Aqueous Solubilities, Vapor Pressures, and 1-Octanol–Water Partition Coefficients for C_9–C_{14} Linear Alkylbenzenes

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Measurements and estimates of aqueous solubilities, 1-octanol–water partition coefficients (K_{ow}), and vapor pressures were made for 29 linear alkylbenzenes having alkyl chain lengths of 9–14 carbons. The ranges of values observed were vapor pressures from 0.002 to 0.418 Pa, log K_{ow} from 6.83 to 9.95, and aqueous solubilities from 4 to 38 nmol·L^{-1}. Measured values exhibited a relationship to both the alkyl chain length and the position of phenyl substitution on the alkyl chain. Measurement of the aqueous concentrations resulting from equilibration of a mixture of alkylbenzenes yielded higher than expected values, indicating cosolute or other interactive effects caused enhanced aqueous concentrations of these compounds.

Introduction

The environmental distribution of high-molecular-weight organic compounds is largely dependent on their physicochemical properties. Among the properties required to predict or understand a compound's distribution are its aqueous solubility, 1-octanol–water partition coefficient (K_{ow}), and vapor pressure. A compound's solubility can affect its transport and bioavailability, including its availability for degradation. Bioaccumulation and sorption by suspended solids and sediments can be predicted from log K_{ow} values. Using water solubility and vapor pressure, the Henry's law constant can be calculated, thereby contributing to estimations of that chemical's exchange across the air–water interface.

The direct measurement of these properties for high-molecular-weight nonpolar organic substances is subject to large errors. These compounds generally exhibit low vapor pressures (*1–3*) and low aqueous solubilities (*3–5*), and their K_{ow} values commonly exceed the upper practical limit for direct determination (log $K_{ow} \geq$ 5–6) (*3, 6, 7*). As a result, a number of alternative methods have been developed for obtaining these parameters. These include the use of (1) a gas chromatographic method to determine vapor pressures (*1, 2, 8*), (2) a reversed-phase high-performance liquid chromatography (RP-HPLC) correlation method to estimate K_{ow} (*6, 7, 9*), and (3) correlation of either molecular size or K_{ow} to estimate solubilities (*10–14*). In the work reported here, we utilize these methods to determine properties of alkylbenzenes having alkyl chain lengths of 9–14 carbons.

The long-chain linear alkylbenzenes (LABs), a mixture consisting of 26 secondary phenylalkanes having alkyl side chains of from 10 to 14 carbon atoms, are produced industrially as precursors of the anionic surfactants, the linear alkylbenzenesulfonates (*15*). The use of these surfactants results in the introduction of (unsulfonated) alkylbenzene residues into the environment as components of municipal wastewater discharges (*15–17*). Since these compounds have relatively restricted sources to the environment, they could be useful in the exploration of transport processes in the field. However, investigation of these environmental processes requires knowledge of their physical properties.

Currently these secondary alkylbenzenes are produced only as mixtures. Thus, both their environmental fate and the determination of the properties of individual components may be affected by interaction with other components of the mixture. The industrial mixture consists of not only the secondary alkylbenzenes but also trace impurities (total of ≤2.5%) thought to be mostly tetralins (*18–20*). Aqueous-phase concentrations of the components in a mixture can be converted to individual solubilities through consideration of the mole fraction and activity coefficient for that component in the organic phase being equilibrated with the aqueous phase. Previous investigations (*21–24*) of aqueous concentrations of mixtures have found that interaction between components in a mixture can result in complex deviations from ideal solution behavior. Reported deviations from ideal behavior have resulted in enhanced (*21, 22*), reduced (*21*), and ideal (*23, 24*) aqueous concentrations for different components in the mixtures studied. If mixtures contain hydrophilic components, these compounds can lead to an increase in the water content of the organic phase which may cause changes in the activity coefficients (*24*) for other mixture components. The solubility of individual compounds could also be affected by interaction in the aqueous phase with other dissolved components. Aqueous-phase interaction with structurally similar (*10*) compounds could result in "accommodation" or colloid formation (*11, 12*). Interaction with structurally dissimilar compounds could result in cosolvency (*25*).

The long-chain linear alkylbenzenes provide an opportunity to investigate the effect of minor structural differences on the physical properties of interest. Here we report the effect of changes in chain length, and the position of phenyl substitution on the alkyl chain, on the values of selected physical properties for these compounds. The experimental results are interpreted on the basis of existing information of structural effects on the properties of alkanes.

Experimental Section

The compounds used in this study came from two sources. The *n*-hexadecane and *n*-alkylbenzenes (nonyl-, decyl-, undecyl-, dodecyl-, tridecyl-, tetradecyl-, and pentadecylbenzene) were acquired from Alltech Associates (97.5–99.9% pure by weight). All compounds used in this work were liquids at

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0021-9568/92/1737-0394$03.00/0

ambient temperature. The secondary alkylbenzenes are not commercially available as pure compounds. Thus, mixtures provided by Monsanto Chemical Co., as described previously (*15*), were used for this work. Potential mixture effects on the measured physical properties of the alkylbenzenes were evaluated by comparing determinations for individual *n*-alkylbenzenes with results obtained for these compounds as components of alkylbenzene mixtures.

