seemed out of line with both the mixture values and the values for tetrahydrothiophene at other temperatures. It is felt that this value is incorrect, but time and funding did not permit further investigation. The value obtained with the mixture is considered probably close to the correct value.

A plot of the experimental *K* values obtained for ethanethiol vs. the inverse of the absolute temperature yields a nominally straight line, as shown in Figure 2. Also included in the figure are values predicted by Hankinson et al. (*3, 4*) using the SRK-III (Soave-modified Redlich-Kwong (*7, 8*)) equation of state and a C_{12} value of 0.06. This constant is an interaction parameter necessary for the calculation, but arbitrarily selected for reasonable agreement with physical data and experimental results. The best least-squares fit to the data is shown and corresponds to the equation

$$\ln K = b + a/T \qquad (1)$$

where a is −906 and b is 1.54, with an average absolute percent error of 7.9%.

A similar plot of *K* values for tetrehydrothiophene is shown in Figure 3. In this case, the predicted values are obtained for an interaction parameter value of 0.035. A least-squares fit of the experimental data using eq 1 gives values of −1953 and 2.998 for a and b, respectively, and an average absolute percent error of 8.5%, if one neglects the 0 °C tetrahydrothiophene-only point.

In both cases, the computer calculations gave surprisingly good agreement with the experimental values, especially considering the low concentration levels involved. Although the interaction parameter can be changed somewhat arbitrarily, the slopes agree quite well. Thus, it is felt that the described method provides a reliable means of determining *K* values for pure odorants in propane as well as mixtures. *K* values in these mixtures, while important in many commercial applications, could not be determined by a titration. The method is simple and inexpensive, yet yields quite reproducible and reliable results, with the main time consideration being the period between mixing and equilibrium.

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Aqueous Solubility of Polynuclear Aromatic Hydrocarbons

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The solubilities of 32 polynuclear aromatic hydrocarbons and indan have been measured in water at 25 °C. The results compare satisfactorily with the available literature values for ten of the compounds. The hydrocarbon infinite dilution coefficient is correlated with carbon number using a parabolic equation. Aqueous solubility can then be calculated directly for hydrocarbons which are liquid at 25 °C. For solid hydrocarbons the ratio of hydrocarbon solid fugacity to hypothetical subcooled liquid fugacity must be estimated. A suitable correlation is suggested.

In assessing the impact of spills and other emissions of oil in the aquatic environment, it is generally accepted that the more soluble monoaromatic or polynuclear aromatic hydrocarbons (PNA's) are likely to have the most significant toxic effects. Fortunately the monoaromatics such as benzene, toluene, and xylenes evaporate fairly rapidly and their concentration in the aqueous phase and thus their impact on aquatic biota may be considerably reduced. There is a possibility that the PNA's, being less volatile, will be retained longer in the aqueous phase and thus exhibit greater toxicity. Some PNA's have been implicated as carcinogens.

Aqueous solubility is a fundamental parameter in assessing PNA dissolution extent and rate and their persistence in the aquatic environment. The extent to which aquatic biota are exposed to a toxicant such as a PNA is largely controlled by the aqueous solubility. In addition, these solubilities are of thermodynamic interest in elucidating the nature of these highly nonideal solutions.

In this work the solubilities of 32 PNA's and indan have been measured in distilled water at 25 °C, and an attempt has been made to correlate the solubility as a function of molecular structure. This enables the solubility of other PNA's to be estimated with sufficient accuracy for environmental calculation purposes.

Experimental Section and Results

All the hydrocarbons used were of the highest grade commercially available and were obtained from Aldrich Chemicals, Eastman Kodak, or K and K Laboratories. They were used without further purification.

