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# Octanol/Water Partition Coefficients and Water Solubilities of Phthalate Esters†

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Measurements of the octanol/water partition coefficients ($K_{ow}$) and water solubilities of di-*n*-octyl phthalate (DnOP) and di-*n*-decyl phthalate (DnDP) by the slow-stirring method are reported. The water solubility was also measured for di-*n*-hexyl phthalate (DnHP). The log $K_{ow}$ values of dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DnBP), di-*n*-pentyl phthalate (DnPP), and DnHP, determined in a previous study, and the log $K_{ow}$ values of DnOP determined again in this study were correlated against the number of carbons in the phthalate side chain. The straight line regression equation (log $K_{ow} = 0.979 + 0.615$, $r^2 = 0.993$) was used to extend the estimate for a carbon number 10; that is, log $K_{ow} = 10.41$ for DnDP. The slow-stirring log $K_{ow} = 8.83 \pm 0.05$ reported here for DnDP suggests that the decrease in solubility of the phthalate in the water layer is nonlinear when the side chain carbon length increases beyond eight carbons. Similarly, the straight line regression equation derived from correlation of the measured water solubilities for DnOP and DnHP reported here and the literature values for DMP, DEP, and DnBP against side chain carbon number predicted a 0.005 $\mu$g/L water solubilty for DnDP. The measured water solubility of DnDP (0.22 ± 0.05 $\mu$g/L) reported here was 44-fold greater.

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## Introduction

The octanol/water partition coefficient ($K_{ow}$) is the physicochemical parameter most commonly measured in the laboratory and used to quantitatively characterize the hydrophobic nature of organic compounds. The slow-stirring method (De Bruijn et al., 1989) is reported to avoid the formation of emulsions, and the measurement of $K_{ow}$ with log > 5 is limited only by the ability to determine the water phase concentration accurately. A measured $K_{ow}$ can be in error by several orders of magnitude for several reasons, including the following: equilibrium between the octanol and water is not achieved due to the common problems of incomplete phase separation; emulsion formation due to excessive mixing; the tendency of some chemicals to self-associate; and sorption of the chemical to very fine (colloidal) particulate matter in the aqueous phase.

A recent critical review (Staples et al., 1997) of water solubility and $K_{ow}$ measurements of 18 commercial phthalate esters, with chain lengths ranging from 1 to 13 carbons, determined that experimental measurements for phthalate esters with alkyl chain lengths < 6 were reliable while corresponding measurements for the esters with alkyl chain lengths ≥ 6 were suspect because of the spread in their reported values. For example, the reported log $K_{ow}$ values for DnHP varied only 1 order of magnitude while the values for DnOP varied over >3 orders of magnitude. A measured value was not even available for DnDP.

The purpose of this study was to measure the slow-stirring water solubilities of DnHP, DnOP, and DnDP and the $K_{ow}$ of DnDP. The slow-stirring $K_{ow}$ values of dimethyl phthalate (DMP), diethyl phthalate (DEP), butylbenzyl phthalate (BBP), di-*n*-butyl phthalate (DnBP), di-*n*-pentyl phthalate (DnPP), DnHP, diethylhexyl phthalate (DEHP), and DnOP were reported previously (Ellington and Floyd, 1996). The $K_{ow}$ measurement for DnOP was repeated in this study concurrently with the measurement for DnDP.

## Materials and Methods

***Reagents.*** Deionized water was distilled with a Barnstead Mega-Pure MP-6A system (Dubuque, IA) and filtered through 0.20 $\mu$m Nylon 66 membrane filter disks (Supelco, Bellefonte, PA). Acetonitrile and methanol were ULTRA RESI-ANALYZED grade for residue organic analysis obtained from J. T. Baker (Phillipsburg, NJ). Octanol >99.5% pure was obtained from Aldrich Chemical Co. (Milwaukee, WI) and was used as received. Di-*n*-hexyl phthalate (DHP, ≥98%) and di-*n*-octyl phthalate (DnOP, ≥98%) were obtained from Chem Service (West Chester, PA) and used as received. Di-*n*-decyl phthalate (DnDP) was supplied by Exxon Chemical Company and was determined to be 99.4% pure when a 1 $\mu$L injection of the neat phthalate was analyzed by gas chromatography/Fourier transform infrared/mass spectrometry analysis (GC/FT-IR/MS). Similarly, the purities of DnHP and DnOP were determined to be 98.6% and 98.7%, respectively.

