

# HANDBOOK OF ENVIRONMENTAL DATA ON ORGANIC CHEMICALS

SECOND EDITION

Karel Verschueren

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**C. WATER POLLUTION FACTORS** Analogous to the previous category, the following data are listed: biodegradation rate and mechanisms; oxidation parameters, such as BOD, COD,  $\text{KMnO}_4$  value, TOC, ThOD; impact on treatment processes and on the BOD test; reduction of amenities through taste, odor, and color of the water or aquatic organisms; the quality of surface water and underground water and sediment; natural sources, manmade sources, waste water treatment methods and results; methods of sampling and analysis.

**D. BIOLOGICAL EFFECTS** Residual concentrations, bioaccumulation values and toxicological effects of exposing the products to: ecosystems, bacteria, plants, algae, protozoans, worms, molluscs, insects, crustaceans, fishes, amphibians, birds, mammals and man.

The "explanatory notes" give a more detailed description of the compiled data, explanations of the definitions and abbreviations used throughout the book, and indicates how the data can be used to prevent or reduce environmental pollution.

### III ARRANGEMENT OF CHEMICALS

The chemicals are listed in strict alphabetical order; those comprised of two or more words are alphabetized as if they were a single word. The many prefixes used in organic chemistry and disregarded in alphabetizing since they are not considered an integral part of the name; these include *ortho-*, *meta-*, *para-*, *alpha-*, *beta-*, *gamma-*, *sec.*, *tert.*, *sym-*, *as-*, *uns-*, *cis-*, *trans-*, *d-*, *l-*, *dl-*, *n-*, *N-*, as well as all numerals denoting structure. However, there are certain prefixes that are an integral part of the names (*iso-*, *di-*, *tri-*, *tetra-*, *cyclo-*, *bio-*, *neo-*, *pseudo-*), and in these cases the name is placed in its normal alphabetical position, e.g., dimethylamine under D and isobutane under I.

### IV EXPLANATORY NOTES

The reader should consult the appropriate sections of this chapter if he is not acquainted with the definitions and abbreviations used throughout the book. The data are given in the following sequence (each item will be discussed in detail):

#### A. PROPERTIES

1. formula
2. physical appearance
3. molecular weight (m.w.)
4. melting point (m.p.)
5. boiling point (b.p.)
6. vapor pressure (v.p.)
7. vapor density (v.d.)
8. saturation concentration (sat. conc.)
9. solubility (solub.)
10. specific gravity (sp. gr.)
11. logarithm of the octanol/water distribution coefficient ( $\log P_{\text{Oct}}$ )

**B. AIR POLLUTION FACTORS**

12. conversion factors
13. odor
14. atmospheric reactions
15. natural sources
16. manmade sources
17. control methods
18. sampling and analysis

**C. WATER POLLUTION FACTORS**

19. biodegradation
20. oxidation parameters
21. impact on biodegradation processes
22. odor and taste thresholds
23. water and sediment quality
24. natural sources
25. manmade sources
26. waste water treatment
27. sampling and analysis

**D. BIOLOGICAL EFFECTS**

- residual concentrations
  - bioaccumulation values
  - toxicological effects
28. ecosystems
  29. bacteria
  30. algae
  31. plants
  32. protozoans
  33. worms
  34. molluscs
  35. insects
  36. crustaceans
  37. fishes
  38. amphibians
  39. birds
  40. mammals
  41. man

**A. PROPERTIES**

Only the most relevant chemical and physical properties are given. Flash points, flammability limits, autoignition temperature etc. have been omitted because they are not of direct concern to the environmentalist. These and other dangerous properties of chemicals can be found in "*Dangerous Properties of Industrial Materials*" by I. Sax.

Chemicals are never 100% pure, but the nature and quantity of the impurities can have a significant impact on most environmental qualities. The following parameters are very sensitive to the presence of impurities:

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water solubility  
odor characteristic and threshold values  
BOD  
toxicity

The following data illustrate this point (from Shell's Chemical Guide):

product: *diethylene glycol*  
 $\text{O}(\text{CH}_2\text{CH}_2\text{OH})_2$

(Shell)

