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Distribution Coefficients at High Dilution for Organic Solutes Between Water and Isobutane or Isobutylene

To facilitate design of an extraction process for removal of organic solutes from petroleum and petrochemical waste streams, distribution-coefficient data were obtained for typical organic pollutants at high dilution. Volatile solvents were chosen because of their low solubility in water and because they are recovered easily. Samples from both the aqueous and the organic phase were analyzed chromatographically. To remove a sample from an equilibrium cell operating at pressures well above atmospheric, a special technique was developed using low-melting Indalloy for microencapsulation.

Distribution coefficients at ambient temperature are given for a variety of solutes, including esters, phenolics, ketones, and aldehydes. The results are correlated by a simple relation based on a perturbed-hard-sphere theory for dilute solutions. Isobutane or isobutylene may be particularly useful in a dual-solvent extraction process wherein a polar organic solvent is used to remove phenolics from water and the volatile C_4 hydrocarbon is used in a secondary extraction to remove the polar solvent from water.

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SCOPE

Extraction of organic solutes from industrial wastewaters provides one possible method for water-pollution abatement and for recovery of solutes having economic value. While extraction processes using conventional organic solvents have often been described, little attention has been given to the use of low-molecular weight hydrocarbon solvents for extraction from aqueous solutions. While an extraction process using volatile solvents must operate at elevated pressure, these solvents offer two important advantages: their solubility in water is extremely low and solvent recovery is simple.

While volatile hydrocarbons may, in some cases, efficiently remove organic pollutants from industrial wastewaters, their maximum utility may be in a dual-solvent extraction process applicable to aqueous waste streams containing phenolics and similar hard-to-remove organic pollutants. In such a process, the primary extraction uses a polar organic solvent of low volatility which effectively

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removes the organic pollutant but which, unfortunately, dissolves to an appreciable extent in water. A volatile hydrocarbon can then be used efficiently in a second extraction step to remove the polar organic solvent from water.

This work describes experimental studies and a simple correlation for establishing distribution-coefficient data as required for rational design of extraction processes wherein isobutane or isobutylene is used as the volatile solvent.

SIGNIFICANCE AND CONCLUSIONS

A new experimental technique was developed for sampling and subsequent chemical analysis of a volatile liquid organic mixture. Distribution coefficients were obtained for a variety of solutes commonly found as pollutants in industrial wastewaters.

Distribution coefficients of organic solutes between water and isobutylene are well above unity for solutes which do not strongly hydrogen-bond to water and for solutes of relatively large molecular weight. Distribution coefficients in isobutylene tend to be higher than those in isobutane because of preferential interaction between the double bond of isobutylene and the polar functional group of the solute. These distribution coefficients are correlated by linear plots on semi-logarithmic coordinates where the independent variable is a characteristic volume of the solute raised to the 0.7 power.

Isobutane and isobutylene are excellent solvents for common polar organic solvents such as methyl isobutyl ketone and butyl acetate. Volatile C_4 hydrocarbons, therefore, may be particularly useful as secondary solvents in a dual-solvent extraction process where a polar organic solvent is used as a primary solvent.

Aqueous waste streams from petroleum or petrochemical processing units may contain soluble organic pollutants in a concentration range between 0.1 and 5 wt. %. For such streams it is frequently advantageous to remove a large fraction of the pollutants by extraction, prior to biological treatment; such removal is particularly desirable if the organic solute has economic value and merits recovery.

This work presents distribution coefficients for a variety of organic solutes between water and isobutane or isobutylene. These solvents were chosen because of their volatility (at ambient temperature their vapor pressures are about 3 atm.) which facilitates solvent recovery. A volatile solvent is particularly useful in a dual-solvent process where a heavier, relatively soluble, polar organic solvent is used in a primary extraction to remove pollutants that have only limited solubility in the volatile solvent. In a secondary extraction the soluble heavy solvent is removed from water by dissolution in the volatile solvent (Earhart, 1974; Won, 1974). For example, in a well-known commercial process, butyl acetate serves as an excellent solvent for extracting phenol, but since butyl acetate dissolves in water to an appreciable extent, it is necessary subsequently to remove the butyl acetate. Extraction with isobutane or isobutylene performs this removal efficiently (Earhart, 1974; Earhart et al., 1974a, b). Figure 1 shows a flow sheet for a dual-solvent process.