***Apparatus and Experimental Procedure.*** A Pyrex cylindrical jar, approximate volume 11.5 L (25.7 cm i.d. × 25.4 cm height, Scientific Products, Stone Mountain, GA), was fitted with a 2-mm i.d. straight bore stopcock that was inserted through the container wall at the bottom and turned down to form a tap for withdrawing water. The jars were cleaned by soaking with an aqueous solution of Micro (Chicago, IL) in laboratory deionized water. The jars were rinsed sequentially with deionized water, with concentrated nitric acid, and again with deionized water. A final rinse was made with the distilled, 0.20-$\mu$m-filtered water. A Teflon-coated magnetic stirring bar (2.54 cm) was added and the jar filled to a level of 6 L for water solubility measurements and 10 L for $K_{ow}$ determinations. In the

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water solubility experiments, 100 $\mu$l of the neat phthalate was added to the water surface and a 30 × 30 cm by 6-mm-thick flat glass plate was placed over the smooth ground open end of the jar to form a tight seal. This prevented both the entrance of airborne particulate matter and the evaporation of water. The water for the $K_{ow}$ experiments was presaturated with octanol by adding 5.5 mL of octanol and slow-stirring for 24 h. The reported water solubility of octanol in water is 0.0347 M (De Bruijn et al., 1989) or approximately 0.5 mL/L. Droplets of octanol were always observed on the water surface at the end of the presaturation. The phthalate, dissolved in 50 mL of octanol at a concentration of 35−75 mg/mL, was carefully layered on the water surface and again covered with the flat glass plate seal. The stirring rate was adjusted in the water solubility experiments in order to move the droplets of phthalate on the surface of the water at approximately 10 cm/min, while in the $K_{ow}$ experiments the rate of stirring was adjusted to create a vortex of approximately 1 cm at the octanol/water interface. To prevent heat transfer from the magnetic stirrer during the experiments, the jar was placed on four 4 × 4 cm by 0.5-cm-thick blocks of wood. The experiments were performed in an Environ-Room (Lab-Line Instruments, Melrose Park, IL) set to maintain a constant room air temperature of 25 ± 0.1 °C, the same temperature that was observed in the octanol/water systems when periodic measurements were made.

***Solid-Phase Extraction (SPE).*** Water samples were collected from the cylindrical jars in either 0.5-L (water solubility measurements) or 1-L ($K_{ow}$ measurements) volumetric flasks. Before the collection of the sample, a volume of methanol was added to the collection flask to make the collected sample 0.5% in methanol. The sample flask also contained 100−300 ng of one of the other phthalates (not being measured) that served as an internal standard. The phthalates were extracted from the collected water sample using a solid-phase disk procedure (Hagen et al., 1990). The solid-phase extractions utilized the 1-L vacuum filtration glassware commonly used to filter liquid chromatography solvents, which was fitted with a ceramic fritted glass support and a 40/35 joint (Sigma-Aldrich). The strength of the applied vacuum was adjusted with a bleed valve attached to a tee joint in the vacuum hose.

The extraction disk (47-mm C18 Empore disk, Varian Analytichem, Harbor City, CA) was placed in the filtration apparatus and cleaned by adding 6 mL of acetonitrile to the reservoir and applying gentle vacuum until the disk was saturated. The disk was soaked for 3 min before drying under a full vacuum. The cleaning step was repeated with methanol then the disk was activated by adding 10-mL of methanol to the reservoir and applying slight vacuum to saturate the disk. At the end of 3 min the level of methanol dropped to 3−5 mm above the surface of the disk. Then the water sample was added to the reservoir and the vacuum adjusted to yield a flow of approximately 20 mL/min until all the water passed through the disk. A sheet of clean aluminum foil was placed loosely over the mouth of the reservoir during the extraction. The foil was pressed tightly over the lip of the reservoir to form a seal, before full vacuum was applied for 30 s to dry the disk. The interior surface of the reservoir and the bottom surfaces of the filter holder were rinsed with acetonitrile to remove residual droplets of water; care was taken to avoid rinsing the extraction disk.