RP-HPLC Estimation of log K_{ow}. A RP-HPLC estimation method was selected because the great hydrophobicities (log K_{ow} values of 6–10) of these compounds make direct determination difficult. We have previously applied this method to the estimation of log K_{ow} for short-chain (C_1–C_4) alkylbenzenes (*9*). The retention volume (time) measurements for the long-chain linear alkylbenzenes were made by the same method, which is briefly discussed here. The estimation method relies upon the linear correlation of a compound's log K_{ow} with the logarithm of its RP-HPLC "aqueous" capacity factor (log k_o') (*9*). The regression line is developed with compounds for which there are directly measured values of both properties. Extrapolation of this relationship to higher log k_{ow} values may introduce some error into the estimated log k_{ow} values; however, data for alkanes (*26*) suggest this error should be minimal. For this study log k_o' values were determined using an acetonitrile–water mobile phase (1.5 $cm^3 \cdot min^{-1}$), a 125-mm × 4.6-mm 5-μm-silica-based octadecyl column, and UV detection (254 nm). log K_{ow} estimates were then derived from log k_o' using the correlation developed previously with the short-chain *n*-alkylbenzenes (benzene through butylbenzene) (*9*).

Vapor Pressure Estimation. Vapor pressures ($P_{GC}°$) were determined using capillary gas chromatographic retention behavior on a nonpolar phase. $P_{GC}°$ values were converted to liquid vapor pressures ($P_L°$) by regressing our $P_{GC}°$ values for 1-phenylnonane and 1-phenyltetradecane against literature data (*27*). This indirect approach to $P_L°$ was chosen because the long-chain linear alkylbenzenes have relatively low vapor pressures at ambient temperatures, and this procedure can be applied to mixtures. The method has been discussed in detail by Bidleman (*1*) and Hinckley et al. (*2*) and, thus, will only be briefly reviewed here. The analyses reported here were performed using a 15-m × 0.32-mm SE-30 (0.25-μm) column. Correlation of the analytes' retention volumes with that of a reference compound which has known vapor pressures at the temperatures used, as well as the desired extrapolation temperature (25 °C), allows the prediction of the vapor pressure of the test compound. Bidleman (*1*) emphasized that the vapor pressure of the selected reference compound needs to be accurately known over the temperature range used for the GC measurements, as well as at the final extrapolation temperature. Several compounds have been used as reference compounds, including two *n*-alkanes (*1*). An extensive literature search (*28–34*) of vapor pressures of *n*-alkanes (C_{15}–C_{20}) over the temperature range of interest for this study (25–150 °C) yielded the largest and most consistent database for *n*-hexadecane (*35*). For this reason, *n*-hexadecane was chosen as the reference compound.

Molecular Surface Area. Molecular surface areas of the alkylbenzenes were determined using a program of originally written by Hermann (*36*) and acquired from the Quantum Chemistry Program Exchange (*37*). Using bond lengths, angles, and atomic radii, the program constructs a three-dimensional model of the molecule. Once the chemical structure is defined, the program rolls a solvent sphere of a given radius over the molecule's exposed surface to determine its solvated surface area (*36*).

For the surface area calculations reported here, it was assumed that all alkyl chains are present in an extended conformation. Using this assumption, the calculated surface area represents a maximum value rather than the total surface area, but permits comparisons among the alkylbenzenes studied. Literature data (*35, 36*) on the surface areas of the propylbenzenes (*n*-propyl and isopropyl) were used to calibrate the bond angles of the structural model used by the program. These molecular conformations were then used as the basis of the long-chain linear alkylbenzene structures by adding methylene groups to the alkyl chains (*35*). All surface areas reported are the "solvated" surface areas using a 0.15-nm solvent radius.

Solubility Estimation and Determination. Numerous studies have demonstrated relationships between aqueous solubility (*S*) and log K_{ow} (*6–9*), molar volume (*11, 12*), or molecular surface area (*13, 14*) for sets of compounds. Estimates of the linear alkylbenzene aqueous solubilities were derived from relationships developed for similar compounds which have known aqueous solubilities, log K_{ow} values, molar volumes, and surface areas. Regression equations relating the aqueous solubilities (*4, 5, 11, 38, 39*) of the short-chain *n*-alkylbenzenes (toluene to hexylbenzene) with their log K_{ow} values (*40–42*), molar volumes, or surface areas were developed. The regression of log *S*–log K_{ow} was performed using a geometric mean linear regression, since both of these variables are subject to measurement error (*43, 44*). The log *S*–molar volume and –surface area relationships were developed using a standard least-squares approach, which assumes that the molar volumes and surface areas are known with relatively small measurement error. These relationships were then used to predict solubilities for the long-chain alkylbenzenes, allowing comparison with direct measurements. Estimates made using the surface areas reported here should be considered relative rather than absolute, since these are maximum rather than total surface areas. The molar volumes were determined by dividing the molar mass by the compound's liquid density (*45*).