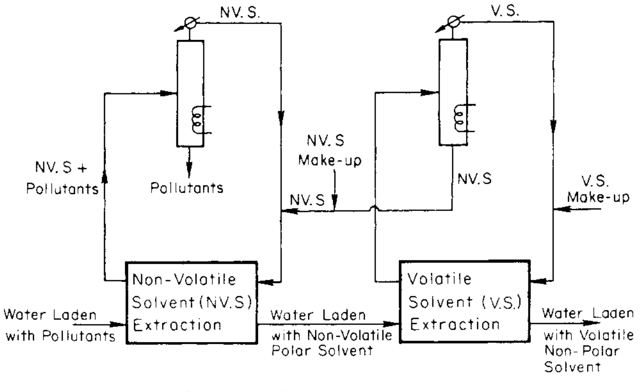

Fig. 1. Dual-solvent extraction.

EXPERIMENT

Because of the solvent's volatility, it is not possible to use standard apparatus to measure distribution coefficients. A special sampling device was constructed to facilitate sampling of the volatile liquid mixture at pressures ranging from 3 to 10 atmospheres.

Apparatus

The equilibrium cell, shown in Figure 2, is a cylindrical, stainless-steel container about 30 cm long and with a 12-cm outside diameter. The inside diameter is about 8 cm and the inside depth is 25 cm. Above the top plate is a rotating holding magnet driven by a variable-speed motor. A stirrer rotating inside the equilibrium cell is magnetically coupled to the variable-speed motor. To allow visual observation of the immiscible mixtures under pressure, two Jerguson sight gauges are bolted to the two opposite sides of the cylinder. The equilibrium cell is completely immersed in a constant-temperature water bath held at 25±0.05°C. A periscope is positioned outside the front sight gauge and a light source is located in the rear. Sampling devices are attached to the side and to the top plate, which also contains a high-pressure, sample-injection port. The pressure is measured by a Heise gauge and the temperature in the cell is measured by a liquid-filled glass thermometer with a 0.1°C graduation. Liquefied gas is introduced from an inverted cylinder into the equilibrium cell driven by its own vapor pressure augmented by helium gas at about 1 or 2 atm. All connections are 3.18-mm and 6.35-mm stainless steel tubing. Ball valves are from Whitey Research Company. Chemical analysis of both aqueous-phase and organic-phase samples is achieved with a Perkin-Elmer 990 Gas Chromatograph.

Procedure

To start, about 1 liter of distilled water is introduced into the equilibrium cell. Organic solute is introduced with a syringe through a rubber septum located at the top of the cell. Liquefied isobutane (or isobutylene) is then introduced from an inverted gas cylinder.

Equilibration between the two phases is obtained by a stirring rod with five propellers, two in each liquid phase and one at the liquid-liquid interface. The two liquid phases are stirred for about ten hours and one hour of settling (no stirring) is allowed before sampling.

Sampling

The aqueous sample is removed at the bottom of the equilibrium cell. After purging twice, a 50-cm^3 sample is removed from the equilibrium cell. From this large sample, six samples, 5 microliters each, are introduced in the chromatograph for chemical analysis. Reproducibility of this analysis is better than 2%.

Because of the high vapor pressure, it is much more difficult to obtain a sample of the organic phase for chemical analysis. Figure 3 shows the special technique devised for sampling of a volatile liquid; this technique is based on the special properties of Indalloy, as suggested by Fleck (1967), based on the work of Nerheim (1964). Initially the flash chamber and the sight gauge are filled with solvent vapor and helium gas. After opening the microcapillary sample valve, the pressure in the flash chamber is reduced by opening the 3-way ball valve to the atmosphere. Liquid is allowed to flow into and through the Indalloy capillary sample tube until it fills the Pyrex-tube sight gage.

The Indalloy capillary sample tube is swaged at both ends and removed. This capillary tube, 12 cm long, with a 1.52-mm outer diameter and 0.254-mm internal diameter, is then swaged at intermediate points so as to provide six encapsulated samples, each about 1.5 cm long, with a volume of approximately 0.5 microliter.