	"normal grade"	"special grade"
distillation range:	240–255°C	242–250°C
acidity (as $\text{CH}_3\text{COOH}$ ):	max. 0.2 wt%	max. 0.002 wt%
ash content:	max. 0.05 wt%	max. 0.002 wt%
BOD <sub>5</sub> :	0.12	0.05
COD:	1.49	1.51
goldfish LD <sub>50</sub> (24 hr):	5000 mg/l	5000 mg/l

product: *ethyleneglycol*  
 $\text{HOCH}_2-\text{CH}_2\text{OH}$

	"normal grade"	"special grade"
distillation range:	194–205°C	max. 2°C, incl. 197.6°C
ash content:	max. 0.002 wt%	max. 0.001 wt%
BOD <sub>5</sub> :	0.47	0.15
BOD <sub>5</sub> after adaptation:	0.81	0.67
COD:	1.24	1.29
goldfish LD <sub>50</sub> (24 hr):	5000 mg/l	5000 mg/l

When no data are available, the distillation range can give a first indication on the presence of impurities. Therefore, in this work, whenever a distillation range (boiling range) is given, the environmental data should be interpreted carefully.

product: *triethanolamine*  
 $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$

	"normal grade"	"85%"
triethanolamine content	min. 80 wt%	min. 85 wt%
BOD <sub>5</sub>	0.02	0.03
BOD <sub>5</sub> after adaptation	0.17	0.90
COD	1.50	1.50

After adaptation of the culture, the "85%" grade is much more biodegradable than the less pure "commercial" grade.

**1. Boiling Points.** The boiling points of the members of a given homologous series increase with increasing molecular weight. The boiling points rise in a uniform manner as shown in Figs. 1 and 2.

If a hydrogen atom of one of the paraffin hydrocarbons is replaced by another atom or a group, an elevation of the boiling point results. Thus alkyl halides, alcohols,

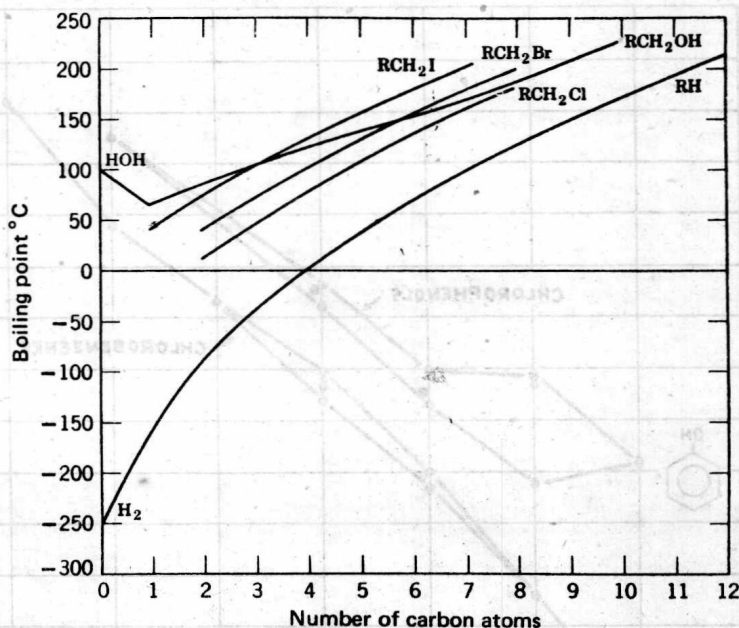


Fig. 1. Relationship of boiling points and molecular weight.

aldehydes, ketones, acids, etc., boil at higher temperatures than the hydrocarbons with the same carbon skeleton.

If the group introduced is of such a nature that it promotes association, a very marked rise in boiling point occurs. This effect is especially pronounced in the alcohols and acids, since hydrogen bonding can occur.

**2. Vapor Pressure.** The vapor pressure of a liquid or solid is the pressure of the gas in equilibrium with the liquid or solid at a given temperature. Volatilization, the evaporative loss of a chemical, depends upon the vapor pressure of the chemical and on environmental conditions which influence diffusion from the evaporative surface. Volatilization is an important source of material for airborne transport and may lead to the distribution of a chemical over wide areas and into bodies of water (e.g., in rainfall) far from the site of release. Vapor pressure values provide indications of the tendency of pure substances to vaporize in an unperturbed situation, and thus provide a method for ranking the relative volatilities of chemicals. Vapor pressure data combined with solubility data permit calculations of rates of evaporation of dissolved organics from water using Henry's Law constants, as discussed by MacKay and Leinonen (1943) and Dilling (1944).

