502. *The Solubility Behaviour of Aromatic Hydrocarbons. Part II.*[1] *Solubilities in Carbon Tetrachloride.*

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The solubilities in carbon tetrachloride of the aromatic hydrocarbons biphenyl, *o*-terphenyl, *m*-terphenyl, naphthalene, phenanthrene, pyrene, fluorene, acenaphthene, and fluoranthene have been measured over a range of temperature. When the solubility data are plotted in the semi-reduced form, log mole-fraction against T_f/T, where T_f and T are the melting point and solution temperature respectively, all the data lie on a single curve. This behaviour is interpreted in terms of the entropies of fusion of the pure solutes. Using known calorimetric heats of fusion, we have determined interchange energies for the various solutes with carbon tetrachloride in order to test for strictly regular solution behaviour. These values are compared with known values determined from corresponding solubilities in benzene.

In Part I[1] the solubilities in benzene of a wide range of aromatic hydrocarbons were determined. It was shown that the effect of melting point on solubility data, for a series of closely related solutes in a common solvent, could be eliminated if log x was plotted against T_f/T, where T_f and x are the freezing point and mole-fraction of solute, respectively, and T is the solution temperature. This corresponding-states behaviour arises because, for a series of closely related non-polar solutes, the entropies of fusion and their deviations from ideality in the same non-polar solvent are approximately the same. In the present work the solubilities of this group of hydrocarbons in carbon tetrachloride are reported. The results are analysed on a similar basis to test for the generality of reduced behaviour and the factors governing it.

[1] Part I, McLaughlin and Zainal, *J.*, 1959, 863.

Experimental

Materials.—Sources of materials and m. p.s of the purified products are: pyrene 148·0° (Rutgerswerke A.G.), fluorene 113·5°, fluoranthene 109·8°, biphenyl 68·8°, acenaphthene 93·8° (Gesellschaft für Teerverwertung), phenanthrene 99·2°, *m*-terphenyl 85·0°, naphthalene 80·1° (B.D.H.), *o*-terphenyl 53·6° (Eastman Kodak). All the compounds were purified by chromatography on alumina, with benzene as eluant except for *o*- and *m*-terphenyl, where light petroleum was used. Solvents were removed by sublimation at 10^{-4} mm., or in cases where the compounds did not sublime, by prolonged heating *in vacuo* near the m. p. " AnalaR " carbon tetrachloride, which was dried ($CaCl_2$) and freshly distilled, was used as solvent.

Apparatus and Technique.—Solubilities were determined by noting the solution temperatures of fixed mole-fractions. The technique previously described [1] was used. This consisted of making up mole-fractions by weight, sealing in Pyrex tubes, and rotating mechanically in a thermostat. The temperature at which the last trace of solid disappeared was noted to the nearest 0·1° with N.P.L. certified thermometers. Temperature was controlled electrically to ±0·05°. Table 1 lists the measured solubilities.

Discussion

Plots of log x against $1/T$ for the data listed in Table 1 are approximately linear within experimental error over the measured temperature range and on extrapolation pass through the melting point.

Table 1. *Solubilities of aromatic hydrocarbons in carbon tetrachloride.*

[x = mole fraction: temp. in °c.]

Biphenyl	Temp.	30·0°	38·4°	45·4°	53·6°	
	x	0·3963	0·4946	0·5998	0·8279	
o-Terphenyl	Temp.	28·8°	34·8°	41·6°	45·4°	49·8°
	x	0·5743	0·6707	0·7493	0·8186	0·8875
m-Terphenyl	Temp.	39·4°	45·0°	55·4°	70·0°	
	x	0·2063	0·2609	0·3718	0·4250	
Naphthalene	Temp.	31·6°	41·0°	49·6°	56·0°	62·8°
	x	0·3129	0·4046	0·5132	0·6010	0·6992
Phenanthrene	Temp.	32·4°	36·8°	40·8°	43·8°	46·0°
	x	0·1768	0·2084	0·2421	0·2664	0·2920
Pyrene	Temp.	41·0	58·4	69·0	79·2	
	x	0·0702	0·1189	0·1639	0·2190	
Fluorene	Temp.	38·2°	46·6°	52·8°	58·2°	64·6°
	x	0·1619	0·2069	0·2499	0·2879	0·3436
Acenaphthene	Temp.	30·0°	41·4°	45·4°	52·0°	
	x	0·1805	0·2627	0·2987	0·3585	
Fluoranthene	Temp.	31·8°	40·2°	47·0°	53·0°	60·4°
	x	0·1032	0·1424	0·1821	0·2278	0·2984

The results have been put in the form

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

and m and c evaluated by the method of least squares subject to the condition that equation (1) passes includes the point $(0, 1/T_f)$. Values of m and c are listed in Table 2.