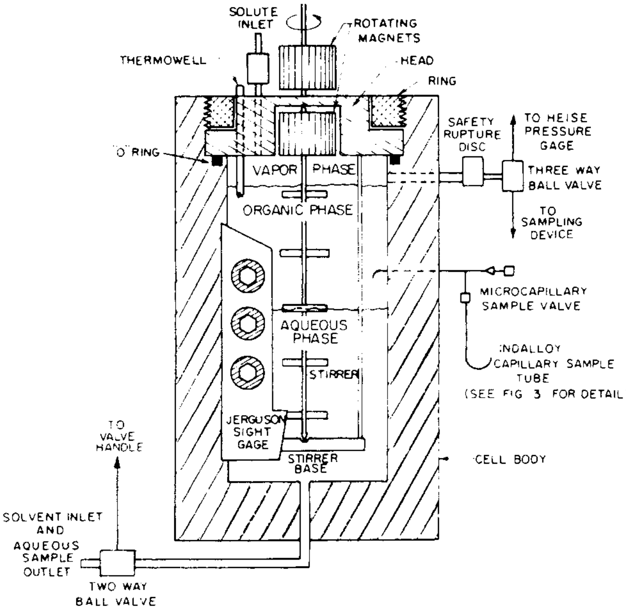

Fig. 2. Equilibrium cell assembly.

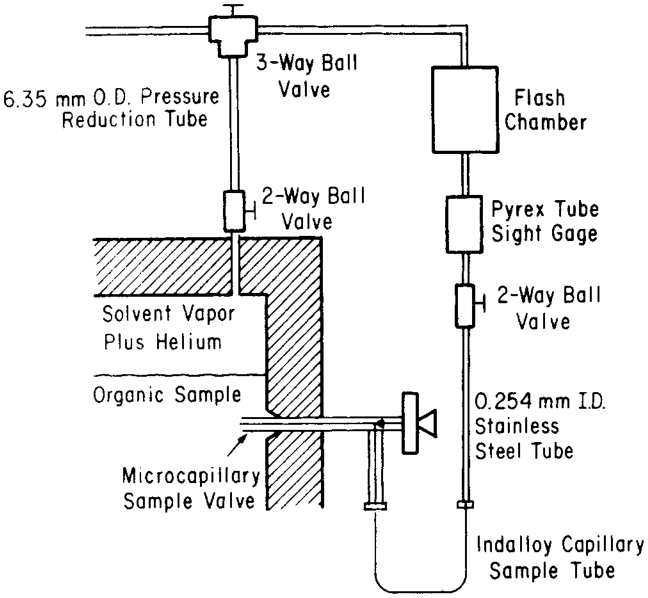

Fig 3. Indalloy encapsulation sampling device.

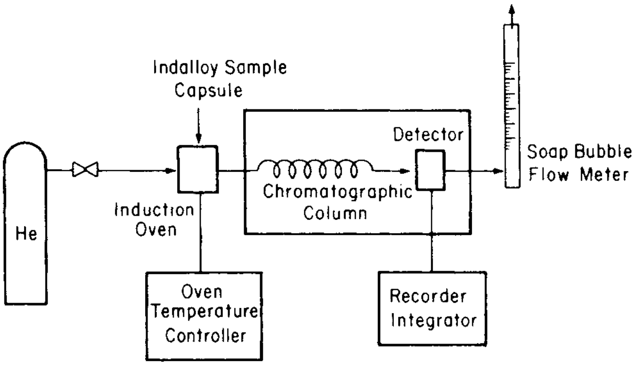

Fig. 4a. Chemical analysis instrumentation. Gas chromatograph and induction oven.

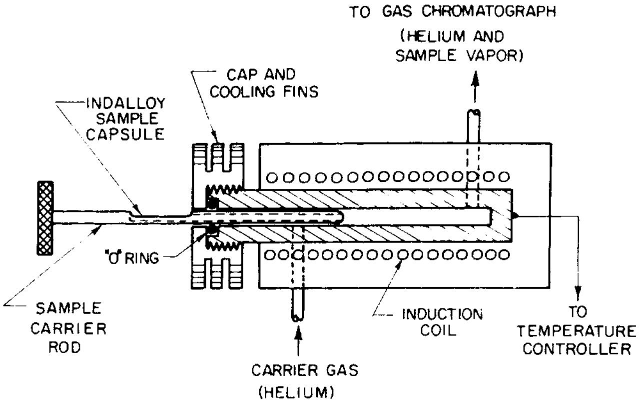

Fig. 4b. Induction oven for melting of sample capsule.

One at a time, each sample is placed into the induction oven as shown in Figures 4a and 4b. The oven [Varian Aerograph Model 695], operating at 250°C, melts the Indalloy (melting point 150°C) and completely vaporizes the sample. Helium gas sweeps the vaporized sample into the chromatograph. Reproducibility is better than 5%. Further details of this analytical procedure are presented elsewhere (Won, 1974).