Direct measurement of aqueous solubilities was performed using a modification of the vapor-phase equilibrium method described by Sutton and Calder (*11*). Briefly, this method involves equilibration of the hydrocarbon phase and the aqueous phase via the vapor phase. The compounds were placed in the bottom of a glass tube inserted into a 5-L flask containing 4 L of (glass-distilled) water. The inserted tube, perforated above the water surface, allowed the alkylbenzenes to equilibrate with the vapor phase above the water in the flask. The water was slowly stirred by a Teflon-coated magnetic stir bar and held at a constant temperature (25.0 ± 1.5 °C). After 7 days, the apparatus was opened, and the water poured into a 5-L separatory funnel. Recovery surrogates (*n*-nonylbenzene, *n*-undecylbenzene, *n*-dodecylbenzene, *n*-tetradecylbenzene) were added, and the solution was extracted four times in succession with 100 mL of dichloromethane. The extracts were combined and reduced in volume by rotary evaporation, transferred to a vial, and further reduced in volume. Just prior to analysis by gas chromatography, the sample was concentrated further under a stream of nitrogen (just to dryness) and taken up in 50 μL of hexane containing a quantitation standard (*n*-pentadecylbenzene). Previous experimentation had shown no significant change in the dissolved concentrations for samples equilibrated for 7, 10, or 14 days.

Since the source of the secondary alkylbenzenes was the commercial mixture, these compounds could not be tested individually. Moreover, the alkylbenzene mixture contains small quantities of cyclic hydrocarbons. Hence, it is possible that the measured aqueous concentrations were affected by cosolute or other effects. To test for such effects, some equilibrations using *n*-decylbenzene and *n*-tridecylbenzene

Table I. Measured log k_0' and Corresponding log K_{ow} estimates of the Alkylbenzenes

	6-phenyl	5-phenyl	4-phenyl	3-phenyl	2-phenyl	1-phenyl[a]
decane						
log k_0'		4.34	4.40	4.40	4.43	4.61
log K_{ow}		6.90	7.00	7.00	7.06	7.38
undecane						
log k_0'	4.66	4.66	4.74	4.70	4.76	5.04
log K_{ow}	7.45	7.45	7.59	7.53	7.63	8.14
dodecane						
log k_0'	4.97	4.97	5.01	5.02	5.08	5.33
log K_{ow}	8.01	8.01	8.07	8.10	8.19	8.65
tridecane						
log k_0'	5.28	5.28	5.32	5.33	5.40	5.74
log K_{ow}	8.56	8.56	8.62	8.65	8.77	9.36
tetradecane						
log k_0'	5.63	5.63	5.68	5.70	5.70	6.07
log K_{ow}	9.16	9.16	9.25	9.29	9.29	9.95

[a] Values for n-nonylbenzene and n-decylbenzene are from ref 9. log K_{ow} of n-nonylbenzene and 7-tetradecylbenzene were estimated to be 6.83 and 9.16, respectively.

Table II. Vapor Pressures ($P_L°$/Pa) for the Alkylbenzenes Determined by GC

	6-phenyl	5-phenyl	4-phenyl	3-phenyl	2-phenyl	1-phenyl[a]
decane		0.418	0.391	0.349	0.251	0.133
undecane	0.171	0.163	0.153	0.134	0.098	0.050
dodecane	0.067	0.064	0.060	0.053	0.038	0.019
tridecane	0.027	0.026	0.020	0.019	0.015	0.008
tetradecane	0.011	0.010	0.010	0.008	0.006	0.002

[a] The vapor pressure ($P_L°$) determined for n-nonylbenzene was 0.338 Pa; that of 7-tetradecylbenzene was 0.011 Pa.

were also performed. These were used individually, together, and in combination (both present) with the commercial alkylbenzenes. Four types of equilibrations were performed: (a) each n-alkylbenzene alone, (b) the two n-alkylbenzenes together, (c) the secondary alkylbenzenes without the n-alkylbenzenes, and (d) the secondary alkylbenzenes with the two n-alkylbenzenes. All solubilities for components of mixtures were adjusted by normalizing to their mole fractions in the hydrocarbon phase and assuming the organic mixture activity coefficients were all equal to 1.

Results

RH-HPLC Estimation of log K_{ow}. log k_0' values were determined for each of the n-alkylbenzenes and secondary alkylbenzenes. The regression equation relating log k_0' and log K_{ow} values for n-alkylbenzenes ranging from benzene to butylbenzene was determined (*9*) to be

$$\log K_{ow} = (1.759 + 0.050) \log k_0' - (0.744 \pm 0.114)$$

$$R^2 = 0.999$$

The resulting log K_{ow} estimates for the C_{10}–C_{14} alkylbenzenes range from 6.9 to 9.95 (Table I).

