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A COMPARISON OF BET, LANGMUIR, AND VIRIAL SURFACE AREAS FOR CARBON POWDERS

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ABSTRACT

Specific surface areas for a series of carbon powders are determined from the BET, Langmuir, and virial models applied to data obtained from nitrogen gas adsorption (77K), acetic acid liquid phase adsorption (296 K), and argon gas chromatography adsorption (265-320 K), respectively. The resultant surface areas obtained from each method differ significantly. A correlation of these areas is reported. The ratio of the Langmuir area to BET area for each powder is found to be proportional to the pore volume. The ratio of the virial area to BET area is found to be proportional to the reciprocal of the gas-solid interaction energy.

INTRODUCTION

Specific surface area is an important consideration in understanding a solid's physiochemical properties. Surface area is used to help characterize a wide variety of solid materials including industrial adsorbents, catalysts, pigments, metallurgical powders, ceramics, and concrete. The techniques used to determine surface area include methods that do not depend on adsorption such as mercury porosimetry and microscopy, as well as methods that depend on liquid or gas phase adsorption (Adamson 1976). Surface area determination requires measuring some property that depends on the exposed surface of a solid. Thus, surface area values are dependent on the method used and different methods can give quite different values for the same material (Young and Crowell 1962). The standard and mostly widely used method for determining surfaced areas is based on the BET, Braunauer-Emmett-Teller, equation (Lowell 1979).

A number of comparisons have been made between the BET method and other methods of determining surface area. Within the range of uncertainty of the two methods, electron micrograph areas of low surface area powders were in general agreement with BET areas. A good correlation was found between the areas for nonporous carbon blacks obtained from nitrogen adsorption using the BET method and from adsorption of methylene blue or phenol in aqueous solution. The use of the Langmuir model in conjunction with the adsorption of fatty acids from hydrocarbon solutions gave areas in good agreement with BET nitrogen adsorption areas for nonporous solids. However, these two methods gave significantly different areas for porous solids (Young and Crowell 1962).

The virial method (Steele and Halsey 1954), based on submonolayer adsorption in the Henry's law region, compared favorably with the BET method for small surface areas. However, a significant discrepancy develops for high BET surface areas. The nitrogen BET area of 2000 m^2/g for an activated saran charcoal was twice the value of the argon virial area (Young and Crowell 1962). Discrepancies between the BET and other methods are more significant as the microporosity of the adsorbent is increased. It has been noted that BET areas above 2500 m^2/g would require every carbon atom in the solid to contribute its full area to the surface of the solid. Since this is impossible it is clear that a significant portion of the adsorbate gas must be condensed in pores rather than adsorbed on walls.

Choudhary (1976) has reviewed the use of liquid phase adsorption methods to determine surface area and porosity. John et. al. (1977) has compared the surface areas obtained from seven different gas adsorption methods applied to a common set of data for a variety of adsorbents.

In the present investigation, the BET method is compared to the Langmuir and virial approaches. Five different carbon powders, selected to span a broad range of surface area and porosity, were used as adsorbents. Three very different methods of obtaining adsorption data were used. The adsorbates included nitrogen gas (77K), acetic acid from aqueous solutions (296K), and argon gas mixed in a helium carrier gas (265-320 K). The adsorbate-carbon systems were analyzed with the BET, Langmuir, and virial models, respectively. The purpose of this investigation is to compare and correlate these BET-Langmuir and BET-virial areas.

THEORY

The BET, Langmuir, and virial models are based on multilayer, monolayer, and submonolayer-Henry's law adsorption, respectively. The way in which each model is used to determine specific surface area, A, is discussed below. For convenience the specific surface areas arising from the BET, Langmuir, and virial approaches are designated as A_B, A_L, and A_V, respectively.

The linear form of the BET equation is

$$\frac{1}{n(P^\circ/P - 1)} = \frac{1}{n_m c} + \frac{(C-1)\,P}{n_m\, C\, P^\circ} \qquad (1)$$

where n is the moles adsorbed at relative pressure P/P^0, n_m is the moles adsorbed at monolayer coverage, P^0 is the saturation pressure of the adsorbate, and C is a constant related exponentially to the magnitude of the adsorbent-adsorbate interaction (Brunauer 1938). The BET model assumes multilayer adsorption can take place at each site and that the Langmuir equation applies to each layer. The heat of adsorption of layers above the first one are set equal to the heat of condensation, while the first layer is assumed to have a unique heat of adsorption. At equilibrium each exposed layer of adsorbate is at a steady state with the next deeper layer. The balancing of adsorption and desorption for each surface layer is used to derive Eq. (1).

For many adsorbents a plot of $1/[n(P^0/P\text{-}1)]$ versus (P/P^0) gives a linear region with is typically from (P^0/P) = 0.05 to 0.3. The slope and intercept are used to find values of n_m and C. Pore size distribution and volumes are determined from the desorption isotherm using the Kelvin equation to estimate the pore radii as function of relative pressure of the adsorbate. In both the BET and Langmuir models the specific surface area, A, is found from

$$A = N_m L a_m \tag{2}$$

where N_m is the moles adsorbed per gram of adsorbent ($N_m = n_m/w$), L is Avogadro's number, a_m is the area occupied by one adsorbate molecule, and w is the mass of adsorbent. For nitrogen adsorption at 77 K the value of a_m is generally taken to be 0.162 nm^2. For acetic acid adsorption from solution the cross sectional area is assumed to be 0.205 nm^2.