The sorbed phthalates were eluted into a collection tube with three 2-mL volumes of acetonitrile. The acetonitrile was transferred to a glass-stoppered, 10-mL, tapered tube. In the water solubility experiments, 25 $\mu$L of octanol was added to the acetonitrile at this time; this was approximately the same volume of octanol retained by the disk when the $K_{ow}$ water layer samples were extracted. This octanol acted as a “keeper” solvent during the subsequent concentration step. Acetonitrile was removed by gentle, nitrogen-gas blowdown while warming the tube with steam. The final concentrated volume used for the water solubility and $K_{ow}$ determinations was 25−50 $\mu$L.

***Solutions for Quantitative Analysis.*** Stock solutions (5−10 g/L) were prepared by weighing each phthalate into separate 5-mL volumetric flasks and bringing to final volume with methanol. Sequential dilutions were made in methanol to yield 100 mg/L and 20 mg/L standards. Similarly, 100 mg/L, 20 mg/L, and 4 mg/L standards that contained all three phthalates together in octanol were prepared. The three mixed phthalate in octanol standards were used to calibrate detector response and linearity and to determine the optimum temperature and pressure programs for GC analysis. The 20 mg/L solutions of the individual phthalates in methanol were used in spiking experiments designed to determine SPE recoveries, and they were also used as the internal standard spiking solutions.

***Gas Chromatography (GC).*** Analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph (Palo Alto, CA) equipped with a programmable pressure, cool on-column inlet, flame ionization detector (FID) fitted with a 30 m, 0.53-mm i.d., 0.5 $\mu$m df XTI-5 Integra-Guard capillary column (Restek, Bellefonte, PA). The on-column inlet was operated in the constant flow mode set at 8.8 psi at the initial column oven temperature of 120 °C. The inlet was programmed to maintain the inlet temperature 3 °C above the column oven temperature. The helium carrier gas velocity was 20 cm/s at this temperature, and nitrogen was used as the FID makeup gas (35 mL/min). The oven was held at 120 °C for 2 min and then programmed at 10 °C/min to 310 °C and held for 10 min. The final pressure was 14.8 psi. Injections (1−5 $\mu$L) were made manually.

***Quantitation.*** The on-column GC inlet makes negligible contributions to deviations and errors in quantitative analyses (Grob, 1991). Calibration only has to consider detector response and possible losses in the column. On-column injection of the mixture of the three phthalates in octanol at the concentrations 4, 20, and 100 mg/L gave chromatograms in which the relative peak areas in each chromatogram varied <5%. The total amount of each phthalate per injection ranged from 4 ng to 600 ng and the volume of octanol from 1 $\mu$L to 5 $\mu$L. Typical peak widths in minutes from injection of 5 $\mu$l of the 20 mg/L solution were 0.033 (DHP), 0.036 (DnOP), and 0.038 (DnDP).

Four separate 1-L samples of water were spiked with 100 ng each of DnOP and DnDP. The phthalates were extracted from the water samples using C18 disks. Acetonitrile was used to elute the phthalates from the disk. The recoveries of DnOP (96.8 ± 3%) and DnDP (102.2 ± 1.2%) were calculated using each alternately as an internal standard for calculating recovery of the other. The absolute recoveries of DnOP and DnDP, which ranged from 41 to 71 ng, were determined by comparison of their FID area response to DHP (100 ng) that was added after the nitrogen-gas blowdown. In the water solubility and octanol/water partition experiments the phthalate closest in volatility to the phthalate of interest was spiked into the water sample and served as the internal standard to determine the water concentration of the phthalate of interest. A

**Table 1. Phthalate Ester Water Solubilities**

| phthalate | molecular weight | $\rho$/g·cm$^{-3}$ (20 °C) | solubility ($\mu$g·L$^{-1}$) | | |
|---|---|---|---|---|---|
| | | | lit.[a] | slow-stirring | no-stirring |
| dimethyl | 194.2 | 1.190 | $4.2 \times 10^6$ | | |
| diethyl | 222.2 | 1.118 | $11.0 \times 10^5$ | | |
| di-*n*-butyl | 278.4 | 1.042 | $1.1 \times 10^4$ | | |
| di-*n*-hexyl | 334.4 | 1.011 | 50.0 | $46.00 \pm 2$ ($n = 3$)[b] | $54.00 \pm 3$ ($n = 3$)[c] |
| di-*n*-octyl | 390.6 | 0.978 | 0.5 | $0.51 \pm 0.08$ ($n = 6$)[d] | $0.49 \pm 0.11$ ($n = 5$)[e] |
| di-*n*-decyl | 446.6 | 0.961 | | $0.22 \pm 0.05$ ($n = 6$)[f] | $0.23 \pm 0.01$ ($n = 2$)[g] |