Vapor Pressure Estimates. The relationship between vapor pressure and temperature determined from literature data for n-hexadecane gave the equation ln $(P/\mathrm{Pa}) = 22.28 - 9176.95/(T/\mathrm{K})$. This equation was used to interpolate vapor pressure values for n-hexadecane at the temperatures used to develop the $P_{GC}°$–T relationships (80–150 °C). The individual equations for each compound studied will not be listed here but are available from us. The liquid-phase vapor pressures ($P_L°$) determined for the alkylbenzenes range widely (Table II), decreasing by more than 1000 times across this set of compounds.

Table III. Surface Areas (A/nm²) Calculated for the Alkylbenzenes in Their Extended Conformations

	6-phenyl	5-phenyl	4-phenyl	3-phenyl	2-phenyl	1-phenyl[a]
decane		5.19	5.27	5.30	5.46	5.50
undecane	5.51	5.52	5.56	5.62	5.78	5.83
dodecane	5.84	5.84	5.90	5.95	6.10	6.15
tridecane	6.16	6.16	6.22	6.27	6.42	6.48
tetradecane	6.49	6.49	6.55	6.59	6.75	6.80

[a] The surface area determined for n-nonylbenzene was 5.18; that of 7-tetradecylbenzene was 6.49.

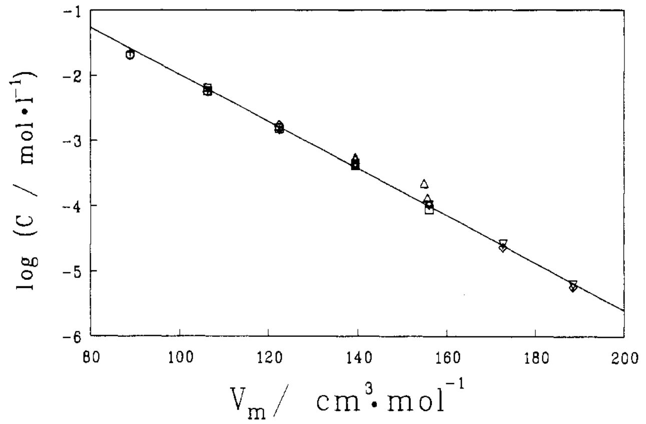

Figure 1. Relationship between log C and V_m for the short-chain alkylbenzenes. Symbols designate literature data from +, McAuliffe (*10*); ○, Sanemasa (*38*); ◇, Owens et al. (*5*); ▽, Tewari et al. (*4*); □, Sutton and Calder (*11*); and △, secondary propyl- and butylbenzenes, data from Sutton and Calder (*11*).

Molecular Surface Area. The calculated "solvated cavity" (*36*) surface areas (Table III) show the long-chain linear alkylbenzenes to be several times larger than benzene (2.41 nm²) (*36*). The calculated surface areas of these alkylbenzenes, however, span a fairly narrow range, from about 5.20 to 6.80 nm².

Solubility Estimation and Determination. The geometric mean regression relating the literature data for aqueous solubility (*4, 5, 11, 38, 40*) and the directly determined log K_{ow} (*40–42*) for the short-chain n-alkylbenzenes gave the equation

$$\log (S/(\mathrm{mol \cdot L^{-1}})) = (0.725 \pm 0.184) - (1.103 \pm 0.044) \log K_{ow}$$

$$R^2 = 0.992$$

The linear least-squares regression between log S and molar volume (V_m) yielded

$$\log (S/(\mathrm{mol \cdot L^{-1}})) = (1.632 \pm 0.049) - (0.036 \pm 0.0004)(V_m/(\mathrm{cm^3 \cdot mol \cdot L}))$$

$$R^2 = 0.998$$

While the log S and V_m of the short-chain n-alkylbenzenes are very well correlated, it is apparent that benzene and the branched isomers of propyl- and butylbenzene fall off this line (triangles in Figure 1). This indicates that the relationship would be somewhat inaccurate for predicting the solubilities of the secondary alkylbenzenes, which would likely also fall above this regression line. The regression between log S and surface area (A) developed using data for the short-chain alkylbenzenes (benzene through n-butylbenzene) gave

$$\log (S/(\mathrm{mol{\cdot}L^{-1}})) = (3.14 \pm 0.04) - (1.88 \pm 0.02)(A/\mathrm{nm^2})$$

$$R^2 = 0.997$$

The surface areas determined were used with this equation to provide solubility estimates for comparison with the other estimates and the directly determined values.