Unlike the BET model which allows for multilayer adsorption, the Langmuir model assumes that adsorption can not extend beyond monolayer coverage (Langmuir 1916). This model is frequently used to represent gas phase chemisorption and adsorption from solution. The linear form of the Langmuir model is written as

$$(C/N) = (C/N_m) + (1/KN_m) \tag{3}$$

where C is the concentration, N is the moles adsorbed per gram of solid at equilibrium concentration, N_m is the moles adsorbed per gram of adsorbent, and K is a constant at a fixed temperature. Linear plots of (C/N) versus (C) are used to find N_m.

In the virial coefficient treatment of physical adsorption for the Henry's law region, the number of moles adsorbed per gram of adsorbent is given by

$$N_m = B_{2s}\,(P/RT) \tag{4}$$

where B_{2s} is the second gas-solid virial coefficient, P is the pressure, R is the gas constant and T is the temperature (Pierotti and Thomas 1971).

Gas phase adsorption isotherms measured in the linear Henry's law region are frequently used to determine very precise second gas-solid virial coefficients. Gas-solid chromatography is an alternative to more traditional adsorption techniques (Rybolt 1984). Gas chromatography provides a convenient method to obtain second gas-solid virial coefficient values since B_{2s} is given as

$$B_{2s} = (tF_1/w) \tag{5}$$

where t is the residence time of an adsorbate gas in a column, F_1 is flow rate of gas in the column, and w is the mass of powder in the column.

In this low coverage Henry's law region, adsorbate-adsorbate interaction is negligible. The B_{2s} values depend only on adsorbent-adsorbate interactions. The relation between the second gas-solid virial coefficient and the gas-solid interaction potential, u_{ls}, is expressed in terms of a configuration integral. If a solid is assumed to have a uniform surface, this integral may be written as

$$B_{2s} = A_V \quad [\exp(-u_{ls}/kT)-1]dz \tag{6}$$

where A_V is the virial surface area, k is the Boltzman constant, and z is gas-solid internuclear separation (Steele 1967).

A Lennard-Jones (3,9) potential,

$$u_{ls} = (\sqrt{27/2})\,E\,[(Z_0/Z)^9 - (Z_0/Z)^3] \tag{7}$$

where E is the maximum depth of the gas-solid interaction potential and Z_0 is the gas-surface distance of closest approach, is frequently used to represent the gas-solid interaction potential. Substitution of Eq. (7) for u_{ls} in Eq. (6) gives an integral equal to (B_{2s}/A_VZ_0). Since $/A_VZ_0$ should not vary with temperature, B_{2s} temperature data can be used to find the value of E which causes the minimum variation of A_VZ_0 for a given gas-solid system. Given a value for the distance of closest approach, Z_0, the surface area can be determined. Unlike the BET and Langmuir models, the virial approach requires no knowledge of adsorbate packing or coverage per adsorbate molecule.

MATERIALS AND PROCEDURES

The carbon powders used included Mexican Graphite (No. 25 Lubricating Graphite from the United States Graphite Co.), Aqua Nuchar, Nuchar S-C, Nuchar S-A (provided by Westvaco Chemical Division), and Super Sorb (provided by Amoco Research). The Nuchar S-C powder was filtered through an 80 mesh (177 micron) sieve to remove larger particles. The other powders were not filtered prior to use.

Degassing the Mexican Graphite (MG), Aqua Nuchar (AN), Nuchar S-C (SC), Nuchar S-A (SA), and Super Sorb (SS) powders for two hours in vacuo at 400K resulted in water weight losses of 0.1, 3, 7, 11, and 3.5 percent, respectively. According to information supplied by Westvaco and Amoco the AN particles averaged about 9 microns in diameter with 96% smaller than 44 microns, the SS particles averaged 50% smaller than 2.7 microns, and the SC and SA particles averaged 75% smaller than 44 microns.

Nitrogen Gas Adsorption

Nitrogen BET surface areas and pore volumes were determined for each of the carbon powders with a Micromeritics Instrument Corporation Digisorb 2500 Automatic Pore Volume and Surface Area Analyzer. This instrument uses a digital Equipment Corporation PDP8/M computer to control the acquisition of adsorption and desorption isotherms at liquid nitrogen temperature. The PDP8/M computer is programmed to use the BET equation and Kelvin equation to calculate surface area and pore volume distributions for an adsorbent.

Aqueous Acetic Acid Adsorption

Langmuir adsorption isotherms for AN, SC, SA, and SS powders were obtained by measuring the adsorption of acetic acid from six solutions in the concentration range 0.015 to 0.150M. Dosages of either 0.5 or 1.0 grams (weighed to the nearest milligram) of adsorbent were added to flasks containing 100 ml of acetic acid solution. The flasks were stoppered, shaken periodically for 30 minutes, then allowed to equilibrate at room temperature (approximately 296 K) for at least one hour. Longer equilibration periods (days) did not significantly shift the amount of acetic acid adsorbed. Solutions were filtered to remove powder and 25 ml aliquots were titrated with 0.100 N sodium hydroxide to a phenolphthalein endpoint (Shoemaker 1981). The decreases in acetic acid concentrations were used to determine the amount of acid adsorbed at each equilibrum concentration.

Argon Gas Chromatography

As described previously (Rybolt 1984), gas chromatography was used to determine the second gas-solid virial coefficients for argon with MG, SC, SA and SS powders. Columns were made from 6.35mm o.d. copper tubing packed with powder and plugged with corning pyrex wool. The gases used were helium, neon, and argon and had reported minimum mole purities of 99.998, 99.998, and 99.8, respectively. A gas sampling value was used to inject a brief pulse of sample gas into the helium carrier gas. Argon was used as the adsorbate gas and neon was used as the marker gas.

