

Temperature Dependence of Solubilities in Water and Heats of Fusion of Solid Aromatic Hydrocarbons

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The solubilities in water of *p*-dichlorobenzene, naphthalene, acenaphthene, biphenyl, fluorene, phenanthrene, anthracene, and pyrene have been measured by extraction and spectrophotometric analysis, from room temperature up to 75°C. At 25°C, smoothed solubilities are, respectively, 83.1, 31.2, 3.88, 7.08, 1.90, 1.18, 0.075, and 0.148 ppm. The data are well described by the expression $R \ln X_2^s = -(\Delta H_m^\circ/T) + (0.000408)(T - 291.15)^2 - c + bT$, where X_2^s is the mole fraction of solute at saturation, ΔH_m° is the molar heat of fusion of the solute, T is the absolute temperature, and b and c are empirical constants. Also, new measurements for the heats of fusion for some of the hydrocarbons, and precise extinction coefficients in the ultraviolet for all of the hydrocarbons in cyclohexane are reported.

The temperature dependence of solubility for most of the larger aromatic hydrocarbons is not known, and such data should provide a greater understanding of the effects of size, and extended aromatic electronic structure, on nonpolar solute-water interactions.

EXPERIMENTAL

Purification of Solutes. The following were recrystallized three times: Baker reagent naphthalene, from ether; Matheson, Coleman and Bell biphenyl, from methanol; Eastman White Label fluorene and phenanthrene, from absolute ethanol; Matheson, Coleman and Bell *p*-dichlorobenzene, from absolute ethanol. Aldrich acenaphthene (mp 90–94°C) was recrystallized five times from absolute ethanol. Each of these products was then vacuum-sublimed twice. Mallinckrodt anthracene (mp 215–17°C) was vacuum-sublimed three times. Aldrich "purissimus" pyrene was used without further purification. Ultraviolet spectra and melting points were identical to published data; however, after shaking the solids with water, the cyclohexane extracts of the aqueous phase showed some extraneous uv peaks, in the case of anthracene and pyrene. In the case of pyrene, no interference with the peak used for analysis occurred, but some overlap with the anthracene peak may have resulted in slightly high (3–5%) solubility values at lower temperatures.

Equilibration and Analyses. Approximately 20 grams of each solid was placed in each of three 250-ml glass-stoppered flasks with distilled deionized water. The flasks were suspended in an open water bath and shaken gently from one to three weeks between measurements. Temperature control was maintained within $\pm 0.5^\circ\text{C}$. Samples of the replicate solutions were withdrawn with pipets through a glass wool plug, immediately emptied into weighed 60-ml separatory funnels, the filled funnels weighed, and the pipets rinsed with cyclohexane into the funnels. (Matheson, Coleman and Bell cyclohexane, mp 5–6°C, proved to be free of interfering uv absorption, and was reusable after distillation through a 1-m helix-packed column.) In the case of *p*-dichlorobenzene above the melting point (52.8°C), the pipet without filter was dipped below the organic layer while being blown through and a sample taken. After the pipets were rinsed, additional cyclohexane was added to the funnels and the aqueous solution ex-

tracted. Final volumes of cyclohexane were chosen such that peak maxima fell in the range $\lambda = 0.5\text{--}1.5$. In all cases, spectra taken of second extracts or of the aqueous layer after extraction indicated complete extraction.

This technique allowed all analyses and Beer-Lambert constant determinations to be performed at room temperature, and minimized losses of solute from aqueous samples by evaporation and adsorption onto glass surfaces (1, 2, 6, 13).

Standard solutions were prepared either by direct weighing using a Cahn electrobalance, or by weighing of 0.1–0.2 gram of samples followed by serial dilution in calibrated glassware. At least two weighings were used for each compound, and absorbance readings were made on at least six solutions in the range 0.5–1.5. Within experimental error (0.5%), all the compounds obeyed Beer's law in the range of concentrations studied. The results of the Beer's law determinations are given in Table I.

