764. *The Solubility Behaviour of Aromatic Hydrocarbons. Part III.*[1] *Solubilities in Cyclohexane.*

By E. McLaughlin and H. A. Zainal.

The solubilities of biphenyl, *o*-terphenyl, *m*-terphenyl, naphthalene, phenanthrene, pyrene, fluorene, fluoranthene, and acenaphthene in cyclohexane have been determined over a range of temperature. Greater deviations from ideality are exhibited than in benzene and carbon tetrachloride. Where heats of fusion are available the excess properties of the solutions have been calculated. If the solubility data are plotted in the reduced form, log solubility against T_f/T, where T_f is the melting point of the pure solute, all the data lie on a single curve with a scatter greater than that for benzene and carbon tetrachloride solutions.

In previous papers[1,2] the solubility behaviour of two series (linked and fused rings) of aromatic hydrocarbons in benzene and carbon tetrachloride were reported for a range of temperature. The solubilities in benzene were more nearly ideal than those in carbon tetrachloride and, in both cases, deviations from ideality arose principally from energies of mixing rather than from entropies. In addition, when both sets of data were plotted as log mole fraction against T_f/T all the points fell on single curves, indicating that the solubilities are the same at the same reduced temperature.

The present work extends these measurements to cyclohexane, where deviations from ideality are greater still.

Experimental.—Sources of materials and m. p.s of the purified products are: naphthalene 80·1°, phenanthrene 99·2°, and *m*-terphenyl 85·0° (B.D.H.); *o*-terphenyl 53·6° (Eastman Kodak); pyrene 148·0° (Rutgerswerke A.-G.); fluorene 113·5°, fluoranthene 109·8°, biphenyl 68·8°, and acenaphthene 93·8° (Gesellschaft für Teerverwertung). All the compounds were purified by chromatography on alumina, with benzene as eluant except for *o*- and *m*-terphenyl for which

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[1] Part II, McLaughlin and Zainal, *J.*, 1960, 2485.

[2] McLaughlin and Zainal, *J.*, 1959, 863.

light petroleum was used. Solvents were removed by sublimation at 10^{-4} mm., or, where the compounds did not sublime, by prolonged heating *in vacuo* near the m. p.

Apparatus and technique. The method consisted [2] of rotating sealed sample tubes containing fixed mole fractions, mechanically in a thermostat. Solution temperatures were noted to 0·1° on N.P.L. certified thermometers. The measured solubilities are given in Table 1.

TABLE 1. *Solubilities of aromatic hydrocarbons in cyclohexane* [x = *mole fraction* : *temp.* (T) *in* °C].

Biphenyl	T	26·3	37·2	45·1	52·0	58·0
	x	0·2013	0·3497	0·5022	0·6527	0·7814
o-Terphenyl	T	22·8	30·0	40·4	49·6	—
	x	0·3537	0·4996	0·7073	0·8955	—
m-Terphenyl	T	38·2	47·4	52·3	56·7	60·2
	x	0·0770	0·1632	0·2421	0·3331	0·4075
Naphthalene	T	27·0	38·0	45·6	52·2	56·4
	x	0·1541	0·2520	0·3479	0·4576	0·5380
Phenanthrene	T	27·4	40·0	55·6	60·5	67·4
	x	0·0402	0·0785	0·1753	0·2394	0·3747
Pyrene	T	21·8	30·5	43·0	49·1	—
	x	0·0084	0·0129	0·0201	0·0251	—
Fluorene	T	33·0	46·6	58·6	69·0	—
	x	0·0502	0·0910	0·1525	0·2435	—
Acenaphthene	T	35·5	50·0	57·0	60·8	—
	x	0·0880	0·2077	0·2812	0·3453	—
Fluoranthene	T	28·6	44·4	52·3	65·0	71·0
	x	0·0204	0·0400	0·0599	0·1191	0·1763

Discussion.—Deviation from ideal solubility behaviour, as determined by replacing the activity a in the solubility equation

$$\ln\frac{1}{a} = \frac{\Delta H_{\mathrm{f}}}{\mathbf{R}}\left[\frac{1}{T} - \frac{1}{T_{\mathrm{f}}}\right] \qquad . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

by the mole fraction of solute x, progressively increases as the solvent is changed from benzene to carbon tetrachloride to cyclohexane. This is illustrated in Table 2 by the average interchange energies $w/\boldsymbol{k}$ defined [3] by the eqn.

$$f = \exp\left[(1 - x)^2 w/\boldsymbol{k}T\right]$$

where for the present case f is the saturation activity coefficient of the solute. These values have been obtained by using the known heats of fusion ΔH_{f} and neglecting their variation with temperature.

TABLW 2. *Interchange energies* ($w/\boldsymbol{k}$)(°K) *of cyclohexane with aromatic hydrocarbons.*

								Average		
							$-\frac{1}{\boldsymbol{k}}\frac{dw}{dT}$	C_6H_{12}	CCl_4	C_6H_6
Fluorene	T	33·0	46·6	58·6	69·0		2·6	408	133	77
	$w/\boldsymbol{k}$	458	422	391	359					
Acenaphthene	T	35·5	50·0	57·0	60·8		4·8	249	121	136
	$w/\boldsymbol{k}$	427	336	327	306					
Phenanthrene	T	27·4	40·0	55·6	60·5	67·4	4·6	469	165	36
	$w/\boldsymbol{k}$	580	519	457	423	366				
Naphthalene	T	27·0	38·0	45·6	52·2	56·4	2·1	275	93	30
	$w/\boldsymbol{k}$	310	286	273	258	248				
Diphenyl	T	26·3	37·2	45·1	52·0	58·0	3·0	264	66	—
	$w/\boldsymbol{k}$	316	281	257	238	227				