The column flow rate was determined from the measured flow rate of the carrier gas, inlet pressure, outlet pressure, atmospheric pressure, flowmeter temperature, and column temperature using the corrected column flow rate equation (Atkins and Curthoys 1978). A bubble flowmeter was used to determine the measured flow rate. A Bourdon pressure gauge and mercury manometer were used to determine the inlet and atmospheric pressure, respectively. Copper-constantan thermocouples which had been calibrated against a platinum resistance themometer were used to monitor the column and flowmeter temperature. The residence time of argon in the adsorbent powder was found by subtracting the measured retention time of the marker gas from the retention time of the argon. Column flow rates and residence times for each powder were substituted into Eq. (5) to determine B_{2s} values at each measured column temperature. Temperature values were in the 265 to 320 K range.

RESULTS AND DISCUSSION

The results of the Digisorb 2500 Analyzer's standard BET, Eq. (1), and Kelvin equation analysis are given in Table 1. BET areas, A_B, and desorption pore volumes, V_p, are reported. Five points were used to calculate each BET area. The pore volumes are based on pores in the 2 to 60 nm range. Nitrogen isotherms spanned the 0.05 to 0.98 relative pressure range. The samples span a wide range of surface area. The Mexican Graphite is primarily a nonporous sample, whereas the other powders have significant porosity. At least half the total pore volume for AN, SC, SA, and SS are found in pores of diameter less than 4.5, 5.0, 4.0, and 2.5 nm, respectively.

TABLE 1. BET Nitrogen Adsorption Results. Pore volumes are for pores in the 2 to 60 nm range.

Solid	Symbol	Area (m^2/g)	Pore Volume (cm^3/g)
Mexican Graphite	MG	26	0.118
Aqua Nuchar	AN	768	0.177
Nuchar S-C	SC	903	0.572
Nuchar S-A	SA	1661	0.925
Super Sorb	SS	3169	0.797

The acetic acid adsorption data was analyzed using Eq. (3) and the results are reported in Table 2. The correlation coefficients for the linear plots for AN, SC, SA, and SS were 0.99, 0.98, 0.98, and 0.95, respectively. The inverse of the slope gives the monolayer coverage, N_m, which is used in Eq. (2) to calculate the Langmuir area, A_L.

TABLE 2. Langmuir Acetic Acid Adsorption Results from C/N versus C plots.

Solid	Intercept (g/l)	Slope (g/mol)	N_m (mol/g)	Area (m^2/g)
AN	10.5	445	0.00225	278
SC	27.9	565	0.00177	218
SA	19.9	521	0.00192	237
SS	31.5	217	0.00461	569

The B_{2s}-temperature data were analyzed using the virial approach and the results are given in Table 3. For each gas-solid system an iterative procedure employing numerical integration based on Eq. (6) was used to find the value of E/k which gave the minimum value of the standard deviation of (log A_VZ_O) and the associated A_VZ_O value. A value of 0.283 nm was used for Z_O, distance of closest approach (Levy 1976), and used to find the A_V values for each powder.

TABLE 3. Virial Argon Chromatography Results

Solid	Standard Deviation of (log Az_o)	E/k (K)	A_VZ_o (m^3/g)	Area (m^2/g)
MG	0.00473	957	0.0044	16
SC	0.00819	1850	0.0431	152
SA	0.00242	1469	0.0979	346
SS	0.00525	1474	0.1812	640

A comparison of the A_B, A_L, and A_V values in Tables 1, 2, and 3 reveals a considerable variation in specific surface areas for each powder. The BET areas are significantly greater than either the Langmuir or virial values. It should also be noted that the trend of increasing BET areas with MG, AN, SC, SA and SS is not matched by the Langmuir areas so that no direct correlation is possible. Although the available MG, SC, SA, and SS virial areas follow a trend of increasing area, a plot of A_B versus A_V cannot be fit by any continuously increasing curve. Thus, for both the A_B-A_L and A_B-A_V data there is no direct correlation of specific surface areas. However, both the Langmuir and virial areas can be correlated with the BET areas if an additional parameter is introduced. A variety of ways to correlate the areas were examined. Two successful correlations are discussed below.

Figure 1 shows an effective Langmuir-BET surface area correlation. The ratio (A_L/A_B) is plotted versus the pore volume V_p for four carbon powders. A least squares fit gave the equation

$$(A_L/A_B) = 0.412 - 0.292(V_p) \tag{8}$$

with a 0.99 correlation coefficient.

FIG. 1 Langmuir Area and BET Area Correlation

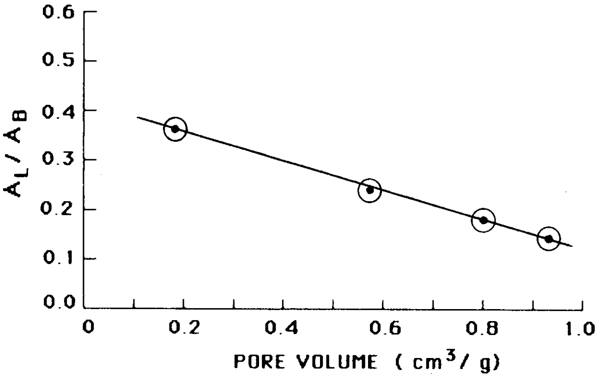


Figure 2 shows an effective virial-BET surface area correlation. The ratio (A_V/A_B) is plotted versus the reciprocal of the interaction energy, $(E/k)^{-1}$ for four carbon powders. A least squares fit gave the equation

