177. *The Solubility Behaviour of Aromatic Hydrocarbons in Benzene.*

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The solubilities in benzene have been determined between room temperature and approximately 80° for diphenyl, *o*-, *m*-, and *p*-terphenyl, 1 : 3 : 5-triphenylbenzene, naphthalene, anthracene, phenanthrene, pyrene, triphenylene, chrysene, fluoranthene, fluorene, and acenaphthene. For the compounds melting below approximately 150° a single curve is obtained when log mole fraction is plotted against T_f/T, where T_f and T are the melting point and solution temperature respectively. This general solubility behaviour of these compounds is interpreted with reference to the entropy of fusion rather than the customary heat of fusion. To test the solutions for strictly regular behaviour the interchange energies of the various solutes with benzene are derived from activity coefficients when calorimetric heats of fusion are known.

There has hitherto been no systematic study of the solubility behaviour of aromatic hydrocarbons in one solvent. Limited data are however available[1] for a few hydrocarbons in different solvents. In view of the importance of these compounds a detailed study of their behaviour in the same solvent was undertaken to obtain information on the influence of structure on solubility. The compounds are representative of three series of aromatic structures, the directly linked phenyl series, the *ortho*-fused benzene series and the fused benzene series with one five-membered ring which are important coal-tar constituents.

Experimental

Materials.—Sources of materials and m. p.s of the purified products are: pyrene 150·2°, triphenylene 198·1° (Rutgerswerke A.G.), fluorene 113·2°, fluoranthene 110·2°, diphenyl 68·9°, acenaphthene 94·1°, chrysene 254·0° (Gesellschaft für Teerverwertung), phenanthrene 98·4° (Synthetic Fuels Research Branch, Bureau of Mines, U.S.A.), *o*-terphenyl 55·5° (Eastman Kodak), *m*-terphenyl 87·0°, *p*-terphenyl 213·0°, naphthalene 80·1° (B.D.H.). 1 : 3 : 5-Triphenylbenzene, m. p. 174·9°, was synthesised by the method of Vorländer, Fischer, and Willie.[2] All the compounds were purified by chromatography on alumina with benzene as eluant, except that hot toluene was used for chrysene and light petroleum for *o*- and *m*-terphenyl. Chromatography was followed by recrystallisation. Solvents were removed by sublimation at 10^{-4} mm. and when the compounds did not sublime by prolonged heating *in vacuo* near the m. p. " AnalaR " benzene which had been dried over sodium wire and freshly distilled was used as solvent.

Apparatus and Technique.—The solubilities were determined by noting the solution temperatures of fixed mole fractions. The mixtures were made up by weight in Pyrex tubes which were then attached to a silica gel drying train. After being embedded in solid carbon dioxide the tubes were sealed at atmospheric pressure. Sealing at atmospheric pressure with liquid nitrogen as coolant frequently led to violent explosions with some compounds, often up to half a day after return to room temperature; no combustion was evident after the explosions; purging the tubes with oxygen-free nitrogen before adding the hydrocarbons did not eliminate the effect.

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[1] Seidell, " Solubilities of Organic Compounds," D. Van Nostrand & Co., New York, 1941.

[2] Vorländer, Fischer, and Willie, *Ber.*, 1929, **62**, 2836.

The solution temperatures were determined by rotating the tubes in a thermostat and noting the temperature at which the last trace of solid dissolved. The thermostat was controlled electrically to ±0·05° and temperatures were determined to the nearest 0·1° with N.P.L. certified thermometers. In general a rough estimate of each solution temperature was first obtained and then approached in 0·1° steps. Table 1 lists the solubilities found.

TABLE 1. *Solubilities of aromatic hydrocarbons in benzene.*

[x = *mole fraction*; *temp.* (T) *in* ° c.]