[a] Staples et al. (1997). [b] The measurements were made at 18, 43, and 66 h. [c] The measurements were made at 18, 65, and 89 h. [d] The measurements were made at 18, 18, 38, 62, 87, and 158 h. [e] The measurements were made at 15, 111, 120, 183, and 327 h. [f] The measurements were made at 17, 184, 504, 736, 736, and 736 h. [g] Duplicate measurements at 353 h. Nonequilibrium values at 41 and 161 h were not included; di-*n*-decyl phthalate was not detected in a measurement made at 17 h.

method detection limit (LOD) was calculated using the SPE extracts of the 1-L presaturation samples that were collected as the first samples taken in the DnDP octanol/water partition experiments. The LOD (0.025 $\mu$g/L) was calculated as the quantity of DnDP to give a response of 3 times baseline noise at the retention time of DnDP.

## Results and Discussion

***Water Solubilities.*** A recent critical review by Staples et al. (1997) of the environmental fate of phthalate esters concluded that for the higher molecular weight esters (i.e. alkyl chains ≥ 6 carbons) most published water solubility values exceed true values. The major source of error was attributed to the introduction of systematic errors associated with the experimental difficulties encountered in the measurements. Table 1 consists of the recommended water solubility data for five dialkyl phthalates from Staples et al. (1997) and the solubility data measured for DnHP, DnOP, and DnDP in this study. The water solubility measurements were performed on the individual phthalates in separate experiments. Equilibrium between DnHP, DnOP, DnDP, and water was established within the first 18 h in the slow-stirring experiments. The 18-h water concentrations measured for DnHP (43 $\mu$g/L), DnOP (0.50 $\mu$g/L), and DnDP (0.20 $\mu$g/L) showed little change in subsequent samples, even though stirring and sampling were continued for 120, 158, and 736 h, respectively (see footnote in Table 1). Droplets of neat phthalate remained on the surface of the water at the completion of all the experiments.

In a recent communication, Letinski et al. (1999) reported slow-stirring water solubilities for DHP (mixed isomers, 70 $\mu$g/L), DnOP ($0.40 \pm 0.04$ $\mu$g/L) and DnDP ($0.047 \pm 0.00$ $\mu$g/L) at 20 °C. While the measured water solubilities for DnOP vary <25%, the Letinski et al. (1999) DnDP water solubility is 4-fold less than the solubility determined in this study. The 5 °C lower temperature for the Letinski et al. (1999) measurements could be a contributing factor to their lower measured water solubilities.

Historically, the establishment of equilibrium between hydrophobic compounds, such as the higher molecular weight phthalate esters and water, is considered to be a slow process. After it was determined that saturation was established in the slow-stirring experiments within the first 18 h for DnDP, the most hydrophobic phthalate, a second set of solubility measurements, referred to as no-stirring, was performed on the three phthalate esters. The no-stirring water solubility experiments were conducted in a manner identical to the slow-stirring experiments except the stirrer motor remained “off”. It took longer to attain saturation in the no-stirring experiments; a concentration that remained constant in subsequent measurements was attained within 48 h for DnHP, 183 h for DnOP, and 353 h for DnDP. The slow-stirring solubilities reported in Table 1 for two phthalate esters, DnHP and DnOP, are essentially the same as the no-stirring values. The very good agreement between the slow-stirring and the no-stirring solubilities is evidence that emulsions were not formed in the stirred samples and any self-aggregation, if present, occurred to the same extent in both systems.

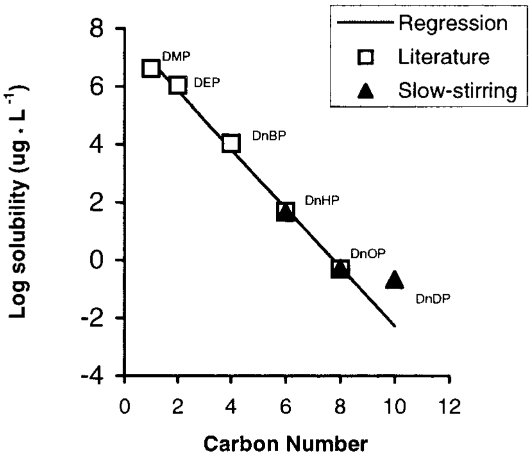

**Figure 1.** Log of Staples et al. (1997) and slow-stirring water solubilities of the phthalates as a function of number of carbons in the alkyl side chain. The regression line extended to DnDP is for literature data.