$$(A_V/A_B) = -0.400 + 947(E/k)^{-1} \tag{9}$$

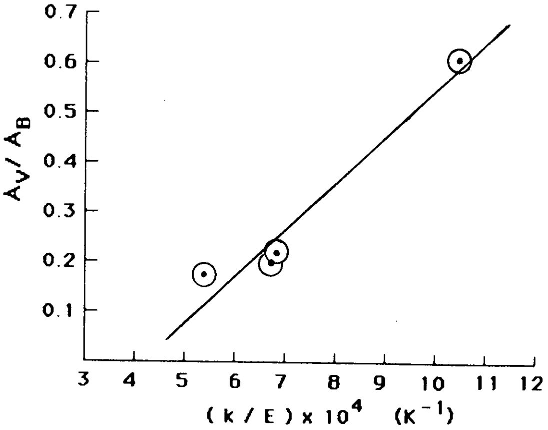
with a 0.97 correlation coefficient.

In Figure 1, the discrepancy between the acetic acid-Langmuir and nitrogen-BET areas is shown to increase as the pore volume increases. As the pore volume increases, a smaller portion of the total BET area comes from adsorption at surface sites which are also available to solution phase adsorption. In Eq. (8) the intercept seems to be related to a ratio of adsorption sites that can also act as sites for both gas phase nitrogen and solution phase acetic acid adsorption. This ratio is further reduced by a term proportional to the pore volume.

It is well known that part of the larger surface are obtained in BET analysis for microporous solids is due to enhanced adsorption in micropores and capillaries. Pore condensation occurs neither for adsorption from solution, used in Langmuir analysis, nor the Henry's law region of adsorption, used in the virial analysis. Pore condensation can cause the BET area to overestimate the "true surface area" for solids with small pores. Even at pressures too low for pore condensation there is enhanced adsorption of individual adsorbate molecules in narrow pores, as well as cooperative processes at higher pressures that are influenced by interaction between adsorbate molecules (Sing 1985).

Figure 2 shows that the virial areas are much less than the BET areas, but can be correlated by considering the interaction energy obtained in the virial analysis. The interaction energy is related indirectly to pore structure since pore structure contributes to the energetic environment in which adsorbate molecules are found. For these porous carbons a better virial analysis would include more complicated gas-solid interaction potentials which would model the three dimensional pore structure. Larger surface areas will be found when the pore structure is included in the virial analysis and so the values of A_V and A_B could be brought more into agreement. However, even with the development of a way to take porosity into account in a virial analysis, the BET area would remain larger due to the pore condensation effects discussed previously.

FIG. 2 Virial Area and BET Area Correlation



The results obtained in this work indicate that the qualitative explanations given may be indicative of more general phenomena which should be explored in an attempt to correlate different types of surface areas for other porous adsorbent systems.

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SOLUBILITIES OF p-DICHLOROBENZENE AND NAPHTHALENE IN SEVERAL AQUEOUS-ORGANIC SOLVENT MIXTURES

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Abstract

The effects of three alcohols, three ketones, pyridine, and ethyl acetate in enhancing the solubilities of p-dichlorobenzene and naphthalene in water are reported. Data were fitted to an equation of the form $S = S_0\ (1+KX^n)$, where S = solubility in aqueous-organic solvent solution, S_0 = solubility in pure water, X = mole fraction organic solvent, and K and n are constants characteristic of the solute-organic solvent pair. Enhancement of solubilities by factors of nearly 90 were observed in some cases.

Introduction

The U.S. apparently contains of the order of 200,000 improperly designed and/or operated hazardous waste landfill sites (US. EPA -1980a), some of which have already contaminated groundwater (U.S. EPA 1977, 1980b). The EPA estimates that "between 1200 and 2000 of these sites pose potentially imminent threats to health and the environment (U.S. EPA 1980c)

Despite the fact that the U.S. alone generates some 200 million tons of hazardous waste (Office of Technology Assessment, 1983), we have relatively little information about sources, environmental pathways, degradation products, and health effects of many of the compounds occur-

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ring in these wastes (Parker, Komarov, and Seuss 1983). The literature on toxic waste transport is quite sparse; most of the published work deals with lab studies, with generic studies using assumed parameters, or with hypothetical cases (Parker, et al. 1983). Some good work has been done on inorganics (Fuller 1978, Griffin and Shimp 1978, for example), and the EPA laboratory at Athens, Georgia has published some informative studies (Burns, et al. 1981, Lassiter, et al. 1974, Baughman and Burns 1980).

However, despite these data, the comprehensive program on Pesticide Transport and Behavior in Aquatic Environments (PEST) developed at Renselaer (Park, et al. 1980) concludes "Unfortunately, the data are not sufficient for either validation or invalidation of PEST." A study of kepone in the James River by O'Connor's group at Manhattan College concluded that "It is strongly recommended that additional data on kepone in the James Estuary and, equally important, organic chemicals in other estuaries, be gathered for further model calibration and validation" (O'Conner, et al. 1983). EXAMS, the U.S. EPA's computer code on transport of hazardous and toxic substances (Burns, et al. 1981) requires a large number of transfer coefficients which are, in general, not available. A paper by Jaffe, et al. (Jaffe, et al. 1982) on the seepage from a hazardous waste disposal site is one of the few papers that have field-determined values. In Conway's excellent and comprehensive text, *Environmental Risk Analysis for Chemicals* (Conway, 1982), not only does the book fail to provide other than generic information, the introduction comments that "the emphasis of the book is on the PROCESS of environmental risk analysis as opposed to a collection of test results with specific chemicals and situations."