Saturated aqueous solutions were prepared by adding an excess quantity of hydrocarbon to doubly distilled water in 250-mL flasks with glass stoppers. The solution was stirred vigorously with a Teflon-coated magnetic bar for 24 h and subsequently settled at 25 °C for at least 48 h before analysis. In some cases the initial dissolution was done at higher temperatures to increase dissolution rate. The saturated aqueous solutions were decanted and filtered through a 5-μ Millipore filter to remove suspended particles. There is a risk that hydrocarbon may be removed from solution by adsorption on the glassware

Table I

		−Ln (f_s/f_r)		Solubilities			Activity coefficient $\gamma_w^\infty \times 10^{-6}$ using (f_s/f_r)	
				Exptl				
Compd	Triple point, K	Lit.	Eq 3	mg/L	x_w, mole fraction $\times 10^9$	Lit., mg/L	Lit.	Eq 3
Indan, C_9H_{10}	221.6	liquid		109.1 ± 1.02	16650		0.060	
Naphthalene, $C_{10}H_8$	353.2	1.188	1.251	31.7 ± 0.26	4460	34.4 (*6*) 31.2 (*5*)	0.0683	0.0642
1-Methylnaphthalene, $C_{11}H_{10}$	251	liquid		28.5 ± 0.3	3550	30.0 (*7*)	0.282	
2-Methylnaphthalene, $C_{11}H_{10}$	307.6	0.1585	0.2148	25.4 ± 0.2	3220		0.265	0.251
1,3-Dimethylnaphthalene, $C_{12}H_{12}$		liquid		8.0 ± 0.5	920		1.09	
1,4-Dimethylnaphthalene, $C_{12}H_{12}$	255.2	liquid		11.4 ± 0.1	1310		0.763	
1,5-Dimethylnaphthalene, $C_{12}H_{12}$	354		1.270	3.38 ± 0.04	377			0.745
2,3-Dimethylnaphthalene, $C_{12}H_{12}$	375		1.747	3.0 ± 0.01	347			0.502
2,6-Dimethylnaphthalene, $C_{12}H_{12}$	381	2.2135	1.883	2.0 ± 0.02	233		0.469	0.653
1-Ethylnaphthalene, $C_{12}H_{12}$	259.2	liquid		10.7 ± 0.3	1240	10.0 (*7*)	0.806	
1,4,5-Trimethylnaphthalene, $C_{13}H_{14}$				2.1 ± 0.1	215			
Biphenyl, $C_{12}H_{10}$	344	0.9180	1.042	7.0 ± 0.06	815	7.48 (*5*)	0.490	0.433
Acenaphthlene, $C_{12}H_{10}$	369.2	1.6988	1.615	3.93 ± 0.014	459	3.88 (*5*)	0.398	0.433
Fluorene, $C_{13}H_{10}$	389	1.896	2.065	1.98 ± 0.04	214	1.90 (*5*)	0.701	0.593
Phenanthrene, $C_{14}H_{10}$	374	1.463	1.724	1.29 ± 0.07	130	1.18 (*5*)	1.76	1.50
Anthracene, $C_{14}H_{10}$	489.2	4.295	4.343	0.073 ± 0.005	7.57	0.075 (*5, 8, 9*)	1.84	1.72
2-Methylanthracene, $C_{15}H_{12}$	482		4.179	0.039 ± 0.004	3.67			4.17
9-Methylanthracene, $C_{15}H_{12}$	354.5		1.281	0.261 ± 0.002	24.4			11.4
9,10-Dimethylanthracene, $C_{16}H_{14}$	455		3.565	0.056 ± 0.0005	4.90			5.77
Pyrene, $C_{16}H_{14}$	429	2.898	2.974	0.135 ± 0.005	12.0	0.148 (*5*)	4.17	3.87
Fluoranthene, $C_{16}H_{10}$	384		1.951	0.26 ± 0.002	22.8	0.265 (*8*)		6.02
1,2-Benzofluorene, $C_{17}H_{10}$	460		3.679	0.045 ± 0.0012	3.75			6.73
2,3-Benzofluorene, $C_{17}H_{10}$	482		4.179	0.0020 ± 0.00003	0.956			16.0
Chrysene, $C_{18}H_{12}$	528		5.225	0.0020 ± 0.00017	0.158	0.006 (*8*) 0.0015 (*9*)		34.1
Triphenylene, $C_{18}H_{12}$	472		3.952	0.043 ± 0.00013	3.39	0.043 (*8*)		5.65
Naphthacene, $C_{18}H_{12}$	630		7.543	0.00057 ± 0.00003	0.037	0.001 (*9*)		14.3
1,2-Benzanthracene, $C_{18}H_{12}$	433		3.065	0.014 ± 0.0002	1.10	0.010 (*8*)		42.4
7,12-Dimethyl-1,2-benzanthracene, $C_{20}H_{16}$	395		2.201	0.061 ± 0.0006	4.26			26.0
Perylene, $C_{20}H_{12}$	550	4.3580	5.725	0.0004 ± 0.00002	0.0283	<0.0005 (*9*)	452	115
3,4-Benzopyrene, $C_{20}H_{12}$	448		3.406	0.0038 ± 0.00031	0.273	0.004 (*9*)		121
3-Methylcholanthrene, $C_{21}H_{16}$	451		3.474	0.0029 ± 0.000021	0.192	0.0015 (*9*)		161
Benzo[g,h,i]perylene, $C_{22}H_{12}$	550		5.724	0.00026 ± 0.00001	0.0173			189
Coronene, $C_{24}H_{12}$	711		9.384	0.00014 ± 0.00002	0.00856			9.82