The measured solubilities of n-decylbenzene and n-tridecylbenzene, tested in various combinations, are similar to, or below, the solubilities predicted using the log K_{ow}, molecular volumes, and surface areas of these compounds (Table IV). The solubilities measured for the secondary alkylbenzenes (mean and standard deviation, Table V) do not agree with those predicted using the log K_{ow} values. Solubilities estimated using the surface areas are similar to the log K_{ow} based estimates (Table V). The lack of reliable molar volume data for the secondary alkylbenzenes precludes the use of that relationship to predict log S values for these compounds.

Discussion

Vapor Pressure. While there were no published vapor pressures available for the secondary alkylbenzenes, there have been other estimates (*46*) and limited direct measurements (*27*) for some of the n-alkylbenzenes (Table VI). Dreisbach (*46*) utilized the Antoine equation, with literature data measured over a wide temperature range (200–800 °C), to estimate vapor pressures at 25 °C. These extrapolations are susceptible to nonlinearity of the relationship between temperature and vapor pressure. Dreisbach (*46*) excluded some of the lower temperature (below 200–300 °C) n-alkane data because they did not fit the equation developed at high temperatures. The published n-hexadecane vapor pressure data (*28–34*) for the "lower" temperature range (25–150 °C), however, gave a linear relationship, within this range. These observations could explain the difference between the estimates of Dreisbach (*46*) and the data reported here (Table VI).

The gas saturation method used by Allemand et al. (*27*) determines the compound's vapor pressure by passing an inert gas over the sample in a tube at a slow, constant rate. The organic content of the gas is analyzed, and the total gas pressure and flow rate are determined. From these parameters the vapor pressure can be determined (*47*). Table VI presents a comparison of our $P_L°$ estimates for n-nonylbenzene and n-dodecylbenzene with values determined by Allemand et al. (*27*). Our values for $P_L°$ of n-nonylbenzene were generally 4–13% less than the direct measurements. The vapor pressures of n-dodecylbenzene were within about 30% of those determined by Allemand et al. (*27*) (Table VI).

Solubility. Comparison of the individual measured solubilities with those predicted using log K_{ow}, molar volume, or surface area did not yield equally good agreement for the two compounds under study (Table IV). The three parameters gave similar predictions for each of the two compounds investigated. The measured n-tridecylbenzene solubilities fell within the ranges predicted for its aqueous concentrations. However, the predicted solubilities for n-decylbenzene were higher than the aqueous concentrations observed. These results suggest that the solubility effects can be quite complex and deserve further study.

While the number of solubility measurements for the individual long-chain compounds is small (Table IV), these values provide the best indication of cosolute effects. Comparison of the solubilities of the two n-alkylbenzenes, when only they were present, with those determined when they were with the mixture, indicates some cosolute or other "multicomponent" influence was responsible for enhancing the measured concentrations.

Table IV. Solubilities (S) for n-Decyl- and n-Tridecylbenzene[a]

experiment	n	S(n-decylbenzene)/ (nmol·L^{-1})	n	S(n-tridecylbenzene)/ (nmol·L^{-1})
individually	2	11.4	1	0.9
together	5	9.9 ± 0.6	5	0.9 ± 0.3
with LAB mix	4	16.1 ± 0.9	4	4.5 ± 1.4
predicted[b] from				
V_m		25.5 (18.1–35.9)		0.9 (0.6–1.3)
log K_{ow}		38.6 (11.9–125.1)		0.3 (0.06–1.0)
A		48.1 (34.1–68.0)		0.7 (0.5–1.0)

[a] The two n-alkylbenzenes were equilibrated individually, combined with each other, and with the secondary LAB mixture for these experiments. Reported solubilities are corrected for the mole fraction these compounds represented in each mixture. [b] The ranges shown are the potential ranges of values given the uncertainties of the regression equations (±1 standard deviation for both coefficients in the regression equation).

Table V. Solubilities (S/(nmol·L^{-1})) Measured[a] Directly and Predicted Using the log S–log K_{ow} and log S–A Relationships

	6-phenyl	5-phenyl	4-phenyl	3-phenyl	2-phenyl
decane					
measured		35 ± 10	36 ± 12	38 ± 15	26 ± 8
predicted					
from K_{ow}		131	100	102	86
from A[b]		190	135	119	60
undecane					
measured	11 ± 3	10 ± 3	9 ± 2	12 ± 3	8 ± 3
predicted					
from K_{ow}	32	32	22	26	20
from A	46	46	37	29	15
dodecane					
measured	4 ± 1	5 ± 2	5 ± 2	7 ± 3	4 ± 1
predicted					
from K_{ow}	8	8	7	6	5
from A	11	11	9	7	4
tridecane					
measured	4 ± 2[c]	4 ± 2	4 ± 2	4 ± 2	4 ± 2
predicted					
from K_{ow}	2	2	2	2	1
from A	3	3	2	2	1
tetradecane					
measured	4 ± 2	5 ± 3	4 ± 2	5 ± 3	4 ± 2
predicted					
from K_{ow}	0.4	0.4	0.3	0.3	0.3
from A	0.7	0.7	0.5	0.4	0.2

[a] Measured values are the mean and standard deviation of mole fraction corrected data from 12 equilibration flasks. Solubilities measured in each flask were corrected for the mole fraction of the component of interest in the hydrocarbon phase being equilibrated with the aqueous phase. [b] A is the surface area in the extended conformation determined here. [c] This value includes contributions from both 6-alkyl- and 7-alkyl-substituted tridecylbenzene, as these two compounds coelute under the analytical scheme used here.