Chemical Analysis

The chromatograph uses two hydrogen-flame-ionization detectors and has linear temperature-programming capability. Two 3.18-mm O.D. stainless steel tubes, each 1 meter long, are packed with 80-100 mesh Porapak Q (or T). Helium, the carrier gas, flows at 30 cm^3/min. at ambient temperature. The detector signals are recorded by a 1.0 mv Brown Electronik recorder equipped with a disk-chart integrator. Temperatures of injector block, detector manifold, and induction oven are normally kept at 250°C. Since the volatilities of solvent and solutes are widely different, temperature programming is normally employed, typically from 125°C to about 50°C above the normal boiling point of the heaviest solute. To convert peak area to mass, the response factor (mv s/mg) of the volatile solvent is obtained as a function of sample size by injecting a known amount of the sample with a calibrated, gas-tight syringe made by Micro-Sampling Corporation. The response factors of the solutes are obtained from chromatograms for mixtures of known composition.

RESULTS

Distribution coefficients were measured for dilute solutions of acetates, ketones, aldehydes, and phenolics. These coefficients, in units of $\frac{\text{mole solute/1000 g solvent}}{\text{mole solute/1000 g water}}$ are shown in Tables 1 to 4.

For polar solutes, the distribution coefficients in isobutylene are larger than those in isobutane because of weak complexing between the double bond in isobutylene and the polar group of the solute. For a homologous series, the distribution coefficient increases sharply as the molecular weight of the solute rises.

Correlation of Results: Theory of Dilute Solutions

To interpret and correlate the experimental results, it is convenient to introduce some simplifying assumptions which are applicable to dilute solutions. Let c stand for concentration of the solute, let single prime refer to the aqueous phase, and let double prime refer to the organic phase.

Let $\Delta \bar{g}$ stand for the change in partial molar Gibbs energy of the dilute solute when it is transferred at constant temperature and pressure from the aqueous phase to the organic phase such that its concentration is the same in both phases: $c' = c''$. The partial Gibbs energy of transfer is related to the solute concentrations and activity coefficients γ by

$$\Delta \bar{g} = RT \ln \frac{c''\gamma''}{c'\gamma'} = RT \ln \frac{\gamma''}{\gamma'} \qquad (1)$$

Note that $\Delta \bar{g}$ is *not* the change in Gibbs energy when phases $'$ and $''$ are in equilibrium.

From the definition of Gibbs energy

$$\Delta \bar{g} = \bar{g}'' - \bar{g}' = \Delta \bar{u} - T\Delta \bar{s} + P\Delta \bar{v} \qquad (2)$$

where

$$\Delta \bar{u} = \bar{u}'' - \bar{u}'$$

and

$$\Delta \bar{s} = \bar{s}'' - \bar{s}'$$

$$\Delta \bar{v} = \bar{v}'' - \bar{v}'$$

In a dilute solution, the partial molar entropy of a solute is determined primarily by its concentration; intermolecular forces between solute and solvent are only of secondary importance. However, the partial molar energy of the solute is strongly dependent on these forces. For the process under consideration here ($c' = c''$), we assume $\Delta \bar{s} = 0$.

At the modest pressures considered here, $P\Delta \bar{v}$ is negligible compared to $\Delta \bar{u}$. To obtain an expression for $\Delta \bar{u}$ we use a concept provided by the perturbed-hard-sphere theory (Reed and Gubbins, 1973). We assume

$$\bar{u}' - u^0 = k'q + U' \qquad (3)$$

and

$$\bar{u}'' - u^0 = k''q + U'' \qquad (4)$$

where superscript zero refers to the ideal-gas state at system temperature, q is a (hard-sphere) size parameter for the solute, and k' and k'' are (temperature-dependent) constants of proportionality. The characteristic energy U' refers to (attractive) interactions between solute and water and U'' refers to similar interactions between solute and organic solvent. Equations (3) and (4) follow from the notion that in order to introduce a solute molecule into the liquid solvent, it is first necessary to create a vacancy (hole) of size q. The work required to make the hole in the aqueous phase is $k'q$ and that to make the hole in the organic phase is $k''q$. Attractive forces between solute and water are responsible for energy U' and those between solute and organic solvent are responsible for energy U''.