or filter. The quantities of solution were sufficiently large that absorption apparently had a negligible effect on the concentration. This was supported by identical results being obtained with and without filtration and by the agreement between these experimental results and literature values for several hydrocarbons. The solutions were then extracted with approximately 5 mL of cyclohexane (ACS spectrograde, Caledon Laboratories Ltd.) in a separatory funnel with 50–100 mL of the saturated aqueous solution. After shaking for 2 h the cyclohexane extract was removed for analysis. No hydrocarbon was detected in a second extract. Replicates and measurement of solubilities of hydrocarbons for which literature values have been reported confirmed the validity of the dissolution and extraction procedure.

An Aminco-Bowman spectrophotofluorometer (American Instuments Ltd.) was used for analysis. Standard calibration solutions were prepared for each hydrocarbon by directly weighting 0.01–0.1 g of the hydrocarbon followed by serial dilution in cyclohexane to concentrations of 1 μg/L. Fluorescence intensity was measured for solutions of concentration 10 mg/L to 1 μg/L. Intensity was found to be a linear function of concentration up to 1 mg/L for most aromatic hydrocarbons. The fluorescence intensity of the cyclohexane extract was measured in the linear region. For hydrocarbons with high aqueous solubilities such as naphthalene and indan, the cyclohexane extracts were also analyzed by gas chromotography for confirmation.

In all cases replicate solubility measurements agreed within 10% and in most cases within 5%. The precision of the method is obviously best for hydrocarbons of relatively high solubility. For hydrocarbons of very low solubility in the parts per billion range the accuracy may be lowered by incomplete equilibration due to slow dissolution of the solid hydrocarbon, by adsorption on the surface of glassware, and by errors in spectroscopic measurement and calibration. It is thus impossible to assign with certainty a level of accuracy to these low solubility measurements.

The measured aqueous solubilities of 32 aromatic hydrocarbons and indan at 25 °C are given in Table I with their formula and melting points (which are here assumed to be equal to the triple points). The values reported are in all cases averages of several (usually three) determinations. The error limits reported indicate the maximum deviations from the average which were obtained in the determinations. There was insufficient replication to calculate a standard error for each hydrocarbon. For nine of these compounds literature data are available for comparison. Agreement in most cases is satisfactory, especially with recent work. The older data of Davis et al. (*2*) were obtained nephelometrically and may be suspect at low concentrations.