Evaluation of the solubility data for the components of the secondary alkylbenzene mixture in light of previous reports (*10, 23–25*) suggests that the solubility of these compounds, particularly the tri- and tetradecylbenzenes, might be enhanced due to either aggregation (*10*) or cosolvency (*25*) in the aqueous phase or nonunity activity coefficients (*23, 24*) in the organic phase.

Physical Property Summary and Interrelationships. The relationship between log $P_L°$ and A for the different linear alkylbenzene isomers appears to be linear (Figure 2). It should be noted, however, that the n-alkylbenzenes plot just below the secondary LABs having an additional carbon. For example, n-nonylbenzene, with a calculated surface area of 5.18 nm^2, has a vapor pressure of 0.338 Pa; this places it just below the cluster of 5-decyl-,

Table VI. Comparison of *n*-Alkylbenzene Vapor Pressures with Literature Data

	$P(25\,°\mathrm{C})/\mathrm{Pa}$	
compound	Dreisbach[a]	this work[b]
n-nonylbenzene	0.573	0.332
n-decylbenzene	0.200	0.127
n-undecylbenzene	0.080	0.046
n-dodecylbenzene	0.032	0.017
n-tridecylbenzene	0.013	0.007
n-tetradecylbenzene	0.005	0.002

Elevated Temperatures

		P/Pa	
compound	$t/°\mathrm{C}$	Allemand et al.[c]	this work[b]
n-nonylbenzene	120	480	420
	130.73	800	738
	142	1350	1291
n-dodecylbenzene	103	22	28
	111	36	49

[a] Using the Antoine vapor pressure equation (*46*). [b] Based on GC retention relative to *n*-hexadecane, corrected to $P_L°$ from $P_{GC}°$. [c] Data from Allemand et al. (*27*) using gas saturation.

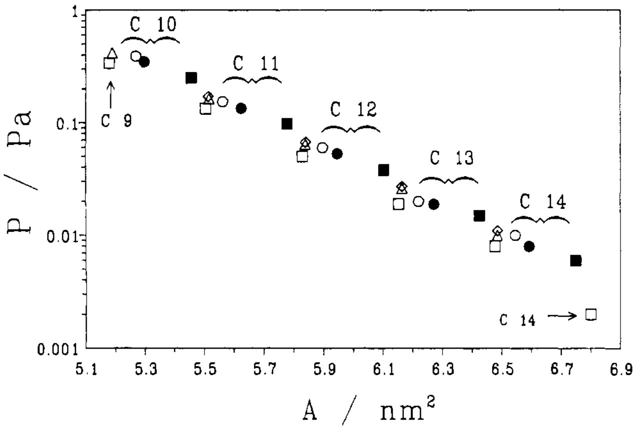

Figure 2. Relationship between P_L and A for the long-chain alkylbenzenes. Symbols designate □, 1-phenyl-; ■, 2-phenyl-; ●, 3-phenyl-; ○, 4-phenyl-; △, 5-phenyl-; and ◇, 6-phenylalkanes.

4-decyl-, and 3-decylbenzenes. The 2-alkylbenzenes were also substantially removed from the internally substituted alkylbenzenes (6-, 5-, 4-, and 3-phenyl substitutions), typically appearing intermediate between its isomers and the next larger homologues of internally substituted alkylbenzenes. It is known that the vapor pressure of alkanes increases with degree of chain branching, presumably due to a decreased area of intermolecular contact for a given molecular weight. These results indicate that the position of phenyl substitution on the alkyl chain mimics branching of the alkyl chain. Thus, the internally substituted alkylbenzenes have greater vapor pressures relative to those with terminal substitution (*n*-alkyl- and 2-alkylbenzene). Another possible factor is that internal substitution of the alkyl chain may limit the association of alkyl chains or the π orbitals of the alkylbenzene molecules. Less intermolecular interaction would result in increased vapor pressures. An investigation of the molecular mechanics of these compounds could provide insight into the causes of these observations.