One of the problems of interest in evaluating the hazard posed by a hazardous waste site is the extent to which synergistic interactions between the chemicals stored at the site may increase the flux of toxic materials out of the site and into the environment, particularly groundwater. To assess this, one needs to know the effect of common industrial organic solvents (often stored at such sites) on the solubilities in water of persistent toxic substances (chlorinated pesticides, PCBs, etc.) of low aqueous solubility. The physical interactions involved were reviewed in some detail in an earlier paper of ours (Nyssen, et al. 1986): we summarize these briefly here.

Generally, "structure making" solutes, which tend to enhance the extent of hydrogen bonding in water, tend also to decrease the solubilities of hydrophobic (non-polar or slightly polar, slightly soluble) solutes; enhancing hydrogen bonding increases the ability of the water to "squeeze out" of the solution those molecules which are non-ionic and which are unable to hydrogen bond with it (Ben-Naim, 1980, for example). Some organic solvents (ethanol, dioxane, tetrahydrofuran, acetone, for example) act as structure makers at low mole fractions but tend to disrupt hydrogen bonding in the water structure at higher concentrations, as shown by activity coefficient, partial molal volume, and proton NMR measurements (Glew, et al. 1968).

The presence of surface-active solutes can increase the solubilities of hydrophobic organics by as much as two to three orders of magnitude (Mukerjee and Cardinal, 1976; Birdi, 1976, Barone, et al. 1966, 1967). Our earlier work (Nyssen, et al. 1986) showed enhancement of the solubilities of hydrophobic organics by factors of as much as 40. Such solubility increases have been shown to lead to correspondingly increased fluxes of the hydrophobic solutes through soils in leaching experiments (Chu and Wilson, 1986; Nyssen and Wilson, 1986). In the following we present data verifying our earlier results (Nyssen, et al. 1986) and extending the study to include some new solvents. It is hoped that these data will be of use in evaluating the potential dangers posed by hazardous waste landfill sites.

EXPERIMENTAL

In this work the solubilities of p-dichlorobenzene (DCB) and naphthalene in aqueous systems containing various concentrations of one of 8 different common industrial organic solvents were determined. All work was done at room temperature. Table 1 lists the solvents and the concentrations used. We note that n-pentanol and 4-methyl-2-pentanone are nearly immiscible with water; for these, saturated aqueous solutions were made by vigorously shaking excess organic solvent with water in a separatory funnel for about 3 minutes, allowing the two phases to separate, and draining off the aqueous phase.

Table 1. Aqueous-Organic Solvent Systems Used

Solvent	Concentrations (mole fractions or % saturation)
n-Propanol	.001, 004, .008, .01, .012, .016, .02, .03, .04, .05, .06, .07, .08, .09, .10
n-Pentanol	.001, .002, .003, .004
n-Hexanol	.0001, .0002, .0004
Acetone	.01, .02, .04, .06, .08, .10
Methyl ethyl ketone	.01, .02
4-Methyl-2-pentanone	saturated
Pyridine	.01, .02, .04, .06, .08, .10
Ethyl acetate	.001, .005, .01

The concentration ranges for n-pentanol and n-hexanol were selected on the basis of the solubilities of these compounds reported by Nishino and Nakamura (1978); from their plots one can calculate solubilities of .0041 and .00075 mole fractions for n-pentanol and n-hexanol, respectively.

Two sets of solutions were prepared, and volumes of approximately 500 mL were placed in glass bottles. Then excess amounts of solid DCB or naphthalene were added to the solutions. The bottles were then closed with screw caps with aluminum foil liners to prevent any evaporation.

It was anticipated that the rate of approach to equilibration of these systems might be slow. Three different procedures were used to bring about equilibration, all of which appeared to be satisfactory. In the first procedure the bottles were shaken vigorously by hand approximately once a day for four weeks. In the second, the bottles were shaken vigrously about once a day for six weeks and were then allowed to stand without shaking for an additional three weeks. In the third procedure, the bottles were vigorously magnetically stirred for about 24 hours; it was found that recrystallization from the vapor phase on the container wall above the solution began to occur after 10 to 24 hours of stirring, indicating saturation of the solution. At this point the solution was allowed to stand quiescent for a week. With all procedures crystallization of the solute on the glass above the liquid was observed before samples were taken for analysis.

All samples were analyzed by gas chromatography. Samples containing DCB were analyzed on a Shimadzu Mini-2 gas chromatograph equipped with a nickel-63 electron capture detector and a 30-meter capillary column coated with SE-30. Analyses for naphthalene were carried out on a Shimadzu Mini-2 gas chromatograph with a flame ionization detector and a 30-meter capillary column coated with SE-30. Initially the following procedure was used; it was found to be quite adequate for the more dilute solutions. In both cases a 100-mL aliquot of the solution was taken in a volumetric flask; DCB was then extracted by adding 3.0 mL of pesticide grade hexane and shaking vigorously several times. Naphthalene was extracted by adding 1.0 mL of pesticide grade hexane, followed by vigorous shaking. The samples were then allowed to separate, and 1.0 microliter of the hexane extract was then injected into the gas chromatograph by the solvent push technique (using 2.0 microliters of hexane). Standard solutions containing the solutes in pesticide grade hexane were used for calibration purposes. This method was satisfactory for the more dilute solutions, but the more concentrated solutions resulted in exceeding the linear ranges of the detectors. For these it was found convenient to use sample volumes between 10 and 25 mL and hexane volumes between 3 and 15 mL. A calibration curve was made each time analyses were done; 1.0 microliter of each standard was injected, and peak areas were plotted versus the known concentrations. These calibration curves were then used to determine the concentrations of solutes in the hexane extracts, after which the solute concentrations in the aqueous solutions was calculated from Eq. (1).