However, while values of $w/\boldsymbol{k}$ are almost temperature-independent for benzene and carbon tetrachloride, Fig. 1 shows that for cyclohexane $w/\boldsymbol{k}$ is linearly dependent on

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[3] Guggenheim, "Mixtures," Oxford University Press, 1952.

temperature with a negative coefficient. This means that in cyclohexane contributions to the excess Gibbs free energy arise from entropy contributions as well as from non-zero heats of mixing. In the event of the solutions being regular at all compositions, the excess entropy of mixing ΔS_e can be calculated from the equation

$$\Delta S_e = -(x)(1 - x)\mathbf{N}\mathbf{k}\, \mathrm{d}w/\mathrm{d}T$$

and the excess heat of mixing from the expression

$$\Delta H_e = x(1 - x)\mathbf{N}\mathbf{k}(w - T\mathrm{d}w/\mathrm{d}T)$$

The maximum values of these functions at $x = 0{\cdot}5$ are in Table 3, where the ΔH_e values are for 50° C. At present, no data from other sources involving direct measurements are available for comparison. The deviations from ideality do not seem to bear any definite relation to the molecular structure of the solute. Phenanthrene, which shows the largest

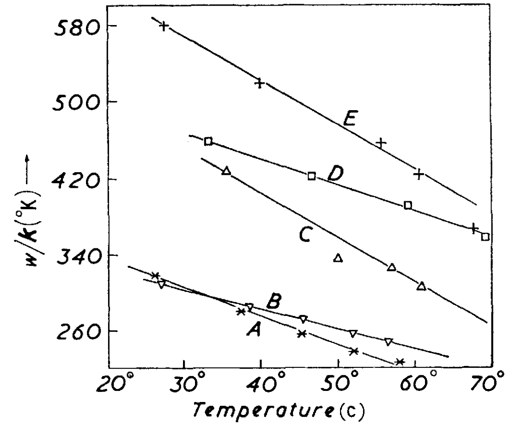

FIG. 1. *Plot of interchange energy $w/\mathbf{k}$ as a function of temp.* (°C).

A, Biphenyl; B, naphthalene; C, acenaphthene; D, fluorene; E, phenanthrene.

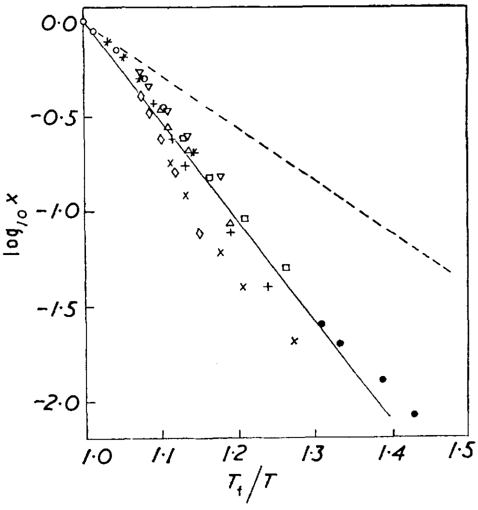

FIG. 2. *Plot of log solubility against T_t/T for aromatic hydrocarbons in cyclohexane.*

* *Biphenyl,* ▽ *naphthalene,* △ *acenaphthene,* □ *fluorene,* + *phenanthrene,* ● *pyrene,* × *fluoranthene,* ○ o-*terphenyl,* ◇ m-*terphenyl.* ---- *Ideal solubility.*

TABLE 3.

	Naphthalene	Biphenyl	Fluorene	Phenanthrene	Acenaphthene
ΔS_e (cal. mole^{-1} deg.$^{-1}$)	1·04	1·49	1·29	2·28	2·39
ΔH_e (cal. mole^{-1})	467	604	622	974	948

deviation of the five molecules for which heat of fusion data are available, exhibits[4] two liquid phases in the binary system with isobutane. For cyclohexane solutions at 27·4°, $w/\boldsymbol{k}T$ is 1·96, which can be compared with the value 2 required for phase separation.

It was shown earlier[1,2] that the ideal solubilities of these series of hydrocarbons all lie on the same curve when log x is plotted against T_f/T. This arises, as can be seen, when the solubility equation (1) is transformed into:

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

because the entropies of fusion for the members of this series are all about 13·0 cal. deg.$^{-1}$ mole^{-1}. This means that ideal solubilities are all the same at the same reduced temperature.

A plot of log a against T_f/T should likewise give a single curve. However, as no independent activity coefficient data are available this has not been tested. For benzene and carbon tetrachloride as solvents, plots of (T/T_f) log a show a smaller scatter compared with the data for cyclohexane given in Fig. 2. The large deviation in the case of cyclohexane may be due to the entropy contribution for each molecule rather than to the non-zero energy of mixing.

As an approximation for estimating the solubility in cyclohexane the data in Fig. 2 have been fitted to the equation

$$\log x = -\frac{24{\cdot}3}{2{\cdot}303\boldsymbol{R}}\left[\frac{T_f}{T}-1\right]$$

by the method of least squares, which enables the solubility to be estimated within about 20%, on an average, for any of the molecules, from its melting point alone.

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[4] Roof and Crawford, *J. Phys. Chem.*, 1958, **62**, 1138.