The relationship between the measured log (aqueous solubilities) and estimated log K_{ow} values for the secondary alkylbenzenes (Figure 3) shows that multicomponent or other effects result in higher than expected concentrations of the C_{13} and C_{14} alkylbenzenes (i.e., the log (aqueous concentrations) level off beyond the dodecylbenzenes). Similar observations have been made regarding the aqueous concentrations of long-chain alkanes (12–26 carbons) (*10*, *48*) and some *n*-alkylbenzenes (*49*). It has been suggested (*10*, *48*) that the increased concentrations of the high-molecular-weight alkanes result from intermolecular association, causing the formation of aggregates or a colloidal phase of alkanes in solution. Ben-Naim and Wilf (*49*) studied the aqueous solubilities of *n*-alkylbenzenes from benzene to *n*-octylbenzene. They reported similar increases in the concentrations of alkylbenzenes beyond *n*-hexylbenzene. They attributed this change in behavior to the length of the alkyl chain becoming sufficient to minimize the effect of the phenyl group on the alkyl chain (i.e., allowing it to be "more aliphatic"), resulting in the alkyl chain dominating the physical behavior of these molecules (*49*).

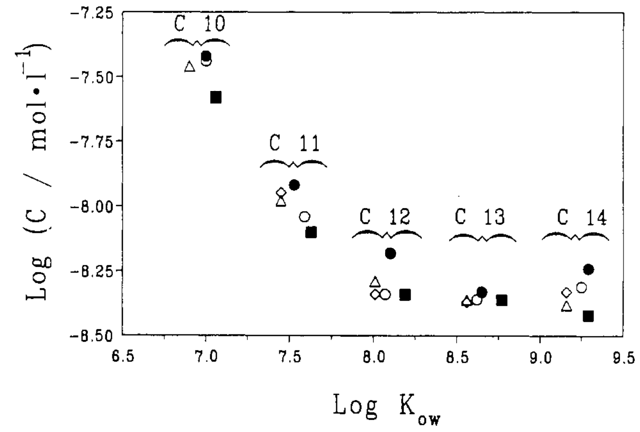

Figure 3. Observed log C–log K_{ow} relationship for the long-chain alkylbenzenes. Symbols are as in Figure 2.

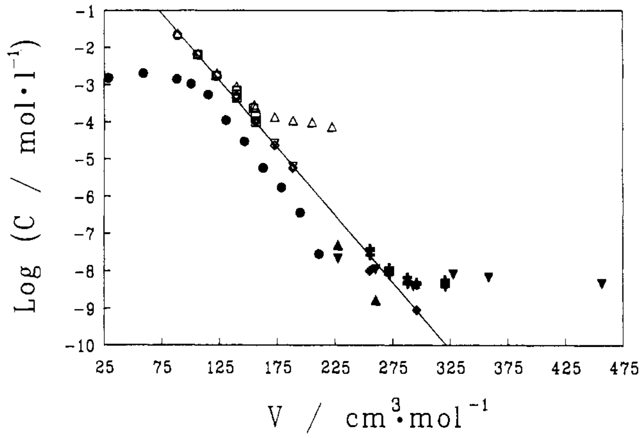

Figure 4. Relationship between log C and V_m for the *n*-alkanes and the long-chain alkylbenzenes. Symbols designate data from *long-chain alkylbenzenes*, this work, ♦, *n*-alkylbenzenes; dark +, secondary alkylbenzenes; *short-chain alkylbenzenes*, △, Ben-Naim and Wilf (*49*); □, Sutton and Calder (*11*); ▽, Tewari et al. (*4*); ◇, Owens et al. (*5*); ○, Sanemasa et al. (*38*); *n-alkanes*, ●, McAuliffe (*10*, *12*); ▲, Coates et al. (*26*); ▼, Sutton and Calder (*48*). Dodecane and tetradecane values reported by Coates et al. (*26*) (▲) and Sutton and Calder (*48*) (▼) point out the aqueous concentration differences discussed in the text.

The comparison of log (dissolved concentration) and molar volume made originally in Figure 1 was expanded to include the dissolved aqueous concentrations of both the *n*-alkanes and the *n*-alkylbenzenes (short- and long-chain, Figure 4). The regression line between log solubility and molar volume developed previously is also plotted in Figure 4. It can be seen that the alkanes and alkylbenzenes plot along parallel lines except at the extremes of molecular volume. The second break in the alkane–molar volume relationship occurs for *n*-alkanes having more than 11 carbons, as discussed by McAuliffe (*10*). This break was not observed by Coates et al. (*26*), as can be seen with the plot of their data for dodecane and tetradecane (Figure 4, filled triangles). Several researchers (*12, 48*) found the dissolved concentrations of *n*-alkanes larger than dodecane to be fairly constant. These results may indicate that there is an effect of aggregate formation despite efforts (*48*) to ensure removal of colloidal or "accommodated" material. RP-HPLC estimation (*26*) of the solubilities of higher molecular weight *n*-alkanes also indicates the observed concentrations for these compounds represent experimental artifacts, rather than true solubilities.