Diphenyl	T	37·0°	47·6°	59·2°	63·2°		
	x	0·5118	0·6478	0·8195	0·8916		
o-Terphenyl	T	28·0°	32·4°	44·8°	50·4°		
	x	0·5852	0·6442	0·8102	0·9013		
m-Terphenyl	T	36·8°	47·0°	60·8°	67·4°	74·2°	77·6°
	x	0·2827	0·3838	0·5466	0·6407	0·7571	0·8344
p-Terphenyl	T	38·0°	60·2°	64·2°	68·0°	77·6°	
	x	0·0071	0·0156	0·0178	0·0204	0·0279	
1 : 3 : 5-Triphenylbenzene	T	25·2°	28·6°	40·4°	46·2°	59·4°	66·6°
	x	0·0299	0·0351	0·0483	0·0562	0·0795	0·0960
Naphthalene	T	35·0°	45·0°	47·4°	63·2°	75·8°	
	x	0·3766	0·4806	0·5094	0·7119	0·9180	
Anthracene	T	35·8°	42·4°	50·6°	59·6°	70·2°	
	x	0·0103	0·0130	0·0173	0·0225	0·0315	
Phenanthrene	T	32·0°	40·2°	41·8°	50·2°	58·0°	
	x	0·2239	0·2836	0·2990	0·3750	0·4572	
Pyrene	T	32·4°	58·6°	66·8°	76·2°	84·6°	
	x	0·0734	0·1506	0·1896	0·2441	0·3014	
Triphenylene	T	39·4°	47·6°	63·8°	69·4°	82·8°	
	x	0·0140	0·0181	0·0289	0·0341	0·0497	
Chrysene	T	35·6°	45·8°	60·6°	72·2°		
	x	0·0021	0·0032	0·0052	0·0079		
Fluorene	T	33·6°	54·4°	58·4°	69·4°	72·8°	
	x	0·1604	0·2778	0·3095	0·4059	0·4405	
Acenaphthene	T	30·6°	41·4°	63·2°	69·4°		
	x	0·1815	0·2540	0·4731	0·5552		
Fluoranthene	T	44·8°	56·0°	64·4°	77·2°		
	x	0·2174	0·3011	0·3826	0·5331		

DISCUSSION

The solubility of a solute of melting point T_f (° K) in a solvent at temperature T (° K) may be written:[3]

$$\ln 1/a = \frac{\Delta H_f}{\boldsymbol{R}} \cdot \left(\frac{1}{T} - \frac{1}{T_f}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a is the activity of the solute and ΔH_f the molar heat of fusion, at temperature T, of the pure solute. In an ideal solution, a is equal to x so that a plot of $\ln x$ against $1/T$ passes through the melting point and has a slope of $\Delta H_f/\boldsymbol{R}$.

For the present series (compounds with melting points below approximately 150°, *viz.*, naphthalene, phenanthrene, pyrene, acenaphthene, fluoranthene, fluorene, diphenyl, and *o*- and *m*-terphenyl) plots of $\log x$ against $1/T$ were linear, within experimental error, over the measured temperature range and on extrapolation passed through the melting point. Equations for the solubilities of these compounds were determined by the method of least squares subject to the condition that the equation satisfies the point $(0, 1/T_f)$.

Table 2 gives the parameters of the solubility equation:

$$\log x = -m(1/T) + C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

for these compounds in benzene. Plots for the other molecules did not pass through the melting point on linear extrapolation and so have not been represented by parameters.

In all cases where heats of fusion are known (see Table 3) it was found that the solubility curves did not have slopes corresponding to ideal values. Reasons for these departures from ideality may be explained on the basis of regular solution theory.

[3] Hildebrand and Scott, " Solubility of Non-Electrolytes," Reinhold Publ. Corp., New York, 1950.

To test the solutions of aromatic hydrocarbons in benzene for strictly regular behaviour the interchange energy W can be derived when heats of fusion are known. The interchange energy is defined[4] such that if, on starting with two pure lattices of molecules A and B, an interior A molecule is exchanged with an interior B molecule the total increase of energy is $2W$, all molecules being assumed at rest on their lattice points. If the solutions are strictly regular then the interchange energy determined by the equation:

TABLE 2. *Parameters of solubility equation.*

Compound	m	C	Compound	m	C
Phenanthrene	1075·5	2·891	Diphenyl	971·8	2·840
Naphthalene	1016·6	2·920	Fluoranthene	1241·8	3·247
Pyrene	1242·6	2·937	Fluorene	1159·6	2·989
o-Terphenyl	840·0	2·554	Acenaphthene	1302·7	3·547
m-Terphenyl	1208·7	3·358			

$$f = \exp [(1 - x)^2 W/kT] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

should be constant within the accuracy of the experimental data. Here f is the activity coefficient of the solute, so that W must be zero for an ideal solution with $f = 1$. In addition, in a strictly regular solution the solvent and solute molecules are assumed[4] to be sufficiently alike in size and shape to be interchangeable on a quasi-lattice. For spherical molecules this requires[4] a ratio of molecular volumes between 1 and 2.