Absorbances of the standard solutions and extracts were measured on a Cary 14 spectrometer, scanning at 5 Å/sec. Values for extracts generally agreed within 2% for replicate solutions, but plots of solubility vs. temperature indicated a scatter for different temperatures of 3–5%, about a smooth curve.

Measurement of Heats of Fusion. The semiempirical equation used to describe the solubility data involves the molar heat of fusion of the solute, and this quantity has not been reported for pyrene. It was measured, along with that of the other compounds for comparison, on a Beckman differential scanning calorimeter. A standard value of 35.6 cal/g for naphthalene was used for calibration (11). Samples (0.3–0.5 gram) were weighed on a Cahn electrobalance, sealed in swaged alum-

Table I. Beer-Lambert Constants for Aromatic Hydrocarbons in Cyclohexane

	λ_{max} , nm	Range, mg/l	Beer-Lambert constant, 1 mg ⁻¹ cm ⁻¹ , ± 10 ³ std dev
<i>p</i> -Dichlorobenzene	273	90–294	0.00378 ± 0.01
Naphthalene	277	10–40	0.0455 ± 0.2
Acenaphthene	289	3.2–7.2	0.0433 ± 0.1
Biphenyl	248	6.2–42	0.1094 ± 0.3
Fluorene	301	2.1–8.3	0.0602 ± 0.4
Phenanthrene	293	0.6–5.0	0.0832 ± 0.3
Anthracene	253	0.3–1.3	1.294 ± 5
Pyrene	335	2.0–8.3	0.278 ± 1

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Table II. Parameters Used to Calculate Smoothed Solubilities

	ΔH_m° , kcal/mol		Least-square coefficients and std dev		Av % dev, obsd-smoothed solubility
	Obsd	Lit.	$10^2 b$	c	
<i>p</i> -Dichlorobenzene ^a	4.34 ± 0.12	4.47 (3), 4.37 (5)	-0.42 ± 0.15	7.1 ± 0.5	2.3
Naphthalene	(8.69 ± 0.04) ^b	4.56 (5), 4.59 (11), 4.50 (12)	1.39 ± 0.05	13.4 ± 0.2	1.9
Acenaphthene	5.23 ± 0.05	4.87 (9), 4.95 (10)	1.86 ± 0.11	17.1 ± 0.4	4.0
Biphenyl	4.52 ± 0.12	4.02 (5), 4.44 (8), 4.46 (11)	2.73 ± 0.12	20.8 ± 0.4	3.7
Fluorene	4.67 ± 0.03	4.80 (?)	3.09 ± 0.10	24.2 ± 0.3	3.2
Phenanthrene	(3.89 ± 0.02) ^c	4.33 (5), 4.46 (8)	3.74 ± 0.13	27.9 ± 0.4	4.7
Anthracene	6.93 ± 0.07	6.90 (5, 8)	1.81 ± 0.15	19.3 ± 0.5	4.4
Pyrene	3.66 ± 0.02	...	4.78 ± 0.09	38.1 ± 0.3	2.7

^a For liquid *p*-dichlorobenzene, Equation 2 was used to calculate solubilities, with $c = 8.90 \pm 0.03$; av dev = 1.1%. ^b Calorimeter peak area (cm²), and av dev; used as standard. ^c Value lower than reliable previous determinations; used 4.46 kcal/mol in calculations.

inum cups, and triplicate runs taken for each compound. Results and literature values are shown in Table II.

Calculations. The solubility data for the solids were smoothed using the semiempirical expression (4)

$$R \ln X_2^s = -(\Delta H_m^\circ/T) + (0.000408)(T - 291.15)^2 - c + bT \quad (1)$$

where X_2^s is the mole fraction of solute at saturation at absolute temperature T , ΔH_m° is the molar heat of fusion of the pure solid solute at the melting point, and b and c are determined by least-squares fit. This equation has been found to describe hydrocarbon solubilities well (4). For liquid *p*-dichlorobenzene, only one empirical constant is required, in an expression derived from the same model as Equation 1 (4),

$$R \ln X_2^s = -(\Delta S_m^\circ) + (0.000408)(T - 291.15)^2 - c \quad (2)$$

where ΔS_m° is the entropy of melting of the pure solute, at the melting point.