Solubility Correlation

The thermodynamic basis for correlating the solubilities of hydrocarbons in water has been discussed by Tsonopoulos and Prausnitz (*7*). An appropriate correlating quantity is believed to be the hydrocarbon infinite dilution activity coefficient γ_w^∞ which

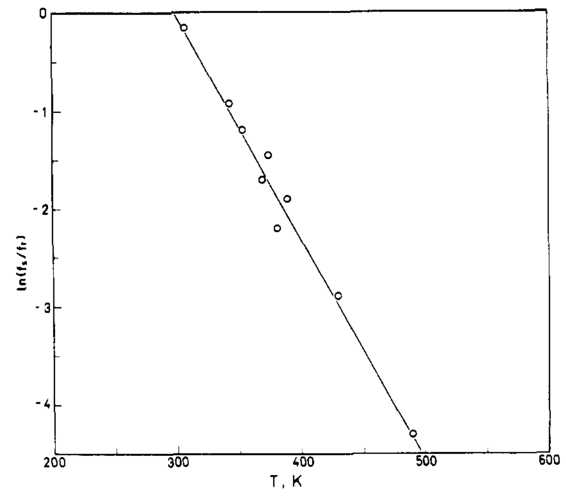

Figure 1. Logarithm of fugacity ratio as a function of temperature.

is essentially a function of the initial slope of the excess free energy curve. Pierotti et al. (*5*), Tsonopoulos and Prausnitz (7), and Leinonen et al. (*4*) have successfully correlated γ^∞ with molecular properties such as carbon number, molar volume, and degree of branching.

For liquid hydrocarbons γ_w^∞ can be assumed to approximate the finite dilution activity coefficient γ_w as defined in the fugacity equation (1) in which subscripts w and h refer to water and hydrocarbon phases, respectively. A small correction for the effect of concentration on γ can be included if desired using the two-suffix Margules equation.

$$f = x_w\gamma_w f_r = x_h\gamma_h f_r \qquad (1)$$

Since the reference fugacities (f_r) cancel and the hydrocarbon mole fraction (x_h) and activity coefficient (γ_h) in the hydrocarbon phase can be assumed to be unity, it follows that γ_w^∞ is simply the reciprocal of the mole fraction solubility.

For solid hydrocarbons the reference fugacity used in the fugacity equation (2) is that of the pure subcooled liquid at the system temperature, an experimentally inaccessible quantity. The solid hydrocarbon fugacity f_s is accessible from vapor pressure data

$$f = f_s = x_w\gamma_w f_r \qquad (2)$$

$$\gamma_w = f_s/(f_r x_w)$$

Since the fugacity ratio (f_s/f_r) is less than unity below the triple point, its magnitude must be estimated from the appropriate thermal properties of the hydrocarbon to permit γ_w or γ_w^∞ to be correlated (Weimer and Prausnitz (*9*)). Unfortunately these properties (heat of fusion and transition and heat capacities) are rarely available although data for some PNA's have been reported by Wauchope and Getzen (*8*). Where such experimental data are available they have been used to calculate γ_w^∞ but in most cases it has been necessary to use a simplified form of the (f_s/f_r) equation for correlating purposes, namely

$$\ln(f_s/f_r) = K(T_{tp} - 298.15) \qquad (3)$$

where K is a constant, T_{tp} is the hydrocarbon triple-point temperature, and 298.15 K is 25 °C. The basis of this equation is the assumption that the entropies of fusion of the PNA's are approximately equal. From available data for some hydrocarbons, K was estimated to average −0.022 73 as shown in Figure 1. This value was then used to calculate (f_s/f_r) for the other solid hydrocarbons. The significance of (f_s/f_r) is apparent from its value of about 0.01 for a PNA with a triple point of 228 °C.