Chemicals with relatively low vapor pressures, high adsorptivity onto solids, or high solubility in water are less likely to vaporize and become airborne than chemicals with high vapor pressures or with less affinity for solution in water or adsorption to solids and sediments. In addition, chemicals that are likely to be gases at ambient temperatures and which have low water solubility and low adsorptive tendencies are less



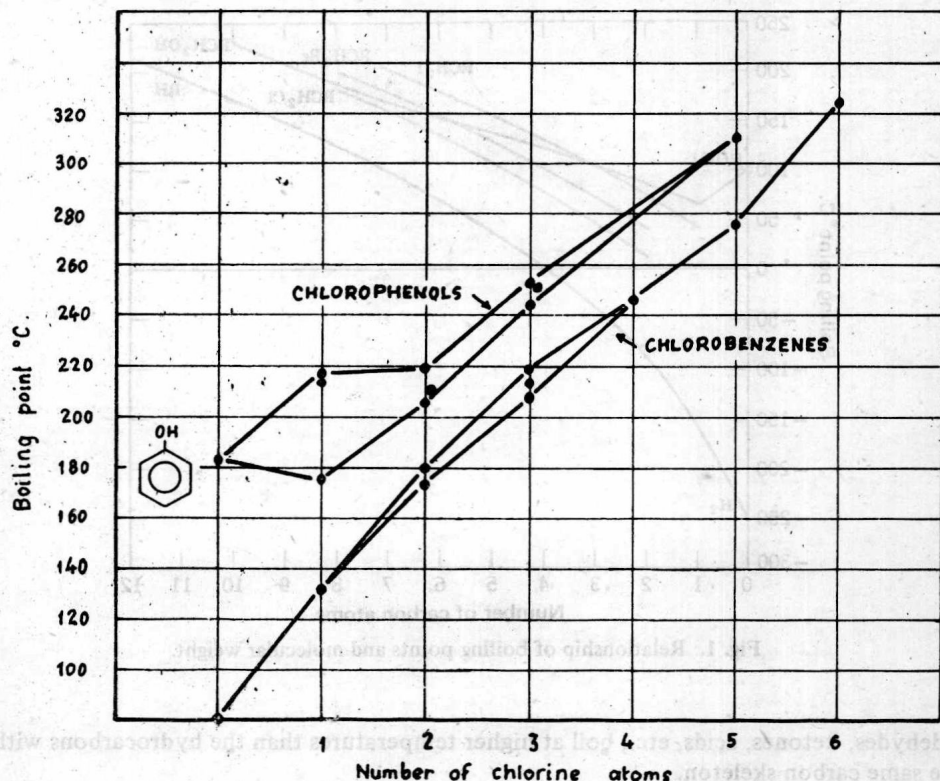


Fig. 2. Relationship of boiling points and molecular weights for chlorinated benzenes and phenols.

likely to transport and persist in soils and water. Such chemicals are less likely to biodegrade or hydrolyze, but are prime candidates for photolysis and for involvement in adverse atmospheric effects (e.g., smog formation, or stratospheric alterations). On the other hand, nonvolatile chemicals are less frequently involved in significant atmospheric transport, so concerns regarding them should focus on soils and water.

Vapor pressures are expressed either in mm Hg (abbreviated mm) or in atmospheres (atm.)

If vapor pressure data for certain compounds are not available, they can be derived graphically from their boiling points and the boiling point/vapor pressure relationship for homologous series. An example is shown in Fig. 3.

**3. Vapor Density.** The density of a gas indicates whether it will be transported along the ground, possibly subjecting surrounding populations to high exposure, or whether it will disperse rapidly.

The concentration term *vapor density* is often used in discussion of vapor phase systems. Vapor density is related to equilibrium vapor pressure through the equation of state for a gas:

$$PV = nRT$$



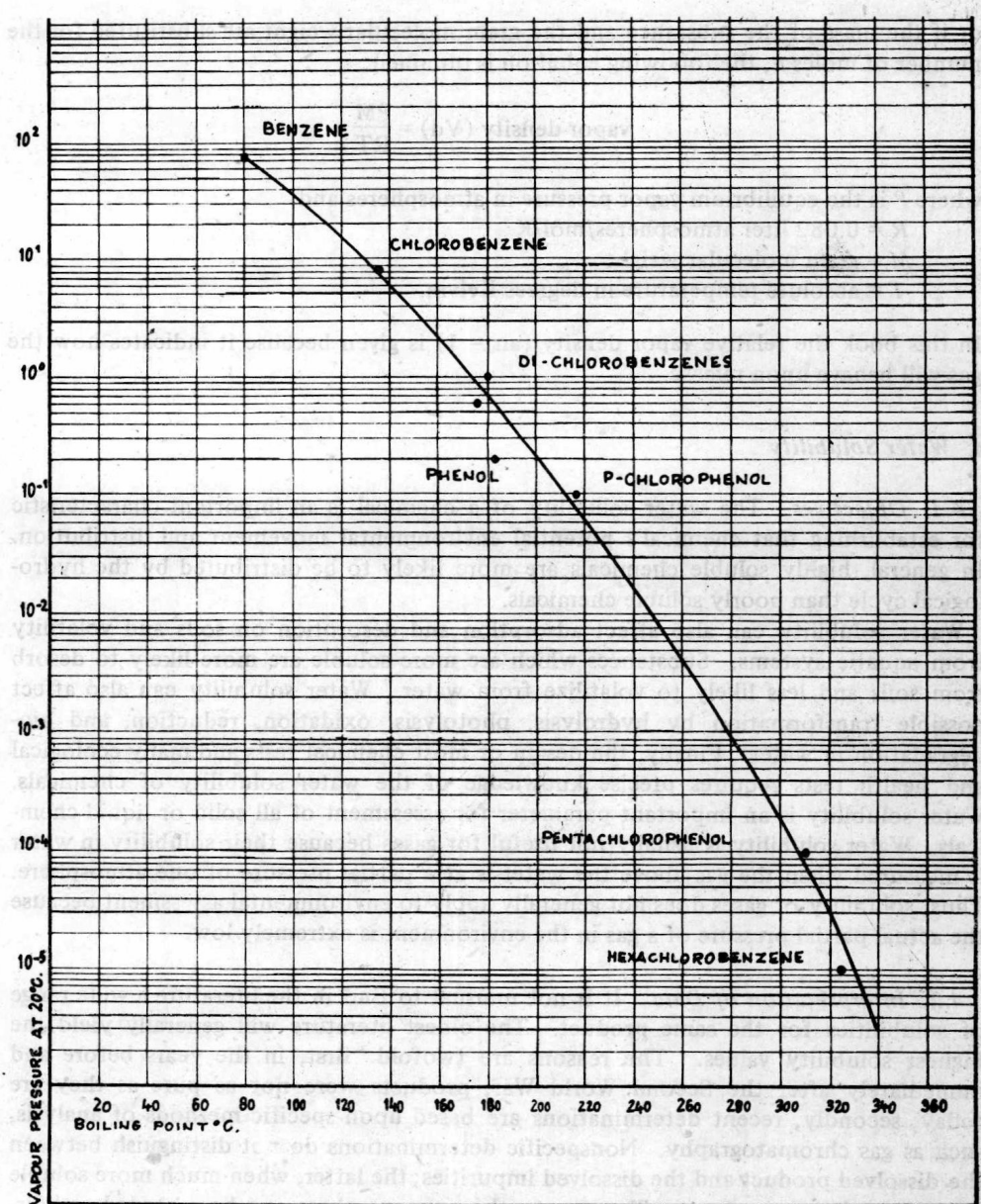


Fig. 3. Relation between boiling point and vapor pressure for homologous series of chlorinated benzenes and phenols.

or if the mass of the substance and the gram molecular weight are substituted for the number of moles  $n$ , the following equation is obtained:

$$\text{vapor density (Vd)} = \frac{PM}{RT}$$

where  $P$  is the equilibrium vapor pressure in atmospheres and

$R = 0.082$  liter atmospheres/mol/K

$M$  = gram molecular weight

$T$  = absolute temperature in degrees Kelvin.

In this book the relative vapor density (air = 1) is given because it indicates how the gas will behave upon release.

#### 4. Water Solubility

**4.1. Objectives.** The water solubility of a chemical is an important characteristic for establishing that chemical's potential environmental movement and distribution. In general, highly soluble chemicals are more likely to be distributed by the hydrological cycle than poorly soluble chemicals.