RESULTS

The fit of the data to Equation 1 is shown in Figure 1; for liquid *p*-dichlorobenzene, the constant, c , varied randomly about the value given in Table II. A plot of the deviations about the model Equation 1 indicated that the three largest hydrocarbons, anthracene, phenanthrene, and pyrene, tended to show some positive deviations in the region at about 50°C and negative deviations near 70°C and higher which could be due either to deficiencies in the model or to a difficulty in obtaining saturation at the highest temperatures. Nevertheless, these deviations are in the range of overall scatter for the solutes in general, and Equation 1 remains a valid description of the data within the upper limit 75°C of our measure-

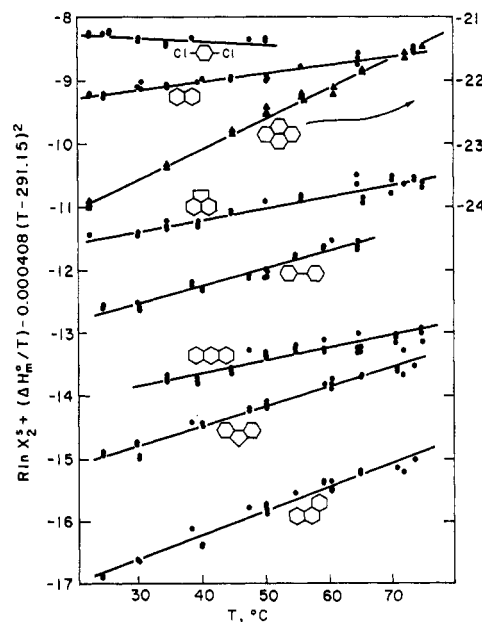


Figure 1. Test of Equation 1

Points are experimental, lines are least-squares fit used to obtain coefficients b and c . Note different ordinate for pyrene

ments. Also, extrapolations to temperatures lower than room temperature may be accurate, since a comparison of calculated solubilities down to 0°C, based on our data, with the low-temperature solubility data of Bohon and Claussen (2) for naphthalene and biphenyl showed very close agreement.

Unsmoothed and smoothed solubilities are given in Table III, along with interpolated solubilities and estimates of preci-

Table III. Observed and Smoothed Solubilities of Solid Aromatic Hydrocarbons in Water

t , °C	Experiment, ppm	Smoothed, ppm with std dev	t , °C	Experiment, ppm	Smoothed, ppm with std dev
	<i>p</i> -Dichlorobenzene(s)			<i>p</i> -Dichlorobenzene(l)	
(00.0)	...	(47 ± 1)	59.2	210	210
22.2	78.0, 77.5	77.5	60.7	219, 216	216
24.6	83.6, 83.3, 83.4	82.2	65.1	228, 231, 231	234
(25.0)	...	(83.1 ± 0.8)	65.2	240, 232, 238	236
25.5	87.8, 85.6	84.1	73.4	281	279
30.0	93.1, 92.1	94.6	(75.0)	...	(289 ± 3)
34.5	102, 103, 101	106.8		Naphthalene	
38.4	121	119.3	(00.0)	...	(13.7 ± 0.2)
47.5	159	156	22.2	28.8, 29.1, 28.8	28.3
(50.0)	...	(170 ± 3)	24.5	30.8 (2), 30.1 (2), 30.7	30.7
50.1	175, 172	170			

(Continued on next page)

Table III. (Continued)