Substitution gives for the Gibbs energy of transfer

$$\Delta \bar{g} = -kq - \Delta U \qquad (5)$$

where

$$k = k' - k'' \quad \text{and} \quad \Delta U = U' - U''$$

The distribution coefficient K is defined by

$$K = \frac{c''_{\text{eq}}}{c'_{\text{eq}}} = \frac{\gamma'_{\text{eq}}}{\gamma''_{\text{eq}}} \qquad (6)$$

where subscript eq stands for equilibrium. Since both

TABLE 1. DISTRIBUTION COEFFICIENTS AND CHARACTERISTIC VOLUMES FOR ACETATES. DISTRIBUTION BETWEEN WATER AND ISOBUTYLENE (AND ISOBUTANE) AT 25°C

	Distribution coefficient K†		V^*,
	Isobutylene	Isobutane	cm³/mole
Methyl acetate	2.56	1.47	80
Ethyl acetate	10.2	5.86	101
Butyl acetate	168	107	144
Amyl acetate	727	(400)	168‡

† $K \equiv \dfrac{\text{mole of solute/1000 g solvent}}{\text{mole of solute/1000 g water}}$

‡ Estimated.

( ) Extrapolated.

TABLE 2. DISTRIBUTION COEFFICIENTS AND CHARACTERISTIC VOLUMES FOR KETONES. DISTRIBUTION BETWEEN WATER AND ISOBUTYLENE (AND ISOBUTANE) AT 25°C

	Distribution coefficient K		V^*,
	Isobutylene	Isobutane	cm³/mole
Acetone	0.63	0.33	74
Butanone-2	2.49	1.35	92
Pentanone-3	13.4	(5.5)	112
Methyl isobutyl ketone	41.5	24.4	134
Heptanone-2	222	(110)	157‡

‡ Estimated.

( ) Interpolated or extrapolated.

TABLE 3. DISTRIBUTION COEFFICIENTS AND CHARACTERISTIC VOLUMES FOR ALDEHYDES. DISTRIBUTION BETWEEN WATER AND ISOBUTYLENE (AND ISOBUTANE) AT 25°C

	Distribution coefficient K		V^*,
	Isobutylene	Isobutane	cm³/mole
Crotonaldehyde	2.48	1.37	88‡
Butyraldehyde	8.05	4.36	92
Furfuraldehyde	1.44	(0.78)	92
Valeraldehyde	(32.2)	17.2	112‡
Hexylaldehyde	130	(68.6)	132‡

‡ Estimated.

( ) Interpolated or extrapolated.

TABLE 4. DISTRIBUTION COEFFICIENTS AND CHARACTERISTIC VOLUMES FOR PHENOLICS. DISTRIBUTION BETWEEN WATER AND ISOBUTYLENE (AND ISOBUTANE) AT 25°C

	Distribution coefficient K		V^*,
	Isobutylene	Isobutane	cm³/mole
Phenol	0.7	0.2	98
o-Cresol	4.8	(1.28)	116
m-Cresol	2.7	(0.7)	119
3,5-Xylenol	(7)	2.14	139

( ) Interpolated or extrapolated.

phases are dilute with respect to solute, we assume that the activity coefficients are constants, independent of concentration; that is, we assume

$$\gamma' \ (\text{at } c') = \gamma'_{eq} \ (\text{at } c'_{eq}) \quad \text{and}$$

$$\gamma'' \ (\text{at } c'') = \gamma''_{eq} \ (\text{at } c''_{eq}) \qquad (7)$$

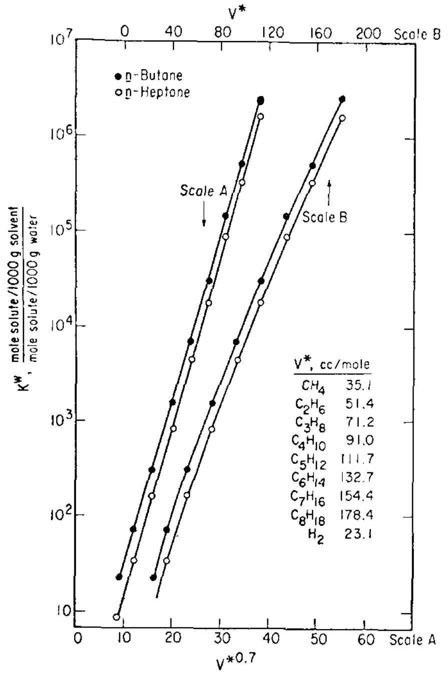

Fig. 5. Distribution coefficients vs. characteristic volumes for n-alkanes between water and n-butane (and n-heptane) at 25°C.