Water solubility can also affect adsorption and desorption on soils and volatility from aquatic systems. Substances which are more soluble are more likely to desorb from soils and less likely to volatilize from water. Water solubility can also affect possible transformation by hydrolysis, photolysis, oxidation, reduction, and biodegradation in water. Finally, the design of most chemical tests and many ecological and health tests requires precise knowledge of the water solubility of chemicals. Water solubility is an important parameter for assessment of all solid or liquid chemicals. Water solubility is usually not useful for gases because their solubility in water is measured when the gas above the water is at a partial pressure of one atmosphere. Thus, solubility of gases does not generally apply to environmental assessment because the actual partial pressure of a gas in the environment is extremely low.

**4.2. Interpretation of Data.** It is not unusual to find in the literature a wide range of solubilities for the same product. The oldest literature will generally yield the highest solubility values. The reasons are twofold: first, in the years before and immediately after the Second World War, products were not as pure as they are today; secondly, recent determinations are based upon specific methods of analysis, such as gas chromatography. Nonspecific determinations do not distinguish between the dissolved product and the dissolved impurities; the latter, when much more soluble than the original product, will move to the aqueous phase and be recorded as "dissolved product". Nonspecific methods include turbidity measurement and TOD.

The measurement of aqueous solubility does not usually impose excessive demands on chemical techniques, but the measurement of the solubility of very sparingly soluble compounds requires specialized procedures. This problem is well illustrated by the variability in the values quoted in the literature for products such as DDT and PCBs. This situation happens to be of some consequence, in that many of those compounds that are known to be significant environmental contaminants, such as DDT and PCBs, are those that have very low water solubilities.

**4.3. Influence of the Composition of Natural Waters.** The composition of natural waters can vary greatly. Environmental variables such as pH, water hardness, cations, anions, naturally occurring organic substances (e.g., humic and fulvic acids, hemicelluloses) and organic pollutants all affect the solubility of chemicals in water. Some bodies of water contain enough organic and inorganic impurities to significantly alter the solubility of poorly soluble chemicals.

The solubility of lower *n*-paraffins in salt water compared with fresh, distilled water is higher by about one order of magnitude, this difference decreasing with and increase in the molecular weight of the hydrocarbon. The increased solubility in seawater is due to simultaneous physical and chemical factors. The solubility of several higher *n*-paraffins ( $C_{10}$  and higher) has been determined in both distilled water and seawater. In all cases, the paraffins were less soluble in seawater than in distilled water. The magnitude of the salting out effect increases with increasing molar volume of the paraffins in accordance with the McDevit-Long theory. This theory of salt effects attributes salting in or salting out to the effect of electrolytes on the structure of water. Since the data in the literature indicate that the lower paraffins (below  $C_{10}$ ) are more soluble, and that the higher *n*-paraffins ( $C_{10}$  and higher) are less soluble in seawater than in distilled water, it is possible to speculate upon the geochemical fate of dissolved normal paraffins entering the ocean from rivers. If fresh water is saturated or near saturated with respect to normal paraffins (e.g., because of pollution), salting out of the higher paraffins will occur in the estuary. The salted out molecules might either adsorb on suspended minerals and on particulate organic matter or rise to the surface as slicks. In either case, they will follow a different biochemical pathway than if they had been dissolved. The salting out of dissolved organic molecules in estuaries applies not only to *n*-paraffins, but to all natural or pollutant organic molecules whose solubilities are decreased by addition of electrolytes. Thus, it is possible that regardless of the levels of dissolved organic pollutants in river water, only given amounts will enter the ocean in dissolved form owing to salting out effects of estuaries. Estuaries may act to limit the amount of dissolved organic carbon entering the ocean, but may increase the amount of particulate organic carbon entering the marine environment.

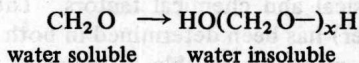
**4.4. Molecular Structure-Solubility Relationship.** Since water is a polar compound it is a poor solvent for hydrocarbons. Olefinic and acetylenic linkages or benzenoid structures do not affect the polarity greatly. Hence, unsaturated or aromatic hydrocarbons are not very different from paraffins in their water solubility. The introduction of halogen atoms does not alter the polarity appreciably. It does increase the molecular weight, and for this reason the water solubility always falls off. On the other hand, salts are extremely polar. Other compounds lie between these two extremes. Here are found the alcohols, esters, ethers, acids, amines, nitriles, amides, ketones and aldehydes—to mention a few of the classes of frequent occurrence.