Table 2. *Parameters of solubility equation.*

Compound	m	c	Compound	m	c	Compound	m	c
Biphenyl	1063·4	3·111	Naphthalene ...	1106·0	3·133	Fluorene	1257·4	3·252
o-Terphenyl ...	975·2	2·979	Phenanthrene...	1245·0	3·345	Acenaphthene	1282·8	3·496
m-Terphenyl...	1689·0	4·461	Pyrene	1431·3	3·398	Fluoranthene...	1458·5	3·819

The slopes of the solubility curves for naphthalene, fluorene, acenaphthene, and phenanthrene, for which heats of fusion ΔH_f are known, do not correspond with the ideal values calculated from the equation

$$\ln 1/a = \Delta H_f(1/T - 1/T_f)/R \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

when the activity a is replaced by the mole-fraction x. These departures from ideality can be interpreted in terms of the activity coefficient f which is given by regular solution theory as [2]

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

W is the interchange energy for solvent–solute molecules in the liquid quasi-lattice and is zero when the solution is ideal and $f = 1$. For a strictly regular solution W is constant. By using the heats of fusion previously given,[1] the interchange energy has been calculated from the present solubility data for naphthalene, fluorene, phenanthrene, acenaphthene, and biphenyl and is given in Table 3 in the form W/k (°K). The experimental solubilities were used and variation of the heat of fusion with temperature was neglected as a first approximation. Constancy of W/k within about 6% indicates that the solutions conform approximately to strictly regular behaviour.

TABLE 3. *Interchange energy W/k* (in °K) *of carbon tetrachloride with aromatic hydrocarbons.*

Compound							Average W/k in CCl_4	Average W/k in C_6H_6
Naphthalene	Temp. (°c)	31·6	41·0	49·6	56·0	62·8		
	W/k	93	97	85	85	107	93	30
Phenanthrene	Temp. (°c)	32·4	36·8	40·8	43·8	46·0		
	W/k	189	177	164	147	146	165	36
Fluorene	Temp. (°c)	38·2	46·6	52·8	58·2	64·6		
	W/k	138	137	129	132	129	133	77
Acenaphthene	Temp. (°c)	30·0	41·4	45·4	52·0	—		
	W/k	128	119	115	121	—	121	136
Biphenyl	Temp. (°c)	30·0	38·4	45·4	53·6	—		
	W/k	72	78	59	56	—	66	—

The average values of W/k for these five solutes in carbon tetrachloride are given in Table 3 together with corresponding values for benzene as solvent. As can be seen, the values for carbon tetrachloride are higher than those for benzene, except for acenaphthene, and the deviations from ideality are therefore greater. This probably arises from two causes. First, benzene is a planar molecule whereas carbon tetrachloride is spherical, so packing of the latter in the solute lattice is less favourable. Secondly, although benzene–solute interactions are mainly between the carbon skeletons of the two molecules, the carbon tetrachloride–solute interactions, however, involve mainly the peripheral chlorine atoms interacting with the carbon skeleton of the solute. This leads to greater deviations from the averaging laws for the heteromolecular interaction for the case of carbon tetrachloride–solute interactions than for benzene–solute interactions and consequently greater deviation of the solutions from ideality.

In a series of closely related molecules where the intermolecular potential is of the same shape it is possible to represent in reduced form by a unique curve the physical properties of the series which are dependent on the characteristics of the potential. This reduction is generally made by choosing the critical state as the reference state. For gases, both equilibrium and transport properties of simple spherically symmetric molecules are found to follow this law of corresponding states.[3] For condensed phases, however, conformity of physical properties to corresponding states has not been so extensively investigated.