$$V_1C_1 = V_2C_2 \qquad (1)$$

Here V_1 = volume of aqueous sample, mL
C_1 = concentration of solute in aqueous sample, mg/L
V_2 = volume of hexane used, mL
C_2 = concentration of solute in hexane extract, mg/L

In the above calculations it is tacitly assumed that all of the solute is extracted by the single extraction. To test this, we took several aqueous solutions after they had been extracted, re-extracted them with a second portion of hexane, and analyzed the second extract. We found that from 97% to 99% of the solutes were extracted during the first extraction, which was felt to be sufficiently complete.

RESULTS AND DISCUSSION

Our results are shown graphically in Figures 1-7. It is seen that generally (but not invariably) increasing the concentration of organic solvent results in increases, sometimes very large increases, in the solubilities of DCB and naphthalene. A number of the plots are fairly flat at low organic solvent concentrations, but are concave upward as the solvent concentration is increased. Figures 4, 6, and 7 show that ethyl acetate, n-pentanol, and n-hexanol have relatively little effect on the solubilities of DCB and naphthalene. The more soluble alcohols, acetone, and pyridine, however, cause extremely large increases in the solubilities of these two compounds over the ranges of solvent concentrations studied.

The shapes of several of the plots suggested the following mechanism for the solubilization of DCB and naphthalene in these solutions; this model was used in our previous work (Nyssen, et al. 1986). We assume that a hydrophobic solute molecule is complexed with n organic solvent molecules, possibly in a micro-micellar structure of some sort. Formally this gives the following "reaction" as representing the solubilization process;

$$\text{Solute} + n\text{Solvent} \rightleftarrows \text{Solute (Solvent)}_n \qquad (2)$$

for which the equilibrium constant is

$$K = \frac{[\text{Solute (Solvent)}_n]}{[\text{Solute}]\ \ [\text{Solvent}]^n} \qquad (3)$$

The total solubility of the hydrophobic organic is the sum of the concentrations of the uncomplexed solute and the complexed solute. This yields

$$\text{Total solute concentration} = S_0\,[1 + KX^n] \qquad (4)$$

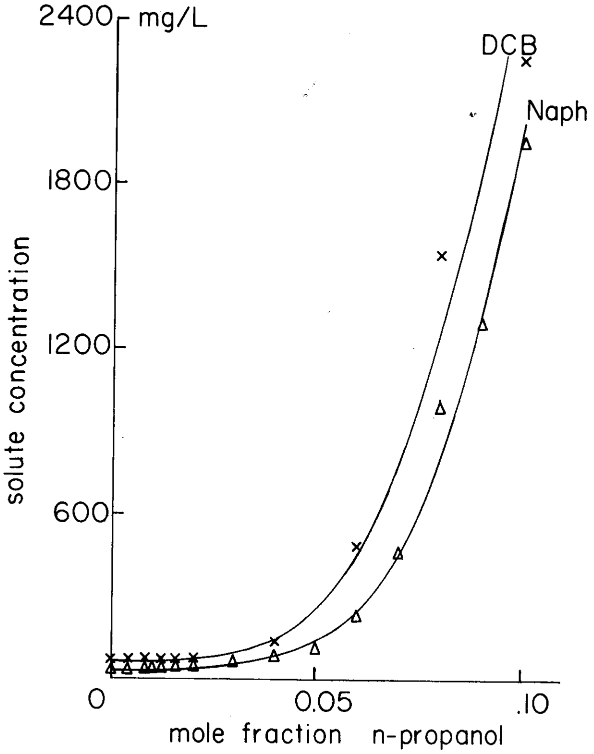

Fig. 1

Plots of DCB and naphthalene solubilities in water/n-propanol mixtures. X-DCB, d-naphthalene in all figures.

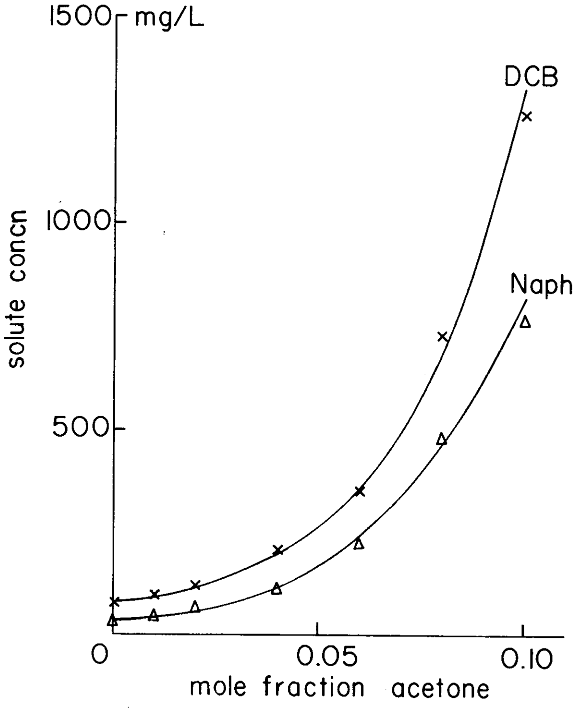

Fig. 2

Plots of DCB and naphthalene solubilities in water/acetone mixtures.