Substitution of Equations (5), (6), and (7) into Equation (1) gives the desired result

$$\ln K = \left(\frac{kq}{RT}\right) + \frac{\Delta U}{RT} \qquad (8)$$

Among others, McGowan (1954) and Deno and Berkheimer (1960) have used Equation (8), setting size parameter q equal to the parachor.

Since the parachor is a poorly understood quantity we prefer to base q on a parameter V^* reflecting the molecular volume. This parameter is calculated from vapor-pressure and density data as outlined in the Appendix. We have found that the experimental results are better correlated with V^* than with any other commonly available measure of molecular size.

It can be argued that the energy needed to make a hole for introducing a solute is proportional not to the volume of a solute molecule but to its surface area. Hence we propose to use for q the characteristic volume V^* raised to a constant power m where m is somewhere between 2/3 and unity. To fix m, we investigated the distribution coefficients of paraffins between water and n-butane (or n-heptane) shown in Table 5; these distribution coefficients were calculated from solubility data for hydrocarbons in water (McAuliffe, 1966) and from Henry's constant data in hydrocarbons (Cook et al., 1957; Aroyan et al., 1951; Hayduk et al., 1970, 1973). As indicated by Figure 5, Equation (8) is obeyed when $q = V^{*m}$ with $m = 0.7$. When $m = 0.7$ a plot of log K vs. V^{*m} gives a straight line. However, considerable curvature is observed when m is set equal to unity. In all subsequent correlations, we use $m = 0.7$. The constants in Equation (8) were evaluated by least-squares; they are shown in Table 6.

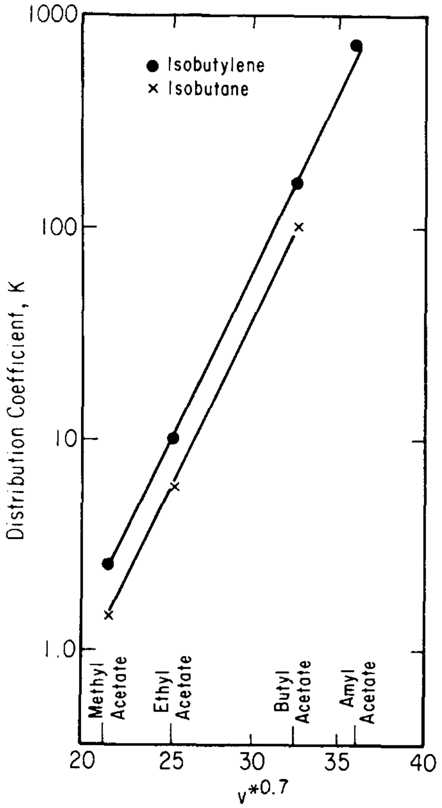

Fig. 6. Distribution coefficients for acetates between water and C_4 hydrocarbons at 25°C.

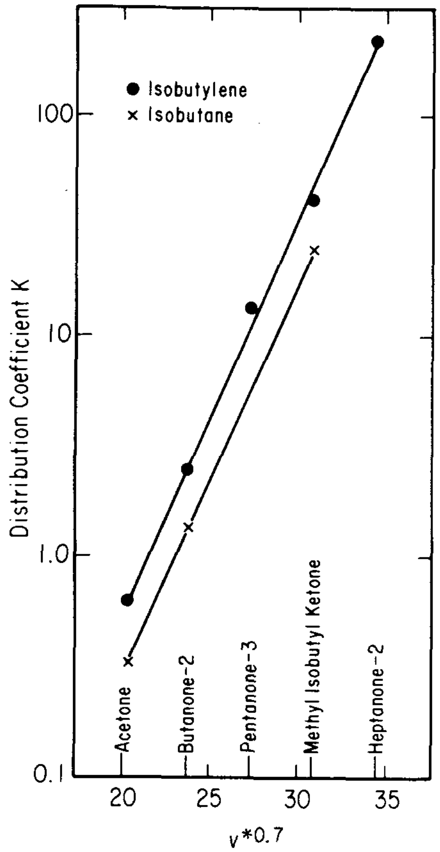

Fig. 7. Distribution coefficients for ketones between water and C_4 hydrocarbons at 25°C.

The experimentally-determined distribution coefficients are plotted on semilogarithmic coordinates as suggested by Equation (8); excellent straight lines are obtained as indicated by Figures 6 to 9. The volumes V° used to prepare these figures are given in Tables 1 to 4. Some additional volumes for organic solutes are given in Table 7.