For the solubility data of solids in liquids it has previously been shown [1] that if the solubility formula (3) is transformed into

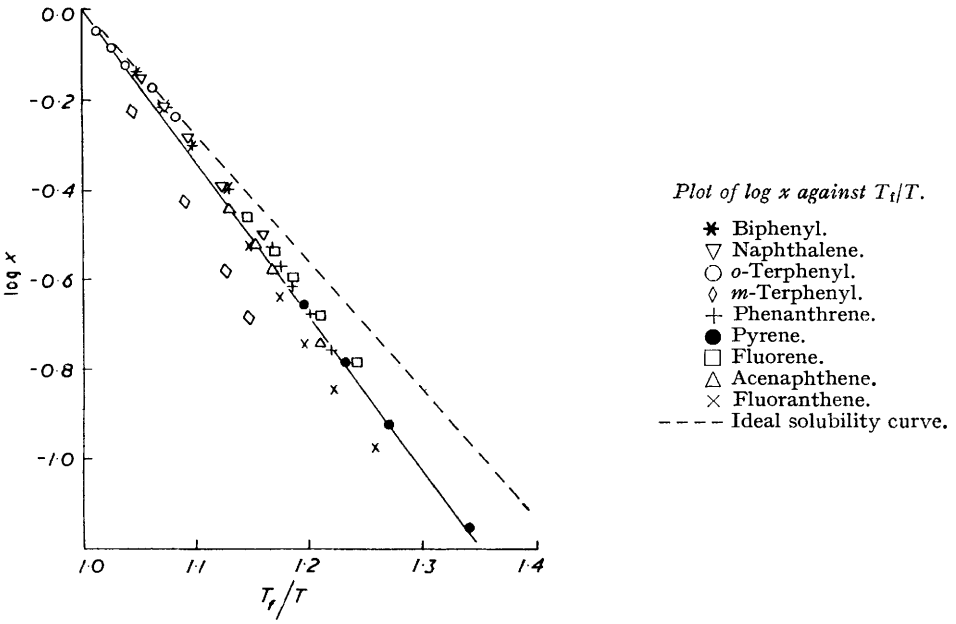
$$\ln a = -\Delta S_f [(T_f/T) - 1]/R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

then the activity is a unique function of the reduced temperature for a series of closely related non-polar molecules in a non-polar solvent. This behaviour arises because in such

[2] Guggenheim, "Mixtures," Oxford Univ. Press, 1952.
[3] Hirschfelder, Curtiss, and Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, 1954, p. 611.

a series the entropies of fusion are all similar, and when $T_f/T \longrightarrow 1$, $\ln a \longrightarrow 0$. In this case the reference temperature for solubility is taken as the melting point of the pure solute. Such an equation has not been tested experimentally owing to lack of sufficient experimental data on entropies of fusion and activity coefficients. If deviations from ideality are small, however, or of the same relative order for each species, then a plot of $\ln x$ against T_f/T would also be expected to be a unique curve for a series of closely related solutes dissolving in a solvent with the same type of force field.

The solubility data of Table 1 are plotted in the Figure as log x against T_f/T and are seen to fall approximately on one curve with a small scatter. The ideal curve, ΔS_f being taken as 13·0 molar entropy units, which is the average value from the known heats of



fusion, is shown as a broken line. The best straight line subject to the condition that it passes through the point (0,1) has been fitted to the experimental results and is given by

$$\log x = -\frac{15{\cdot}9}{2{\cdot}303\boldsymbol{R}}\left[\frac{T_f}{T} - 1\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The corresponding equation for the solubilities in benzene has the factor outside the bracket replaced by $13{\cdot}8/2{\cdot}303\boldsymbol{R}$. Although log solubility is not in general linear in $1/T$, yet deviations from linearity for such systems as are considered here are small, so that use of equations (5) is justified in the first approximation for small temperature ranges. Equations such as (5) can be determined for a series of solvents to enable an estimate of the solubility to be made within about 5%.

This behaviour indicates that, at the same value of reduced temperature T_f/T, the solubilities of these hydrocarbons in carbon tetrachloride are all equal irrespective of their melting points.

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