As might be expected, acids and amines generally are more soluble than neutral compounds. The amines probably owe their abnormally high solubility to their tendency to form hydrogen-bonded complexes with water molecules. This theory is in harmony with the fact that the solubility of amines diminishes as the basicity decreases. It also explains the observation that many tertiary amines are more soluble in cold than in hot water. Apparently at lower temperatures the solubility of the hydrate is involved, whereas at higher temperatures the hydrate is unstable and the solubility measured is that of the free amine.

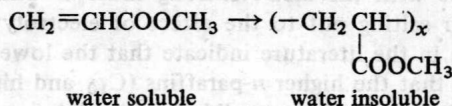


Monofunctional ethers, esters, ketones, aldehydes, alcohols, nitriles, amides, acids, and amines may be considered together with respect to water solubility. As a homologous series is ascended, the hydrocarbon (nonpolar) part of the molecule continually increases while the polar function remains essentially unchanged. There follows, then, a trend toward a decrease in the solubility in polar solvents such as water.

In general an increase in molecular weight leads to an increase in intermolecular forces in a solid. Polymers and other compounds of high molecular weight generally exhibit low solubilities in water and ether. Thus formaldehyde is readily soluble in water, whereas paraformaldehyde is insoluble:



Methyl acrylate is soluble in water, but its polymer is insoluble:



Glucose is soluble in water, but its polymers—starch, glycogen, and cellulose—are insoluble. Many amino acids are soluble in water, but their condensation polymers, the proteins, are insoluble.

Lindenberg (1803) proposed a relationship between the logarithm of the solubility of hydrocarbons in water and the molar volume of the hydrocarbons. If the logarithm of the solubilities of the hydrocarbons in water is plotted against the molar volume of the hydrocarbons, a straight line is obtained. This relationship has been worked out further by C. McAuliffe, and solubilities as a function of their molar volumes for a number of homologous series of hydrocarbons have been presented graphically (242).

From the given correlation between molecular structure and solubility the following conclusions may be drawn:

*Branching* increases water solubility for paraffin, olefin and acetylene hydrocarbons, but not for cycloparaffins, cyclo-olefins, and aromatic hydrocarbons.

For a given carbon number, *ring formation* increases water solubility.

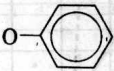

*Double bond* addition to the molecule, ring or chain increases water solubility. The addition of a second and third double bond to a hydrocarbon of given carbon number proportionately increases water solubility (Table 2).

*A triple bond* in a chain molecule increases water solubility to a greater extent than two double bonds.

Cary T. Chiou et al. (382) found a good correlation between solubilities of organic compounds and their octanol/water partition coefficient. Furthermore functional groups such as chlorine atoms, methyl groups, hydroxyl groups, benzene rings, etc. showed additive effects on the logarithm of the octanol/water partition coefficient ( $\log P_{\text{oct}}$ ) of the parent molecule.

This allowed the calculation of  $\log P_{\text{oct}}$  values for many organic compounds based on the  $\log P_{\text{oct}}$  value for the parent compound and the additive effects of the functional groups. Because of the correlation between solubilities of organic compounds

TABLE 1. Influence of Functional Groups on Solubility of benzene derivatives.

Functional group		$S_{\text{mg/l}}$ solubility mg/l (temp. °C)	$\log S_{\text{mg/l}}$	$\Delta \log S_{\text{mg/l}}$ $\log S_{\text{C}_6\text{H}_5\text{X}} - \log S_{\text{C}_6\text{H}_6}$
aniline	-NH <sub>2</sub>	34,000 (20°)	4.53	1.28
phenol	-OH	82,000 (15°)	4.91	1.66
benzaldehyde	-COH	3,300	3.52	0.27
benzoic acid	-COOH	2,900	3.46	0.21
nitrobenzene	-NO <sub>2</sub>	1,900	3.28	0.03
benzene	-	1,780	3.25	0.00
fluorobenzene	-F	1,540 (30°)	3.19	-0.06
thiophenol	-SH	470 (15°)	2.67	-0.58
toluene	-CH <sub>3</sub>	515	2.71	-0.54
chlorobenzene	-Cl	448 (30°)	2.65	-0.60
bromobenzene	-Br	446 (30°)	2.65	-0.60
iodobenzene	-I	340 (30°)	2.53	-0.72
diphenylether		21 (25°)	1.32	-1.93
diphenyl		7.5 (25°)	0.88	-2.37

and  $\log P_{\text{Oct}}$ , it is not surprising to find the same additive effects of functional groups on their water solubility. Table 1 shows this influence of functional groups on the solubility of benzene derivatives. Solubilities of homologous series of organic compounds are plotted in Figs. 4 to 9.

