table 4. Effect of Temperature on the Partitioning of PAHs between Diesel Fuel and Liquid Water

		K_{fw} (% RSD)[b]				
	c/g·L^{-1}[a] (% RSD)[b]	21 °C	100 °C	150 °C	200 °C	250 °C
naphthalene	1.6 (10)	4400 (21)	980 (5)	280 (7)	95 (11)	33 (17)
2-methylnaphthalene	11 (11)	29000 (41)	5800 (38)	960 (16)	230 (31)	59 (27)
1-methylnaphthalene	4.2 (11)	23000 (31)	2200 (21)	470 (8)	160 (37)	53 (26)
phenanthrene	1.9 (11)	*c*	5400 (14)	1100 (28)	240 (24)	75 (37)
anthracene	0.66 (10)	*c*	*c*	2100 (40)	360 (32)	81 (33)
fluoranthene	0.36 (9)	*c*	*c*	3500 (37)	370 (15)	92 (26)
pyrene	0.50 (3)	*c*	*c*	3500 (41)	490 (47)	100 (21)
chrysene	0.33 (18)	*c*	*c*	*c*	1000 (42)	110 (20)
benzo[*b*]fluoranthene	0.56 (29)	*c*	*c*	*c*	2900 (43)	430 (35)
perylene	0.41 (32)	*c*	*c*	*c*	1300 (49)	210 (39)
benzo[*ghi*]perylene	0.34 (41)	*c*	*c*	*c*	3400 (58)	500 (40)

[a] Concentrations are in the original fuel before equilibration with water. [b] % RSDs are based on analyses of triplicate samples. [c] Not detected in the water phase. Detection limit was ~0.05 μg·mL^{-1} water.

Table 5. Comparison of Partitioning Coefficients of PAHs between Diesel and Water at Ambient Temperature with Reference Data

	c/g·L^{-1}		log K_{fw}				
			Lee et al., 1992				
	Lee et al., 1992 concn range of four diesel samples	this work	DF1	DF2	DF3	DF4	this work
naphthalene	0.35−1.5	1.6	3.67	3.62	3.71	3.71	3.65
2-methylnaphthalene	3.5 −9.0	11	4.47	4.29	4.44	4.49	4.46
1-methylnaphthalene	2.0 −4.0	4.2	4.31	4.21	4.36	4.33	4.36

tures ranging from 21 to 200 °C using the pressurized cell method developed in this study. As shown in Table 2, K_{fw} is reproducible, since the % RSDs are typically less than 10% on the basis of analyses of triplicate samples. The BTEX partitioning coefficients (K_{fw}) for the gasoline−water system were previously determined at ambient temperature and pressure (Brookman et al., 1985; Cline et al., 1991). As shown in Table 3, the K_{fw} values for benzene obtained in this study and in the literature (Cline et al., 1991) agree very well within the experimental error. For all of the remaining BTEX components, our K_{fw} values lie between the values reported by Brookman et al. (1985) and Cline et al. (1991), as shown in Table 3. The good agreement in K_{fw} between literature and our values demonstrates again that our technique is a reliable method to determine organic partitioning coefficients. Since K_{fw}s in Table 3 were obtained at different pressures (1 bar in Brookman et al. (1985) and Cline et al. (1991) and 50 bar in this work), pressure (1 vs 50 bar) may not affect K_{fw} even though different gasoline and different sets of measurements were used for determining K_{fw}s.

The effect of temperature on the fraction of each organic compound found in the water phase is shown in Figure 2, top (the fraction in water = the mass of each organic compound found in 3 mL water after equilibration divided by the mass of the same organic in 1.5 mL of the fuel before equilibration. Values on the graphs are given in mass %). Only 0.5 mass % of the total benzene from the gasoline was found in the water phase after equilibration at ambient temperature, while 99.5 mass % benzene still remained in the gasoline phase. However, the fraction of all of the organic compounds in water increased in a logarithmic manner by raising the temperature (Figure 3, top). At 100 °C, partitioning into water was increased approximately two to four times compared with that at 21 °C. Further increases were achieved by raising the temperature to 150 °C (4 to 16 times higher than that obtained at 21 °C). At 200 °C, more than 5 mass % of the benzene partitioned into the water phase, an increase of ~10-fold. The enhancement in partitioning at 200 °C vs 21 °C was even higher for toluene (~18-fold), ethylbenzene and xylenes (~30-fold), and naphthalene (~60-fold).

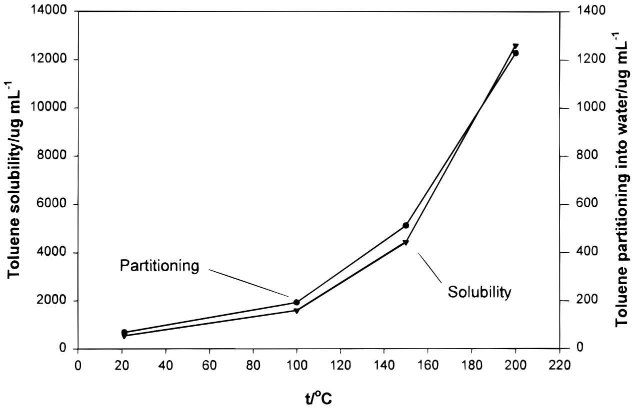

Figure 5. Temperature influence on toluene solubility in water and toluene partitioning from gasoline into water at 50 bar.