The literature (lit.) values and correlated (eq 3) values (from the equation above) of (f_s/f_r) given in Table I were used to calculate γ_w^∞ for each compound. For liquid hydrocarbons γ_w^∞ is the reciprocal of the experimental mole fraction solubility. For solid hydrocarbons, the values of (f_s/f_r) used (together with the experimental mole fraction solubility) to calculate γ_w^∞ were from the literature or from eq 3. Values of γ_w^∞ are plotted in Figure 2 as a function of carbon number, the dotted line being the correlation derived by Tsonopoulos and Prausnitz for seven PNA's. The figure suggests that no simple carbon number correlation is capable of representing the data satisfactorily for all PNA's since there is a scatter of over an order of magnitude for the higher molecular weight compounds. Interestingly, the methyl substituted hydrocarbons tend to have high γ_w values, suggesting that the presence of these substituent groups reduces the capacity of the water matrix to accommodate the hydrocarbon, possibly by interfering with the aromatic–water interaction which enhances the solubility of aromatic compounds over that of alkanes. Interesting in this respect is the behavior of the substituted naphthalenes which show the profound effect of the (f_s/f_r) ratio and the effect of substitution in reducing solubility.

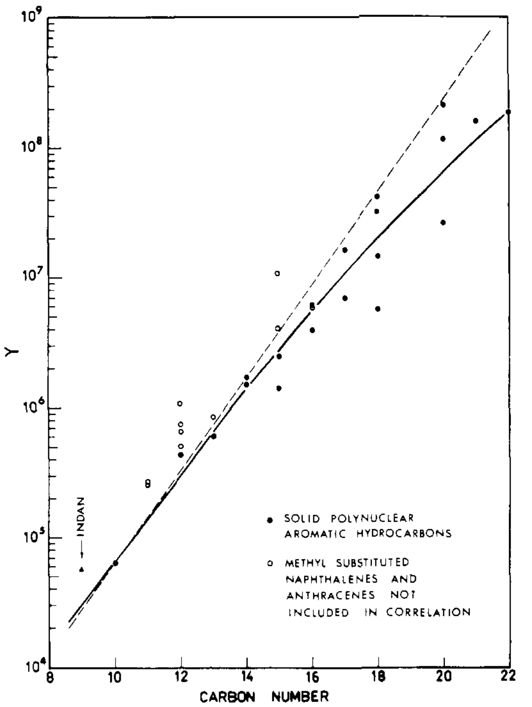

Figure 2. Logarithm of activity coefficient, calculated using eq 3 in the case of solid hydrocarbons, as a function of carbon number.

Although part of the data scatter in Figure 2 is undoubtedly attributable to errors in the (f_s/f_r) correlation it appears that the significant effect may be shape and size of the molecule in determining the ability of the water structure to accommodate and interact with hydrocarbons. Perhaps the molar volume of the subcooled hydrocarbon or its partial molar volume would provide a better basis for correlation than carbon number.

In view of the lack of thermodynamic data for PNA's the only presently feasible approach to correlation is to use carbon number, as shown by Tsonopoulos and Prauznitz, and degree of alkyl substitution. The Tsonopoulos and Prausnitz correlation shown dashed in Figure 2 tends to overestimate γ at carbon numbers over 15 and it underestimates γ for alkyl-substituted compounds, the correlations having been developed only for the parent PNA's. It is thus suggested that the best available procedure for correlating γ and thus estimating the solubility of other compounds is to use a parabolic equation for γ^∞ as a function of carbon number which approaches the Tsonopoulos and Prauznitz correlation at low carbon numbers. In the regression the alkyl-substituted naphthalenes and anthracenes were excluded since they distort the curve in the C_{10} to C_{14} region. For

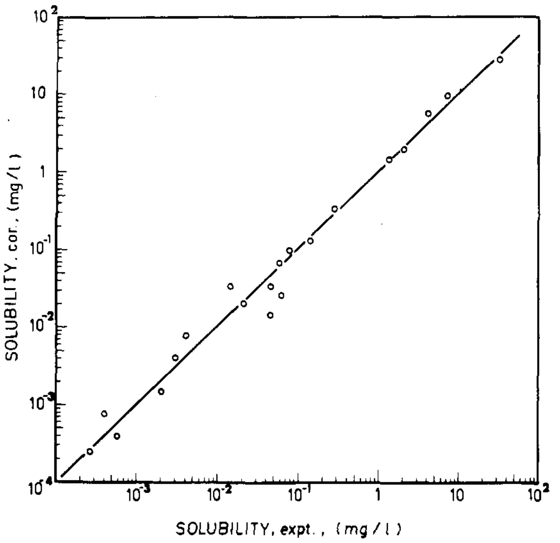

Figure 3. Comparison of correlated and experimental solubilities.