Even though the experiments are called no-stirring measurements, movement of the droplets of phthalate on the water surface was continuous. All experiments were conducted in a controlled-temperature room with the stirrers located on metal shelves. The shelves were supported by metal brackets that were inserted in slots in a wall-mounted, metal track. The slow-stirring jars/stirrers were alternated on the metal shelf with the no-stirring assemblies. Vibrations caused by the stirring motors were clearly transferred from the operating stirrers to the nonstirred vessels. The vibration, which was evident by placement of the hand on the outer surface of the jar, was sufficient to cause continual movement of the droplet of phthalate on the water surface and exposure to the maximum surface area of the water. This apparently enhanced diffusion of the phthalate to the lower depths of the water.

Plots of the log values of the Staples et al. (1997) and the measured slow-stirring water solubilities in Table 1 against carbon number (DMP = 1, DEP = 2, etc.) are shown in Figure 1. A straight line regression equation was derived from the Staples et al. (1997) log water solubility values and was used to extend the estimate for a carbon number of 10, that is, DnDP ($Y = -1.0234X + 7.904$, [DnDP] = 0.005 $\mu$g/L). A similar plot (not shown) was made of the Staples et al. (1997) log water solubilities against the molar volumes, the phthalate molecular weight divided by its liquid density at 20 °C, and the regression line extended to 10 carbons ($Y = -0.0309X + 12.164$, [DnDP] $= 0.006$ $\mu$g/L). The molar volumes of a homologous series of molecules increase approximately linearly with each added carbon atom, and the decrease in water solubility for each additional carbon has been reported to be approximately 0.54 log units (Kamlet et al., 1986; Barton, 1983). For the phthalate esters in Table 1, this would equate to approximately a 2.16 log unit decrease for each two-carbon increment; this is approximately the decrease observed in the measured solubilities of DMP through DnOP.

The water solubilities measured in this study for DnHP and DnOP are essentially the same as the Staples et al. (1997) recommended values. However, the 0.22 $\mu$g/L measured water solubility of DnDP is 40−70-fold greater than that predicted by the two regression equations, which were based on measured values and molar volumes. The 0.006 $\mu$g/L water solubility of DnDP predicted from the molar volume is based on the assumption that the volume occupied by the phthalate in aqueous solution is equal or proportional to the volume it occupies as a neat liquid.

It is well-known that chain-branching increases the water solubility in monofunctional, C1-substituted hydrocarbons, such as the alkyl isomeric alcohols butanol, isobutanol, *sec*-butanol, and tertiary butanol (Mittal, 1997). One explanation for the elevated water solubility of DnDP could be that the alkyl side chains in the DnDP rotate and assume conformations of lower energy that more closely resemble a branched alkyl chain rather than a straight chain. Aggregation of individual phthalate molecules into units that contain two or more molecules would be a second explanation. The molecular volume of the aggregates would be less than the sum of the molecular volume of the monomers. Also, the alkyl side chains of DnDP are flexible and can rotate to configurations of lower energy that have less than fully extended chains. The “average” molar volume of the “collapsed” configuration of DnDP would be less than the molar volume of neat DnDP and is closer to the molar volume of DnOP; this is reflected in the approximately one and a half orders of magnitude higher measured water solubility (0.22 $\mu$g/L) for DnDP than was predicted by the molar volume regression equation (0.006 $\mu$g/L).