The solubilities of *n*-pentylbenzene through *n*-octylbenzene determined by equilibrating the *n*-alkylbenzenes directly with water (*49*) are higher than those obtained using a generator column (*4, 5*). This may have resulted from the formation of *n*-alkylbenzene colloids or aggregates in the aqueous phase in the former experiments (*49*). The secondary (internally substituted) alkylbenzenes are also included in Figure 4 (dark plus). Since the molar volume of these compounds is at present undetermined, they are plotted using the molar volume of the *n*-alkylbenzenes of the same alkyl chain length. The similar behavior of the longer chain (C_{13}, C_{14}) secondary alkylbenzenes and the *n*-alkanes beyond dodecane (C_{12}) suggests that these solubilities may be controlled by the same effects. The *n*-alkylbenzenes (filled diamonds, Figure 4), when equilibrated separately from the secondary alkylbenzenes, fit the regression line (developed using the short-chain *n*-alkylbenzenes) better than do the secondary alkylbenzenes. This suggests that interaction in either the aqueous or organic phase of the equilibration is causing these effects for the longer chain secondary alkylbenzenes.

Conclusions

Measurements and estimates of the aqueous solubilities, vapor pressures, 1-octanol–water partition coefficients (log K_{ow}), and surface areas of the long-chain linear alkylbenzenes have been made. These parameters all show relations to chain length and are affected to varying degrees by the phenyl substitution pattern of the alkyl chain. For example, the vapor pressure always increased as the phenyl substitution became more internal on the alkyl chain. Some irregular trends were also observed. Solubility showed slightly increased values when the phenyl substitution was in the 3-position (3-phenyl) of the alkyl chain. There appears to be cosolute or other interaction effects prohibiting accurate, direct measurement of the solubilities of individual components of the secondary alkylbenzene mixture. Special attention needs to be paid to assessing such low-solubility compounds.

Acknowledgment

We thank L. E. Bailey, A. E. McElroy, G. B. Gardner, and J. W. Farrington for assistance with various portions of the work reported here. Portions of this work were performed while R.P.E. was at the Southern California Coastal Water Research Project.

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Received for review November 26, 1991. Accepted May 11, 1992. P.M.G. gratefully acknowledges support from the MIT Sea Grant College Program, a part of the National Oceanic and Atmospheric Administration, and from the National Science Foundation, Grant No. 8714110-CES.

Registry No. $Ph(CH_2)_{10}CH_3$, 6742-54-7; $Ph(CH_2)_{11}CH_3$, 123-01-3; $Ph(CH_2)_{12}CH_3$, 123-02-4; $Ph(CH_2)_{13}CH_3$, 1459-10-5; $PhCH(CH_3)(CH_2)_7CH_3$, 4537-13-7; $PhCH(CH_3)(CH_2)_8CH_3$, 4536-88-3; $PhCH(CH_3)(CH_2)_9CH_3$, 2719-61-1; $PhCH(CH_3)(CH_2)_{10}CH_3$, 4534-53-6; $PhCH(CH_3)(CH_2)_{11}CH_3$, 4534-59-2; $PhCH(CH_2CH_3)(CH_2)_6CH_3$, 4621-36-7; $PhCH(CH_2CH_3)(CH_2)_7CH_3$, 4536-87-2; $PhCH(CH_2CH_3)(CH_2)_8CH_3$, 2400-00-2; $PhCH(CH_2CH_3)(CH_2)_9CH_3$, 4534-52-5; $PhCH(CH_2CH_3)(CH_2)_{10}CH_3$, 4534-58-1; $PhCH(Pr)(CH_2)_5CH_3$, 4537-12-6; $PhCH(Pr)(CH_2)_6CH_3$, 4536-86-1; $PhCH(Pr)(CH_2)_7CH_3$, 2719-64-4; $PhCH(Pr)(CH_2)_8CH_3$, 4534-51-4; $PhCH(Pr)(CH_2)_9CH_3$, 4534-57-0; $PhCH(Bu)(CH_2)_4CH_3$, 4537-11-5; $PhCH(Bu)(CH_2)_5CH_3$, 4537-15-9; $PhCH(Bu)(CH_2)_6CH_3$, 2719-63-3; $PhCH(Bu)(CH_2)_7CH_3$, 4534-50-3; $PhCH(Bu)(CH_2)_8CH_3$, 4534-56-9; $PhCH(n\text{-}C_5H_{11})(CH_2)_4CH_3$, 4537-14-8; $PhCH(n\text{-}C_5H_2)_5CH_3$, 2719-62-2; $PhCH(n\text{-}C_5H_{11})(CH_2)_6CH_3$, 4534-49-0; $PhCH(n\text{-}C_5H_{11})(CH_2)_7CH_3$, 4534-55-8; $PhCH(n\text{-}C_6H_{13})(CH_2)_6CH_3$, 4534-54-7; $H_3C(CH_2)_7OH$, 111-87-5; $Ph(CH_2)_9CH_3$, 104-72-3.