<i>t</i> , °C	Experiment, ppm	Smoothed, ppm with std dev	<i>t</i> , °C	Experiment, ppm	Smoothed, ppm with std dev
Naphthalene (Contd.)			Fluorene (Contd.)		
(25.0)	...	(31.2 ± 0.2)	59.2	10.5, 10.5	10.2
29.9	38.1, 38.2, 38.3	37.3	60.5	10.7, 11.0, 11.6	10.9
30.3	38.1, 37.6, 37.6	37.8	65.1	14.2, 14.1, 14.2	14.1
34.5	44.6, 43.8	44.3	70.7	18.5, 18.5, 18.9	19.3
39.3	52.6, 52.8	53.3	71.9	18.8	20.6
40.1	54.8	55.0	73.4	21.5	22.5
44.7	66.0, 65.5, 65.3	66.2	(75.0)	...	(24.7 ± 0.4)
(50.0)	...	(82.4 ± 0.4)	Phenanthrene		
50.2	78.6	83.1	(00.0)	...	(0.39 ± 0.01)
55.6	106	105	24.6	1.12, 1.11	1.16
64.5	166, 151, 157	156	(25.0)	...	(1.18 ± 0.02)
73.4	240, 247, 244	239	29.9	1.49, 1.49	1.49
(75.0)	...	(258 ± 3)	30.3	1.47, 1.48	1.52
Acenaphthene			38.4	2.44, 2.45	2.27
(00.0)	...	(1.45 ± 0.04)	40.1	2.27, 2.28, 2.25	2.47
22.2	3.57	3.46	47.5	3.87, 3.88, 3.87	3.63
(25.0)	...	(3.88 ± 0.07)	(50.0)	...	(4.14 ± 0.04)
30.0	4.76, 4.60, 4.72	4.80	50.1	4.30, 4.38, 4.32	4.16
34.5	6.00, 5.68, 5.73	5.83	50.2	4.08, 4.04, 4.11	4.19
39.3	6.8, 7.1, 7.0	7.2	54.7	5.66, 5.64, 5.63	5.34
44.7	9.4, 9.4, 9.3	9.2	59.2	7.17, 7.19, 7.21	6.85
(50.0)	...	(11.9 ± 0.1)	60.5	7.2, 7.2, 7.6	7.4
50.1	12.5, 12.4, 12.4	11.9	65.1	9.8, 9.7, 9.8	9.6
55.6	15.8, 16.3, 15.9	15.6	70.7	12.4, 12.6, 12.4	13.3
64.5	25.9, 27.8	24.3	71.9	12.9	14.2
65.2	23.7, 23.4, 22.8	25.2	73.4	15.2	15.6
69.8	30.1, 34.3, 33.6	32.1	(75.0)	...	(17.2 ± 0.3)
71.9	35.2	35.9	Anthracene		
73.4	39.1, 40.1	39.0	(00.0)	...	(0.022 ± 0.001)
74.7	40.8, 39.3	41.8	(25.0)	...	(0.075 ± 0.002)
(75.0)	...	(42.5 ± 0.7)	35.4	0.125, 0.122, 0.119	0.123
Biphenyl			39.3	0.152, 0.151, 0.148	0.159
(00.0)	...	(2.64 ± 0.07)	44.7	0.208, 0.210, 0.206	0.214
24.6	7.13, 7.29, 7.35	6.96	47.5	0.279	0.249
(25.0)	...	(7.08 ± 0.09)	(50.0)	...	(0.286 ± 0.003)
29.9	8.77, 8.64, 8.95	8.73	50.1	0.301, 0.297, 0.302	0.288
30.3	8.55, 8.54, 8.48	8.88	54.7	0.391, 0.389, 0.402	0.372
38.4	13.2, 13.3, 13.5	12.7	59.2	0.480, 0.488, 0.525	0.481
40.1	13.1, 13.4, 13.4	13.8	64.5	0.72, 0.62, 0.64	0.66
47.5	18.8, 19.0, 18.7	19.5	65.1	0.67, 0.64, 0.67	0.68
(50.0)	...	(22.0 ± 0.2)	69.8	0.92	0.90
50.1	20.6, 21.6, 21.8	22.1	70.7	0.90, 0.97, 0.96	0.95
50.2	20.7, 21.8	22.2	71.9	0.91	1.02
54.7	28.3, 28.8, 28.8	27.7	74.7	1.19, 1.13, 1.26	1.21
59.2	36.4, 36.3, 36.0	34.8	(75.0)	...	(1.23 ± 0.02)
60.5	40.4	37.2	Pyrene		
64.5	43.7, 44.7, 46.6	45.9	(00.0)	...	(0.049 ± 0.001)
Fluorene			22.2	0.129, 0.128, 0.124	0.130
(00.0)	...	(0.66 ± 0.01)	(25.0)	...	(0.148 ± 0.002)
24.6	1.93, 1.87, 1.88	1.86	34.5	0.228, 0.235	0.235
(25.0)	...	(1.90 ± 0.03)	44.7	0.397, 0.395, 0.405	0.399
29.9	2.41, 2.33, 2.34	2.37	(50.0)	...	(0.532 ± 0.004)
30.3	2.10, 2.25, 2.23	2.41	50.1	0.558, 0.576, 0.556	0.534
38.4	3.72, 3.73	3.53	55.6	0.75, 0.75, 0.77	0.73
40.1	3.88, 3.84, 3.85	3.84	56.0	0.74	0.74
47.5	5.59, 5.62, 5.68	5.54	60.7	0.96, 0.95, 0.90	0.97
(50.0)	...	(6.29 ± 0.05)	65.2	1.27, 1.29	1.27
50.1	6.31, 6.42, 6.54	6.32	71.9	1.83, 1.86, 1.89	1.90
50.2	6.27	6.35	74.7	2.21	2.26
54.7	8.31, 8.41, 8.56	8.02	(75.0)	...	(2.31 ± 0.03)