\* Effects which cannot be taken into account by this additive-constitutive character of the solubility are:

- steric effects which cause shielding of an active function
- intra- and intermolecular hydrogen bonding (see trihydroxyphenols)
- branching
- inductive effects of one substituent on another
- conformational effects, e.g., "balling up" of an aliphatic chain.

TABLE 2. Influence of Double Bonds on Aqueous Solubility of Cyclic Hydrocarbons (at room temperature) (242).

Hydrocarbon	Solubility mg/l
cyclohexane	55
cyclohexene	213
1,4-cyclohexadiene	700
benzene	1,780

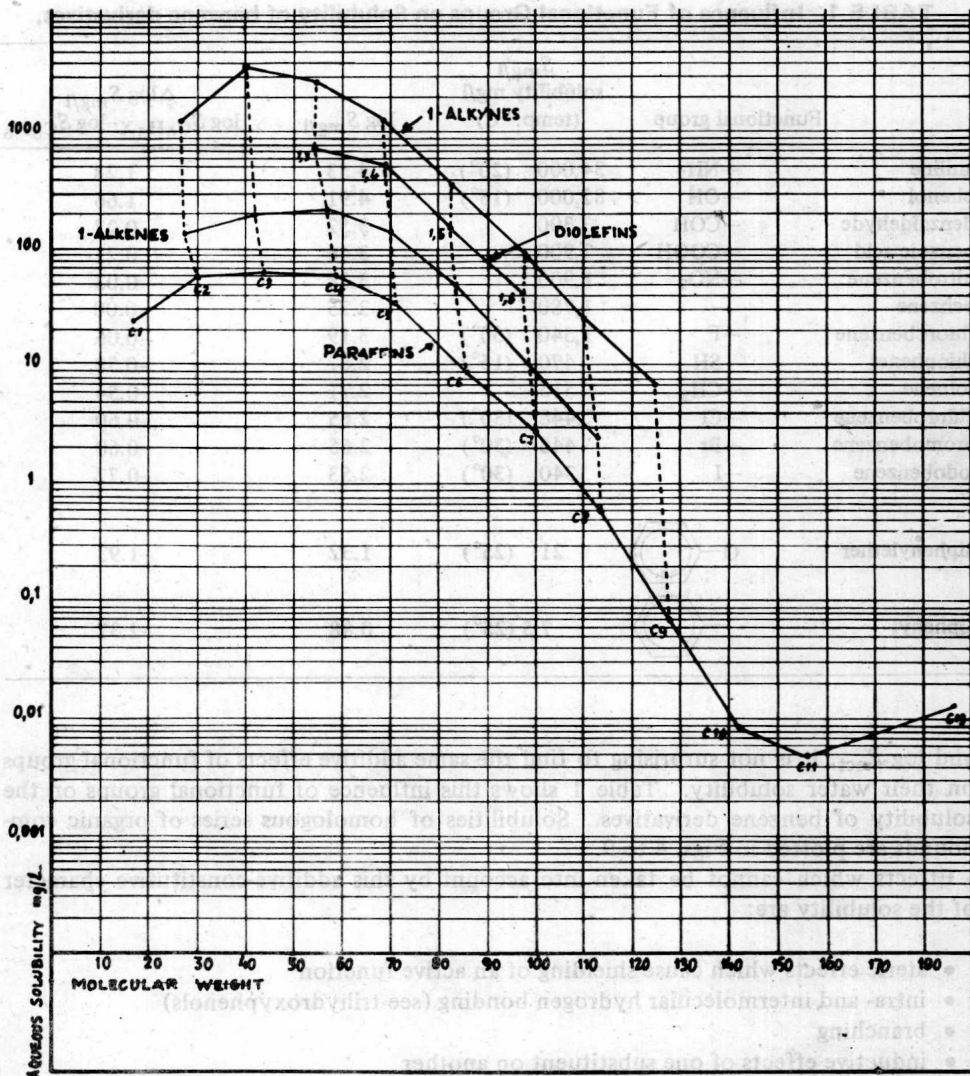


Fig. 4. Relationship between aqueous solubility and molecular weight for saturated and unsaturated straight-chain hydrocarbons.