***Octanol/Water Partition Coefficients.*** The SPE disk extraction efficiency experiments performed for the water solubility measurements were repeated with water that had been equilibrated with a layer of octanol. The results were essentially the same as those for pure water. The octanol dissolved in the aqueous layer did not interfere with the SPE but instead was beneficial in the on-column GC analyses. Figure 2 contains two FID chromatograms of eluates of SPEs of 1 L samples of water. The lower chromatogram is the 1-L blank SPE of water taken at the end of the 24 h presaturation of water with octanol; the upper chromatogram is from the determination of the $K_{ow}$ of DnDP in the same system. In both chromatograms, the large solvent peak is from octanol retained on the C18 disk. The final sample volume after elution of the C18 disk with acetonitrile and nitrogen blowdown was in the 25−50 $\mu$L range, a concentration factor of 20 000−40 000, respectively. The 5 $\mu$L typical volume injected combined with the capillary retention gap and GC inlet and oven temperature parameters yielded symmetrical, narrow peaks. A typical peak width (0.035 min), for DnDP, which eluted at 310 °C, greatly enhanced quantitation due to the increased peak height and resolution. DnOP was added as an internal standard to the volumetric flask before collection of the water layer and was used to calculate the recovery of DnDP; DnHP was added after blowdown of the SPE eluent to final volume but prior to GC analysis. The DnHP was used to determine the absolute recovery of the DnOP internal standard. In the $K_{ow}$ experiments for the three phthalates, the absolute recovery of the phthalate internal standard ranged from a low of 25% to a high of 90%.

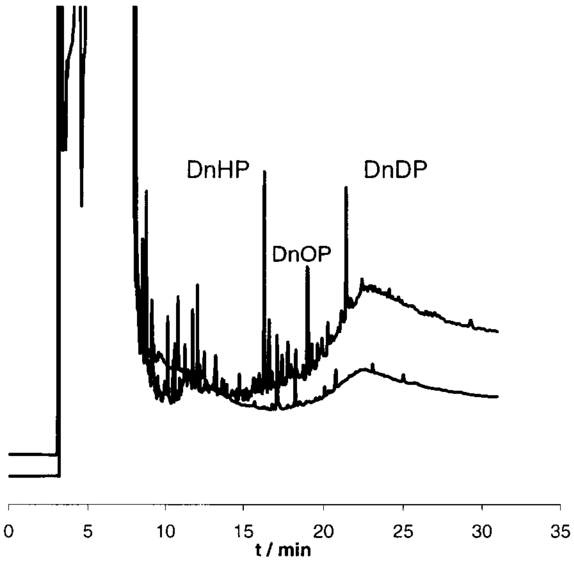

**Figure 2.** GC/FID chromatograms of 5 $\mu$L injections of SPE extracts of 1-L water samples. The lower trace is an octanol/water presaturation blank, and the upper trace is from determination of the log $K_{ow}$ of DnDP.

**Table 2. Phthalate Ester Octanol/Water Coefficients**

| | log $K_{ow}$ | | |
|---|---|---|---|
| phthalate | lit.[a] | slow-stirring | no-stirring |
| dimethyl | 1.61 | 1.60 ± 0.04 ($n = 12$)[b] | |
| diethyl | 2.38 | 2.42 ± 0.04 ($n = 9$)[b] | |
| di-*n*-butyl | 4.45 | 4.50 ± 0.03 ($n = 9$)[b] | |
| di-*n*-pentyl | | 5.62 ± 0.04 ($n = 6$)[b] | |
| di-*n*-hexyl | 6.30 | 6.82 ± 0.10 ($n = 6$)[b] | |
| di-*n*-octyl | 8.06 | 8.18 ± 0.06 ($n = 5$)[c] | 8.16 ± 0.05 ($n = 5$)[d] |
| di-*n*-decyl | | 8.83 ± 0.05 ($n = 4$)[e] | 9.27 ± 0.11 ($n = 4$)[f] |

[a] Staples et al. (1997). [b] Ellington and Floyd (1996) butylbenzyl phthalate log $K_{ow} = 4.73 \pm 0.06$ ($n = 6$) and diethylhexyl phthalate log $K_{ow} = 7.27 \pm 0.04$ ($n = 3$) were in the 1996 report but not used in this table. [c] The measurements were made at 20, 92, 164, 260, and 260 h, respectively. [d] The measurements were made at 20, 92, 164, 260, and 260 h, respectively. [e] The measurements were made at 20, 44, 336, and 504 h, respectively. [f] The measurements were made at 39, 123, 195, and 263 h, respectively.