In contrast to the aromatics, *n*-alkanes did not partition significantly into water (<detection limit: ~0.7 μg·mL^{-1} water) at temperatures lower than 150 °C. For example, only 0.046 mass % of the *n*-octane was found in water at 200 °C. Similar class-selective extractions were previously reported for environmental samples such as soil, sludge, sediments, and air particulates using water at temperatures from 100 to 150 °C (Hawthorne et al., 1994; Yang et al., 1997). Figure 4 shows the comparison of chromatograms of the original gasoline and the aqueous phase organics (after water−gasoline equilibration) at different temperatures. These chromatograms also clearly demonstrate that the organic partitioning into water is increased by raising water temperatures and that only the aromatic components show significant partitioning into the water at any temperature.

The similarities between the effect of temperature on the solubility of toluene and on the partitioning of toluene from gasoline into water are shown in Figure 5. Both toluene solubility and partitioning from gasoline are increased by the same proportions by raising the temperature. Linear regression analysis shows a direct relationship between solubility and partitioning, since the correlation coefficient (r^2) is 0.995. In addition, the K_{fw}s of toluene in the gasoline−water system (Table 2) are only 8 to 36% lower than that in toluene−water system (Table 1) for all of the four temperatures tested. Therefore, there are no significant cosolute effects on toluene partitioning from gasoline into water.

PAH Partitioning from Diesel Fuel into Water. PAH partitioning between diesel fuel and water was determined at 50 bar and temperatures ranging from 21 to 250 °C, and the K_{fw} values are shown in Table 4. Lee et al. determined the K_{fw} values for naphthalene from four diesel samples in ambient water using a batch equilibration technique (Lee et al., 1992). As shown in Table 5, our log K_{fw} values agree very well with the range of the four diesel fuels previously reported (Lee et al., 1992). The lower molecular weight PAHs showed enough partitioning into water that K_{fw} could be determined at all temperatures. However, K_{fw} for the higher molecular weight PAHs could not be determined at the lower temperatures because the equilibrium concentrations in water were below the detection limit of ∼0.05 μg of PAH per mL of water.

As shown in Figure 2 (bottom), the PAH fraction in water was low for naphthalene and methylnaphthalenes at 21 °C, ranging from 0.007 to 0.045 mass % of the original fuel concentration. However, the PAH partitioning into water increased logarithmically when the fuel−water system was heated (Figure 3, bottom). Each additional 50 °C increase in temperature increased partitioning into water by approximately three to four times. The partitioning of naphthalene and methylnaphthalenes into water was increased 130- to 470-fold by raising the temperature from 21 to 250 °C. The higher molecular weight PAHs did not significantly partition into water ($<0.05\ \mu g \cdot mL^{-1}$ water) at lower temperatures (e.g., 21 °C). For example, phenanthrene was not detected in water until 100 °C, while anthracene, fluoranthene, and pyrene could be detected in water at 150 °C. When the temperature was 200 °C or higher, all of the PAHs were detected in the water, although the partitioning into water decreased with the molecular weight of PAHs. Since naphthalene was present in both the gasoline and diesel fuel, the K_{fw} values can be compared to determine if the fuel composition affects the partitioning behavior. As shown in Tables 2 and 4, the K_{fw} values are similar (on the basis of triplicate samples of each fuel) for naphthalene in gasoline−water and in diesel−water at each temperature (e.g., 21 °C, 4700/4400; 100 °C, 880/980; 150 °C, 280/280; 200 °C, 77/95, for gasoline−water/diesel−water, respectively), indicating that the fuel composition does not have a significant effect on the naphthalene partitioning into water.

Conclusions

A liquid fuel−water equilibration system using a pressurized cell and a magnetic stir bar was developed to determine liquid organic solubility and partitioning in water. This equilibration device can be operated over a wide range of temperatures (from ambient to 250 °C) and pressures (1−50 bar). This newly developed method is reliable since toluene solubility and organic partitioning coefficients from gasoline and diesel fuel obtained by this method agreed well with literature values at ambient conditions. Raising the water temperature has a significant effect on enhancing toluene solubility, while water pressure has no significant effect. The partitioning of both BTEX and PAHs from liquid fuel into water was greatly increased at higher temperatures. The toluene partitioning coefficients for toluene/water and gasoline/water systems were similar, demonstrating no large cosolvent effect.

Acknowledgment

The authors appreciate instrument loans from ISCO.

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Received for review December 9, 1996. Revised March 11, 1997. Accepted May 21, 1997.[⊗] The authors thank the American Petroleum Institute and the U.S. Department of Energy for financial support.

JE960395V

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.