sion based on variance about the model equation. We believe these data will provide a basis for comparison of the thermodynamics of solution for these solid hydrocarbons, with that of the much more studied gaseous and liquid hydrocarbons.

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Some Properties of Binary Systems of Hexane and Normal Chloroalkanes

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Viscosities, densities, refractive indices, and refractivity intercepts at 25°C are presented for nine binary liquid systems of *n*-hexane with 1-chloroalkanes from 1-chlorobutane through 1-chlorooctadecane. These, and the derived properties excess molar Gibbs free energy of activation for flow and excess molar volume, are related to halide chain length and composition. Behavior in the present systems is compared with that reported previously for those systems containing the same halides with *n*-hexadecane as the *n*-alkane component.

The viscometric (2), volumetric (9), and refractometric (11) properties at 25°C have been reported previously for mixtures in nine binary liquid systems of *n*-hexadecane (C₁₆) with 1-chloroalkanes from 1-chlorobutane (C₄Cl) through 1-chlorooctadecane (C₁₈Cl). (For convenience *n*-alkanes will generally be abbreviated in the text as C_{*n*} and 1-chloroalkanes as C_{*n*}Cl.) In the present paper the work is extended by the substitution of C₆ as the *n*-alkane, with the same halide components. C₁₆ is of greater chain length than most of the present 1-chloroalkanes, and C₆ is of shorter chain length than most of them. The purpose is to establish the effect of this alteration of the relative chain lengths of the *n*-alkane and the 1-chloroalkanes.

EXPERIMENTAL

Equipment. The equipment and techniques parallel that of earlier work (7, 8). A water bath thermostatically controlled to ±0.01°C was used. Bath temperature was monitored with a Beckman thermometer set with a calibrated

thermometer. The calibration of the latter was against an NBS certified standard. Times were measured with an electric stopclock which had been calibrated against an electronic time standard. The cathetometer used in density determinations indicated height to ±0.05 mm. Weighings were made with a Mettler 300-gram-capacity precision balance with certified balance weights.

Viscosities were determined with Cannon-Fenske ASTM viscometers with different capillary diameters because of the 20-fold increase in viscosity in the 1-chloroalkane series. Three freshly obtained NBS oils of certified viscosity were employed as primary calibration standards for the ASTM 50 and 100 viscometers. Kinetic energy corrections compared favorably with those predicted for the given capillary diameters (17).

Densities were determined with a 4.5-ml. Lipkin pycnometer with precision capillary arms of 1-mm i.d. The pycnometer was calibrated with air-free distilled water, with heights of the liquid in the capillary arms measured relative to a single etched mark on each arm. The calibration was rechecked periodically. The precision of the results obtained with the pycnometer was dependent upon precautions previously described (10).

The viscometers and pycnometer were maintained in the bath until constant flow time or liquid volume, respectively, was obtained. As room temperature was only slightly lower than

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