**4.5 Solubility of Mixtures.** Mixtures of compounds, whether they are natural such as oil or formulations such as many pesticides, behave differently from the single compounds when brought into contact with water. Indeed each component of the mixture will partition between the aqueous phase and the mixture.

Components with a high aqueous solubility will tend to move toward the aqueous phase while the "unsoluble" components will remain in the other phase. From this follows that the fractional composition of the "water soluble fraction" (WSF) will



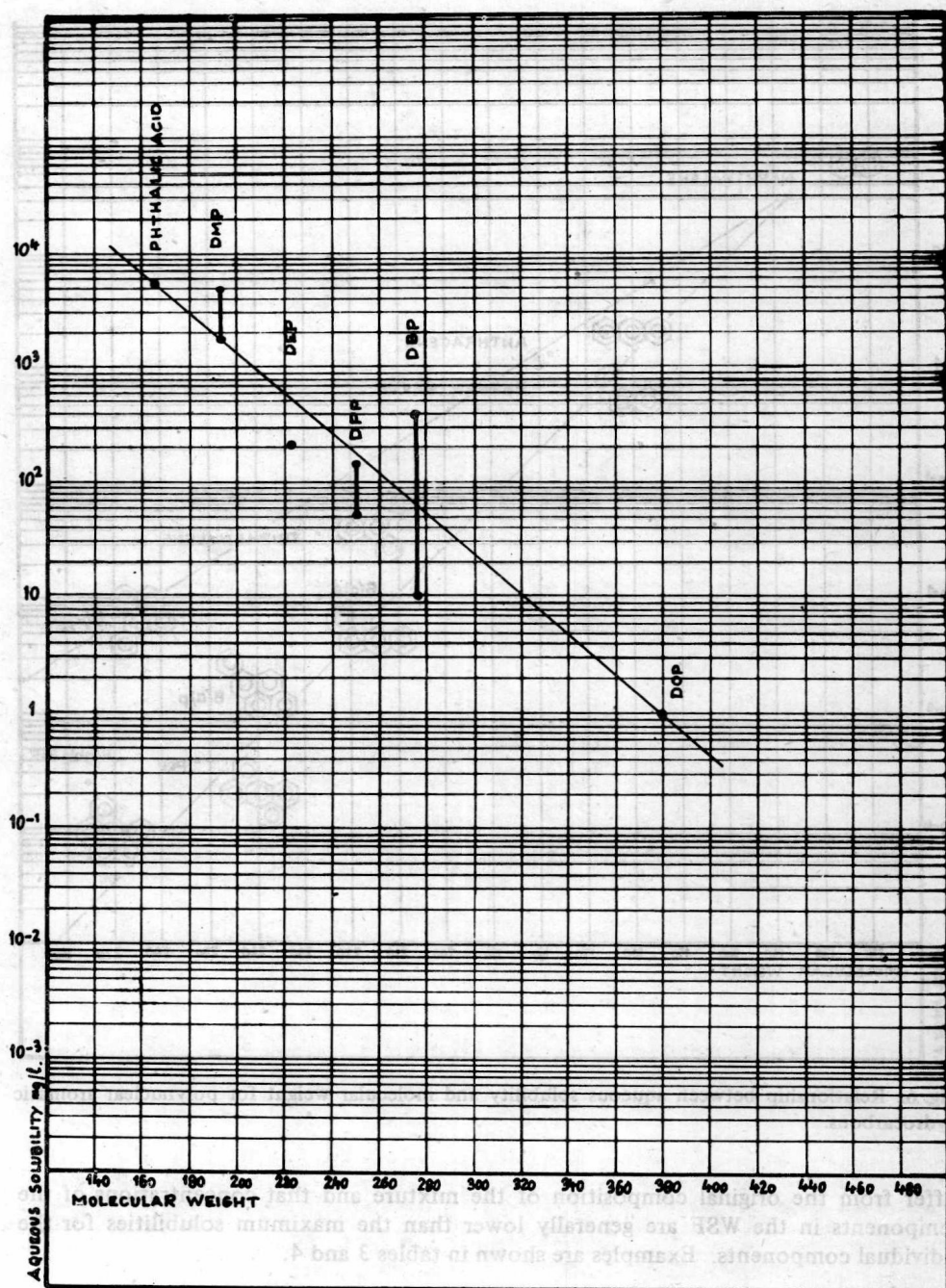


Fig. 5. Relationship between aqueous solubility and molecular weight for phthalic acid and phthalates.