TABLE 3. *Heats and entropies of fusion of aromatic hydrocarbons.*

Compound	T_f (° K)	ΔH_f (cal./mole)	ΔS_f (cal. deg.$^{-1}$ mole^{-1})
Naphthalene[a]	353·5	4490	12·7
Anthracene[b]	489·2	6890	14·1
Phenanthrene[b]	372·3	4450	12·0
Diphenyl[c]	342·1	4460	13·0
Acenaphthene[d]	367·3	4950	13·5
Fluorene[e]	388·1	4800	12·4

[a] Ward, *J. Phys. Chem.*, 1934, **38**, 761. [b] Parks and Huffman, *Ind. Eng. Chem.*, 1931, **23**, 1138. [c] Spaght, Thomas, and Parks, *J. Phys. Chem.*, 1932, **36**, 882. [d] Skau, *ibid.*, 1935, **39**, 761. [e] Mortimer, *J. Amer. Chem. Soc.*, 1923, **45**, 633.

TABLE 4. *Interchange energy* (W/k) *of benzene with aromatic hydrocarbons.*

Compound	Molar volume (ml.) at T_f	Temp. (° c)					
		10°	20°	30°	40°	50°	60°
Fluorene	163·7	81	78	76	75	76	78
Acenaphthene	148·7	140	135	131	131	132	147
Phenanthrene	169·2	35	34	34	35	37	41
Anthracene	178·9	134	130	128	128	127	129
Naphthalene	127·1	25	25	26	28	33	43

Table 3 gives values of the known heats of fusion of the compounds and Table 4 the values of W/k (° K) determined from these values and the experimental solubilities at 10° intervals. The solubilities were interpolated by using equation (2), and variation of the heat of fusion has been neglected as a first approximation. W/k has not been derived for diphenyl owing to some uncertainty about the value of the latent heat of fusion.[5]

Examination of the values for W/k given in Table 4 shows that the solutions conform roughly to regular behaviour, W/k being constant within an average of 4% over the measured range. Deviations from ideal behaviour may therefore be attributed to the existence of a finite interchange energy on mixing the solvent and solute quasi-lattices.

Although the molecules listed in Table 4 are mostly planar their volumes are approximately twice that of the solvent molecules (benzene has mol. vol. 87·3 ml.) at the melting

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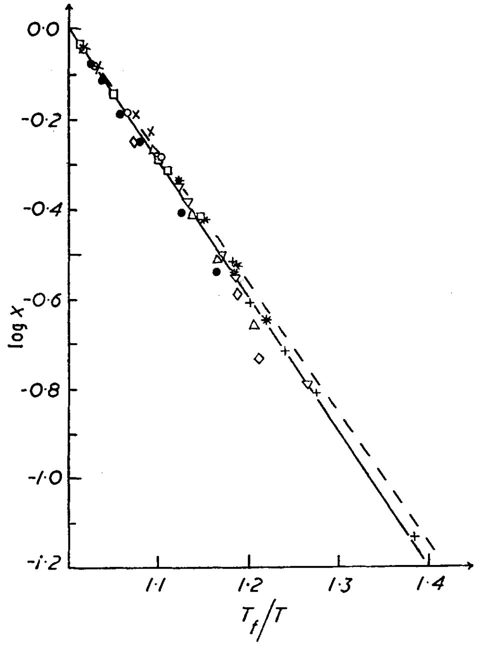
[4] Guggenheim, " Mixtures," Oxford Univ. Press, 1952.

[5] Warner, Scheib, and Svirbely, *J. Chem. Phys.*, 1934, **2**, 590.

point, so that conformity to strictly regular behaviour may seem a little surprising. However, from an examination of the volume requirements for rotation about the three principal axes it has been shown [6] that the fused-ring aromatic hydrocarbons do not, on an average, have sufficient room in the liquid state to assume completely random configurations. As the volume for rotation about the axis in the plane of the molecule is generally much greater than the molar volume of the liquid the molecules adopt a quasi-parallel configuration in the liquid state over small regions. This is borne out by the *X*-ray structure of liquid benzene [7] and by the relatively low viscosities of melts of aromatic hydrocarbons.[6] In these layer liquids the interlayer distance should be approximately constant whatever the molecule, so that mixtures with benzene are " two-dimensional " solutions. This peculiarity may facilitate conformity to regular solution behaviour despite the difference in molecular volume between solvent and solute.