such compounds one procedure is to calculate γ for the PNA of equal carbon number, then multiply this value by about 2.0, effectively halving the solubility. An alternative procedure is to follow the approach of Pierotti et al. (*5*) and calculate the activity coefficient of the parent (unsubstituted) hydrocarbon for alkylbenzenes, then increase log γ by 0.622, i.e., a factor of 4.2 on γ, for each alkyl carbon present. The correlation obtained is shown in Figure 2 and has the form

$$\log \gamma_w^\infty = 3.5055 + 0.3417(N - 6) - 0.002640(N - 6)^2 \quad (4)$$

where N is carbon number. Correlated and experimental values of solubility excluding the alkyl subsituted naphthalenes and anthracenes are compared in Figure 3. The average deviation in log solubility is about 0.26 which corresponds to a factor of 1.8 but in some cases the deviation may be as high as a factor of 3. Although these deviations are large, the calculated solubilities are sufficiently accurate for many environmental calculation purposes. Since the correlation extends over 5 orders of magnitude and uses only carbon number and melting point, the accuracy is regarded as satisfactory. More accurate correlations will probably be developed when more thermal, solubility, and volumetric data are available for these compounds.

In conclusion, aqueous solubility data have been obtained for 32 PNA and indan. For approximate solubility estimation, the best procedure presently available for liquid hydrocarbons is to calculate γ_w^∞ from eq 4. The mole fraction solubility is then the reciprocal of γ_w^∞. For solid hydrocarbons (i.e., melting point above 25 °C) γ^∞ can be calculated from eq 4, (f_s/f_r) from eq 3, and the solubility then calculated from eq 2. For alkyl-substituted naphthalenes or anthracenes the correlated solubilities are about double the experimental values and a correction of this magnitude is needed for such compounds.

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Vapor–Liquid Equilibrium of the Methane–*n*-Hexane System at Low Temperature

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Measurements of the bubble-point compositions are reported and combined with earlier dew-point data from this laboratory to give *K* values for the methane–*n*-hexane system at seven temperatures, 0, −25, −50, −63, −75, −80, and −82.65 °C, from 20 up to 2675 psia. The data may also be evaluated isobarically without interpolation. Two liquid phases were observed in the temperature region between −77.24 (UCST) and −90.69 °C (LCST); detailed composition measurements were made over this entire three-phase region and associated two-phase regions at a total of five temperatures. Equilibrium constants are reported for all three binaries encountered: G–L_1, G–L_2, and L_1–L_2.

A number of studies of the vapor–liquid equilibrium of the methane–*n*-hexane binary system have been reported in the literature. Both liquid and gas phases were studied by Boomer and Johnson (*1*) at 25, 55, and 85 °C and by Poston and McKetta (*9*) over the range 100–340 °F. The lowest temperatures were studied by Shim and Kohn (*11*) in the range −110 to 150 °C, but they did not measure dew points below 0 °C or any bubble points near the critical pressure. Shim and Kohn did not report the two liquid phases existing at temperatures between −77.24 and −90.69 °C. Davenport and Rowlinson (*7*) reported, in a study of hydrocarbon solubilities in methane, that the methane–*n*-hexane system exhibited limited immiscibility, with an LCST of −90.6 °C. Earlier dew point studies in this laboratory (*5*) defined the three-phase region.

Experimental *K* values, obtained by combining the vapor-phase measurements of the elution method (*5*) with those obtained for the liquid phases by use of gas chromatography measurements, are presented here for the CH_4–*n*-C_6H_{14} binary system. Equilibrium constants κ between the liquids for each component in this system are also evaluated.

Experimental Method and Procedure

The recycle equilibrium apparatus is the same as used by Elliot et al. (*8*) in the methane–*n*-butane investigation with some modifications. The boiling point of *n*-hexane is 68.95 °C.