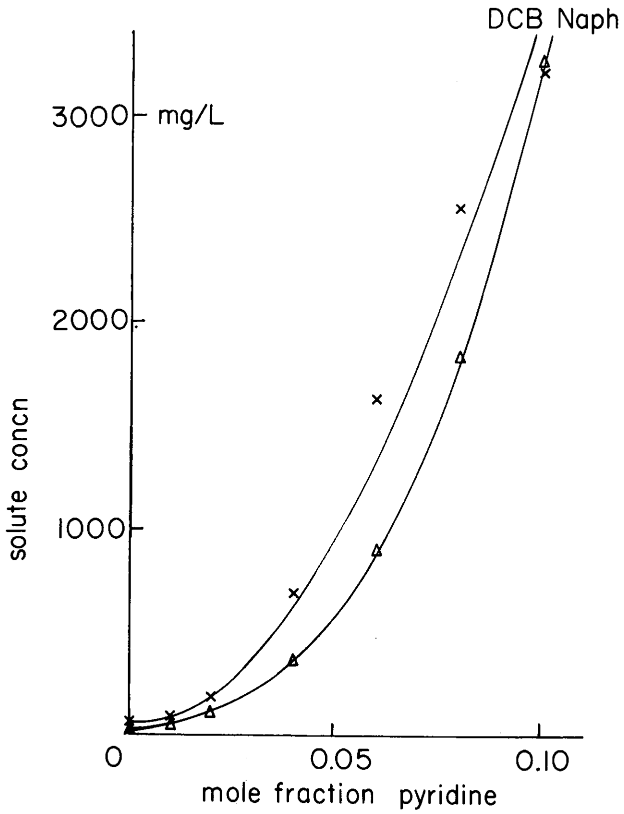

Fig. 3

Plots of DCB and naphthalene solubilities in water/pyridine mixtures.

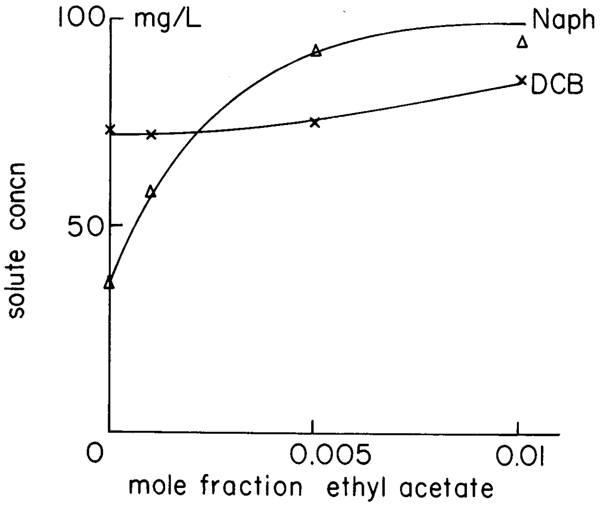

Fig. 4

Plots of DCB and naphthalene solubilities in water/ethyl acetate mixtures.

where S_0 is the saturation concentration of the solute in pure water, and X is the mole fraction of the organic solvent. We rewrite this in the general form

$$\text{Total solute concentration} = A + BX^n \qquad (5)$$

where A, B, and n are constants to be fitted to the data. A should be independent of the identity of the organic solvent, since it is simply the concentration of the solute in pure water. The values of n are of particular interest; these are the average numbers of organic solvent molecules which are assumed to complex with (or micellize) a single solute molecule. Values of these constants were calculated for all the sets of data by means of a non-linear least squares pro-

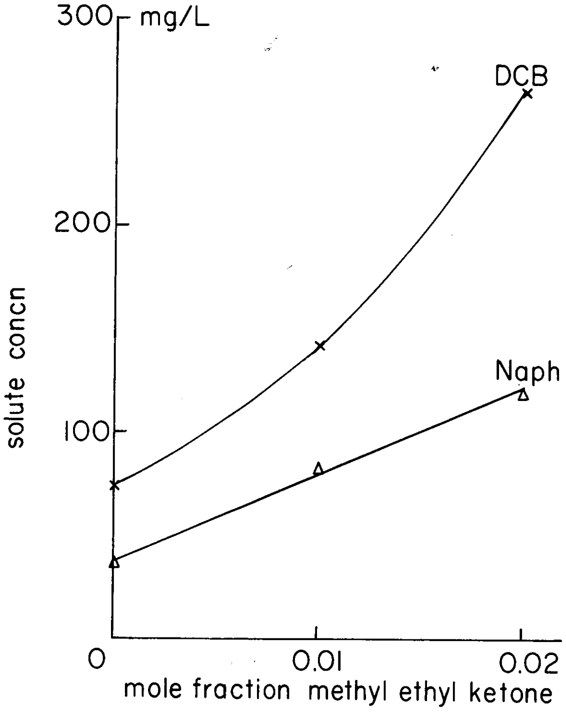

Fig. 5

Plots of DCB and naphthalene solubilities in water/methyl ethyl ketone mixtures.