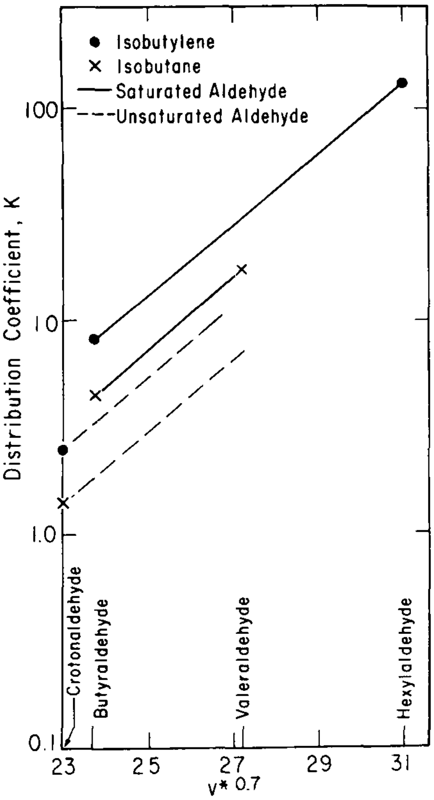

Fig. 8. Distribution coefficients for aldehydes between water and C_4 hydrocarbons at 25°C.

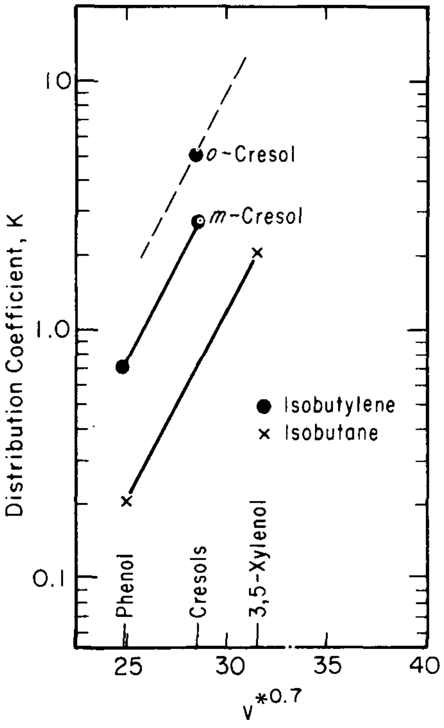

Fig. 9. Distribution coefficients for phenolics between water and C_4 hydrocarbons at 25°C.

Figures 6 to 9 provide a useful method for interpolation and extrapolation toward providing good estimates of distribution coefficients for those solutes where no experimental data are available.

The double bond in crotonaldehyde and the two double bonds in furfuraldehyde tend to lower the distribution coefficient as shown in Figure 8 and in Table 3. However, if the double bond is well removed from the polar functional group, its effect is reduced.

The effect of steric hindrance is evident in Figure 9. When chain branching is close to the polar functional group, the distribution coefficient tends to rise. However, for a fixed value of V^*, branching well removed from the polar functional group has little influence on the distribution coefficient.

TABLE 5. DISTRIBUTION COEFFICIENTS AND CHARACTERISTIC VOLUMES FOR n-ALKANES BETWEEN WATER AND n-BUTANE (AND n-HEPTANE) AT 25°C

	Distribution coefficient K		
	n-Butane	n-Heptane	V°, cm^3/mole
Methane	70.6	33.2	35.1
Ethane	400	159	51.4
Propane	1,577	825	71.4
Butane	7,040	4,000	91.0
Pentane	3.24×10^4	1.67×10^4	111.7
Hexane	1.5×10^5	9.05×10^4	132.7
Heptane	5.33×10^5	3.4×10^5	154.4
Octane	2.53×10^6	1.7×10^6	178.4
Hydrogen	21.2	8.7	23.6

TABLE 6. CONSTANTS IN EQUATION (8) WITH $q = V^{\circ 0.7}$

	$k/RT, \left(\frac{\text{cm}^3}{\text{mole}}\right)^{-0.7}$	$-\frac{\Delta U}{RT}$
Isobutylene		
Acetates	0.387	7.42
Aldehydes	0.41	7.62
Ketones	0.412	8.81
Phenolics	0.34	8.72
Isobutane		
Alkanes	0.41	0.713
Acetates	0.388	7.98
Aldehydes	0.403	8.08
Ketones	0.411	9.45
Phenolics	0.348	10.2
Alcohols‡	0.41	11.27

‡ Estimated from correlation of Pierotti et al., *Ind. Eng. Chem.*, **51** 95 (1959).