Table 2 contains the recommended log $K_{ow}$ values from Staples et al. (1997) and values determined here by the slow-stirring and no-stirring methods. Plots of log $K_{ow}$ against carbon number are shown in Figure 3. The slow-stirring log $K_{ow}$ values in Table 2 up to and including DnOP were plotted against the carbon number; the regression line equation $Y = 0.9788X + 0.6152$ yielded an estimated log $K_{ow}$ of 10.45 for DnDP. The calculated regression value for DnOP was 8.44. After 20 h in the slow-stirring experiments, a log $K_{ow}$ of 8.17 was determined for DnOP and 8.78 for DnDP. That these values did not change, within experimental error, in subsequent samples (i.e. after longer equilibration times) was evidence that the phthalates in the two phases were at equilibrium between the water and

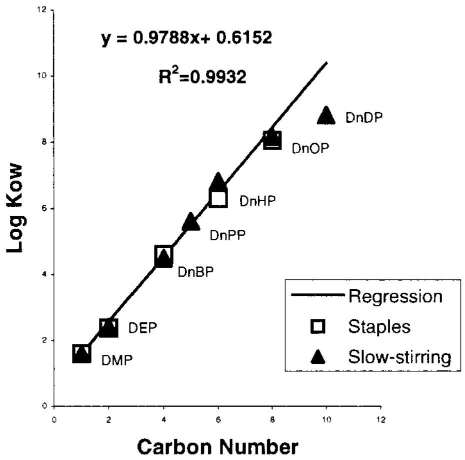

**Figure 3.** Log of Staples et al. (1997) and slow-stirring $K_{ow}$ values as a function of number of carbons in the alkyl side chain. The regression line extended to DnDP is for slow-stirring data.

octanol within the first 20 h of stirring. Slow-stirring and $K_{ow}$ determinations were continued for 260 h for DnOP and 336 h for DnDP, and the subsequent values are included in the respective means and standard deviations in Table 2. Similar to the water solubility studies, no-stirring experiments were conducted in parallel with the slow-stirring experiments. Surprisingly, DnOP quickly reached equilibrium with the octanol/water without stirring and a log $K_{ow}$ of 8.16 was determined for DnOP after 20 h. A log $K_{ow}$ of 9.35 was determined for the no-stirring DnDP after 39 h. The DnOP was sampled at 92 and 164 and twice at 260 h, and the log $K_{ow}$ of 8.16 ± 0.05 ($n = 5$) was included in Table 2. The no-stirring log $K_{ow}$ of DnDP was determined again at 123, 195, and 263 h, and the results were averaged with those for the 39-h sample to give a log $K_{ow}$ of 9.27 ± 0.1 ($n = 4$). After the 263-h sample was analyzed, slow-stirring was started and continued for 118 h. The aqueous layer was sampled 1 h after stirring was stopped, and a log $K_{ow}$ of 8.45 was determined. The aqueous layer was sampled again at 24 and 144 h, and log $K_{ow}$ values of 8.92 and 8.93 were determined, respectively. Apparently, DnDP is prone to aggregation or formation of microemulsions upon stirring that increase the water layer concentration of the phthalate. The 24 h of standing was sufficient to reestablish the equilibrium concentrations attained in the original slow-stirring experiments.

***Octanoic Acid Experiments.*** Formation of micelles and microemulsions would enhance the solubility of the phthalates in the aqueous phase. Micelles are formed by surfactant-type molecules (amphiphiles) such as octanoic acid, an alkyl carboxylic acid which has a polar head and a hydrophobic hydrocarbon tail and achieves segregation in aqueous media by self-aggregation (Palit, 1947). Micelles enhance the water solubility of a chemical by sequestering nonionic neutral molecules in the hydrocarbon core. To test the effect of octanoic acid on the partitioning of DnOP into the aqueous layer, a calculated amount of octanoic acid, based on the log $K_{ow}$ for octanoic acid, was dissolved in 1-mL of octanol and added to the octanol layer of the "no-stirring" experiments. The log $K_{ow}$ of octanoic acid is 3.03 and was used to determine the amounts of acid needed to achieve desired water concentrations (Dunn, 1986).

The first addition of octanoic acid yielded an equilibrium water concentration of the acid of 120 $\mu$g/L. A log $K_{ow}$ of 8.13 was determined for DnOP after 91 h of "slow-stirring". Octanoic acid was added twice more to yield acid water concentrations of 6 mg/L and 12 mg/L. The log $K_{ow}$ values of DnOP after 62 and 48 h of stirring were 8.16 and 8.31, respectively. The water used in these experiments was deionized and distilled; apparently the lack of counterions to support formation of micelles caused the octanoic acid to have no effect on the water concentration of the phthalates, even at these relatively high surfactant concentrations.

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