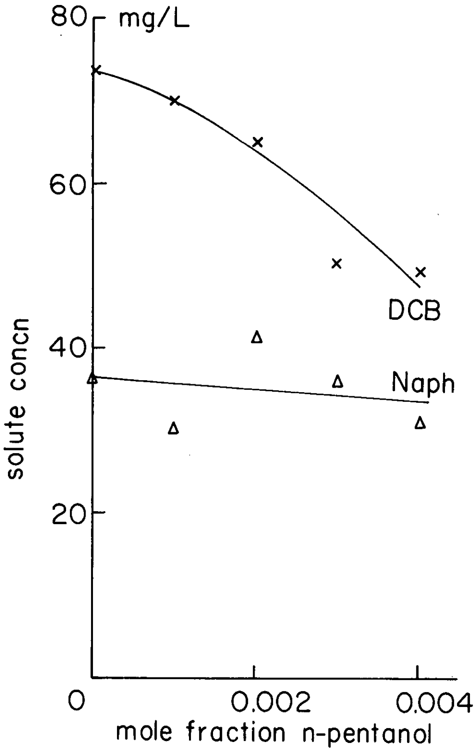

Fig. 6

Plots of DCB and naphthalene solubilities in water/n-pentanol mixtures.

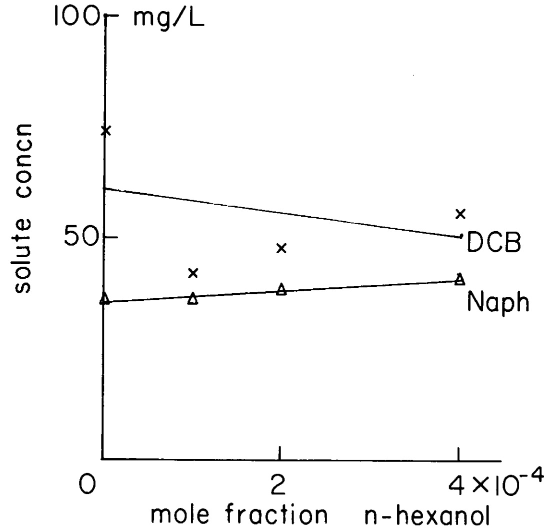

Fig. 7

Plots of DCB and naphthalene solubilities in water/n-hexanol mixtures

gram in BASIC which was run on an Apple IIe microcomputer. The values of n so determined are given in Table 2.

Table 2. Effective Coordination Numbers of DCB and Naphthalene with Organic Solvents in Aqueous Solution

Solvent	Values of n and K			
	p-DCB		Naphthalene	
	n	K	n	K
n-Propanol	4.50	9.3×10^5	3.86	3.8×10^5
n-Pentanol	0.559	-7.1	9.5×10^{-4}	-1.4×10^{-2}*
n-Hexanol	-.44	-8.3×10^{-3}	3.16	2.0×10^{10}*
Acetone	2.78	9.7×10^3	2.53	6.7×10^3
Methyl ethyl ketone	1.51	9.4×10^2	2.45	3.4×10^4
4-Methyl-2-pentanone	----	--------	----	--------
Pyridine	1.38	9.6×10^2	2.60	3.5×10^4
Ethyl acetate	2.35	8.1×10^3	.37	8.8×10^0

*The negative K values for these two solvents indicate that our model apparently does not apply to them.

The reported solubilities of DCB and naphthalene at 25°C are 80 mg/L and 30 mg/L, respectively (Lawless, et al. 1975). The values which we obtained in this study are 74 mg/L and 36.5 mg/L, which we regard as fairly good agreement. In Table 3 are shown the highest concentration used of each solvent, the corresponding solubilities of DCB and naphthalene, and the ratios of these solubilities to the solubilities of the two compounds in water. (In calculating these ratios we used our own values for the solubilities in pure water.)

Table 3. Ratios of Maximum Solution Solubilities to Solubilities in Pure Water

Solvent	Highest concn. (mole fraction)	Solubility (mg/L)		Factor Increased	
		DCB	Naph	DCB	Naph
n-Propanol	.100	2250	1960	30	54
n-Pentanol	.004	50	36	.67	.98
n-Hexanol	.0002	48	38	.64	1.04
Acetone	.10	1260	760	17	20
Methyl ethyl ketone	.02	264	121	3.6	3.3
4-Methyl-2-pentanone	sat'd	73	53	.99	1.46
Pyridine	.10	3030	3260	41	89
Ethyl acetate	.01	86	95	1.2	2.6

It was observed that the maximum mole fraction of methyl ethyl ketone which could be used without the appearance of a second liquid phase was about .02; solutions prepared containing mole fractions of methyl ethyl ketone of .04 and .06 dissolved quite large quantities of DCB or naphthalene, and a liquid layer separated from the aqueous phase. This settled below the aqueous phase when DCB was the solute; it floated when naphthalene was the solute. Evidently, the rather small amount by which the solubilities of DCB and naphthalene are enhanced by .02 mole fraction of methyl ethyl ketone does not give a true measure of the ability of this solvent to affect the movement of hydrophobic compounds. A study of the mobility of the second, organic solvent-rich phase in soils would certainly be in order.

In conclusion, we note the following. It appears that organic solvents which themselves are of low solubility in water are not very effective in enhancing the solubilities of hydrophobic solutes. Acetone and pyridine, along with the lower alcohols studied by Nyssen, et al. (1986), are very effective in enhancing the solubilities of these hydrophobic organic compounds in water, and can be expected to greatly enhance the movement of hydrophobic organics from hazardous waste sites. The occurrence of phase separations, seen here with methyl ethyl ketone, requires further study, particularly with regard to the ability of the solvent-rich phases to move through soils.

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