Plot of log *x against* T_f/T.

□ *Naphthalene.* ○ *Diphenyl.* ▽, Fluorene. ◇, Acenaphthene. ×, *o*-Terphenyl. +, Pyrene. △, Fluoranthene. ●, *m*-Terphenyl. *, Phenanthrene. *Ideal solubility curve* — — —.

To examine the general pattern of the solubility of these aromatic hydrocarbons in benzene and the effect of structure on solubility equation (1) may be transformed into

$$\ln a = -\Delta S_f[(T_f/T)-1]/\boldsymbol{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

by multiplying the right-hand side above and below by T_f and rearranging the result. Here ΔS_f is the molar entropy of fusion. It is seen from Table 3 that the average molar entropy of fusion is $13{\cdot}0 \pm 0{\cdot}6$, in agreement with Walden's rule [8] which predicts this value for many compact organic molecules. As the solubility curves pass through the point $(0, 1/T_f)$ of plots of log x against $1/T$(° K) and are linear for compounds melting below approximately 150°, a plot of ln a for each substance against T_f/T would be expected to fall on a single curve with a slight scatter due to small deviations from the average entropy of fusion.

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[6] McLaughlin and Ubbelohde, *Trans. Faraday Soc.*, 1957, **53**, 628.
[7] Pierce, *J. Chem. Phys.*, 1937, **5**, 717.
[8] Walden, *Z. Elektrochem.*, 1908, **14**, 713.

No independent data on the saturation activity coefficients obtained by other techniques are available, so that equation (4) cannot be directly tested. However, if log x is plotted against T_f/T it is found that the data for these compounds melting below 150° lies on a single curve. This is illustrated in the Figure where the best straight line, subject to the condition that it passes through the point (1, 0), has been fitted by the method of least squares. The ideal curve ΔS_f, being taken as 13·0 molar entropy units, is also shown. For compounds with melting points above 150° the scatter (not shown) from the best straight line is somewhat greater. This is probably due to the relatively larger heats and entropies of fusion of these compounds (cf. anthracene in Table 3). As a first approximation, nevertheless, the solubility of all the aromatic hydrocarbons in benzene studied can be represented approximately by the equation:

$$\log x = -\frac{13{\cdot}8}{2{\cdot}303\boldsymbol{R}} \cdot \left[\frac{T_f}{T} - 1\right] \qquad \ldots \ldots \ldots \quad (5)$$

Solubilities calculated from equation (5) agree with experimental values, on an average, within about 5% for compounds melting below 150° but for higher-melting compounds may be in error by a factor of three.

The limited solubility data available for the low-melting compounds in carbon tetrachloride also fall on a single line in a plot of log x against T_f/T. This indicates a similarity in the entropy of solution of these compounds in non-polar solvents. In alcohol the plots are different for each compound and non-linear in general, indicating other factors as operative.

In the absence of solubility data for aromatic hydrocarbons in any solvent where deviations from ideality are expected to be small, the entropy term in equation (5) can be assumed to have an ideal value of 13, to afford an estimate of the solubility from the melting point alone.

Two well-known generalisations concerning the solubility of solids can be made [3] from the ideal solubility equation which is obtained from equation (1) when $a = x$: (1) If the heats of fusion of two substances are similar the one with larger T_f should have the smaller solubility in any solvent. (2) If two solids have similar melting points the one with lower ΔH_f should be the more soluble. However, as the melting point is a function of the lattice cohesion energy of the solid, such rules give no information on the effect of structure on solubility except in so far as structure influences the melting point. For example, any branched terphenyl has a much lower melting point that the straight-chain member and would therefore have a greater solubility; also the more compact a fused-ring system the lower its melting point and hence the greater its solubility, as, for example, with pyrene and triphenylene. However, the Figure brings out the point that if solubilities of all these compounds, both fused and directly linked, are compared at the same reduced temperature T/T_f they all have the same solubility, irrespective of their structure.

Thanks are offered to Professor A. R. Ubbelohde, F.R.S., for helpful advice and encouragement and to the National Coal Board for financial support for chemicals. One of us (H. A. Z.) thanks the Government of Iraq for a grant.

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[*Received, October 3rd,* 1958.]