TABLE 7. CHARACTERISTIC VOLUMES V° FOR SOME OTHER ORGANIC SOLUTES (cm^3/mol)

Benzene	91.2	Resorcinol	103.2
Toluene	112.6	Acetic acid	61.2
m-Xylene	133.8	n-Propionic acid	82.3
Aniline	102.6	n-Butyric acid	103.7
Methanol	41.1	n-Hexanoic acid	147.7
Ethanol	60.2	n-Octanoic acid	192.1
n-Propanol	78.7	Benzoic acid	123.0
n-Pentanol	118.1	Fluoromethane	36.2
n-Octanol	180.2†	Chloromethane	47.9
n-Decanol	228.8	Trichloromethane	80.6
Benzyl alcohol	117.6	Trichlorofluoromethane	87.8
Ethylene glycol	62.0	Tetrachloromethane	98.6

† Liquid density data extrapolated with the Rackett equation.

IMPLICATIONS FOR EXTRACTION PROCESSES

For efficient solute removal by extraction, the distribution coefficient should be large, in excess of unity. When isobutylene is the solvent, favorable distribution coefficients are observed for hydrocarbons and for many monofunctional organic solutes, especially those of relatively high molecular weight. For a variety of wastewaters from petroleum-refining petrochemical plants, therefore, extraction with easily recovered isobutylene presents a possibly attractive method of water pollution abatement or solute recovery. However, for difficult-to-extract organic solutes like phenol, direct extraction with isobutylene is not attractive. For wastewaters containing phenol in significant (0.1 to 5 wt. %) concentration, it is preferable to use a dual-solvent process: phenol is removed with a favorable but slightly water-soluble solvent (for example, butyl acetate) and that solvent is subsequently removed from the aqueous phase by extraction with volatile isobutane or isobutylene. Details of such a process are given by Earhart (1974) and Earhart et al. (1974a).

ACKNOWLEDGMENT

We are grateful to C. J. King and J. P. Earhart for helpful discussions and to the Environmental Protection Agency and to the National Science Foundation for financial support.

NOTATION

A, B, C, D, E = empirical constants
c = concentration of solute, $\dfrac{\text{g mole solute}}{\text{1000 g solvent}}$
$\bar{g}$ = partial molar Gibbs energy, cal/mole
k = proportionality constant
K = distribution coefficient, $\dfrac{\text{concentration in organic phase}}{\text{concentration in aqueous phase}}$
P = vapor pressure
q = molecular-size parameter
R = gas constant
$\bar{s}$ = partial molar entropy, cal/mole °K
T = absolute temperature
$\bar{u}$ = partial molar internal energy, cal/mole
U = characteristic interaction energy, cal/mole
V = molar liquid volume, cm^3/mole
V^* = characteristic volume, cm^3/mole
$\bar{v}$ = partial molar volume, cm^3/mole
γ = activity coefficient, activity/concentration

Subscripts

eq = equilibrium
c = critical

Superscripts

0 = ideal-gas state
$'$ = aqueous phase
$''$ = organic phase
m = exponent

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APPENDIX. EVALUATION OF SIZE PARAMETER V^*

The molecular-size parameter V^* is the molar volume of a saturated liquid in a standard state specified by Hildebrand's rule (Hildebrand, 1939). The standard state chosen here is that state where the vapor volume in equilibrium with the saturated liquid is 100 liters/mole. This state is useful because it corresponds to a temperature range where liquid density data are most frequently available.

The liquid volume V^* is determined from vapor-pressure and liquid density data. The vapor pressure P is represented as a function of temperature T by the Antoine equation

$$\ln P = A - B(C + T)^{-1} \tag{A1}$$

where A, B, and C are empirical constants. When the vapor volume is 100 liters/mole, the pressure is given by the ideal-gas law

$$P = RT(100)^{-1} \tag{A2}$$

Simultaneous solution of Equations (A1) and (A2) fixes the temperature.

The molar liquid volume V is given as a function of temperature by an equation of the Rackett form (Rackett, 1970):

$$\ln V = D + E(1 - T/T_c)^{2/7} \tag{A3}$$

where T_c is the critical temperature and where D and E are empirical constants. When the temperature determined from Equations (A1) and (A2) is substituted into Equation (A3), we obtain the parameter V^*. The compilation by Francis (1959) is particularly useful for obtaining constants D and E from density data for organic liquids.

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