



1984

## Setchenov parameters for naphthalene : a thesis ...

Gerardo Gold Bouchot  
*University of the Pacific*

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SETCHENOV PARAMETERS FOR NAPHTHALENE

A Thesis

Presented to

the faculty of the Graduate School

University of the Pacific

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Gerardo Gold Bouchot

May 1984

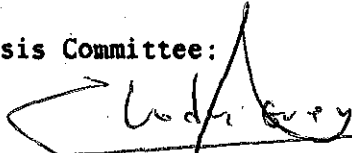
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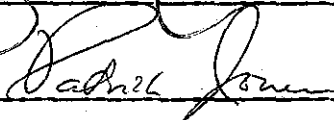
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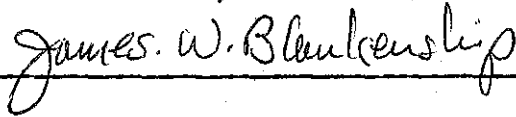
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Dated

May 18, 1984

## ACKNOWLEDGEMENTS

I wish to thank Dr. Silvio Rodriguez for being more than a research advisor, for his encouragement and friendship.

I also wish to thank Dr. Patrick Jones and Dr. Michael Minch for the use of several pieces of equipment from their laboratories, Dr. Richard Dodge for the use of his program L/B, and Dr. David T. Hughes from the Mathematics Department for his help with the use of the programs in the SPSS package.

Finally, in appreciation of her continuous support and love, I dedicate this thesis to my wife, Esther.

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Setchenov Parameters for Benzene and Toluene  
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## INTRODUCTION

### Oil Pollution in the Ocean. A General Overview

#### Sources of Hydrocarbons in the Marine Environment

Public concern over the increasing pollution by petroleum hydrocarbons in the marine environment has grown as its visible effects--oil films and tar balls in surface waters, soiling of beaches, etc.--have in turn increased and received wider mass-media coverage. However, there is not a corresponding increase in the volume or quality of the information available to assess the long-term effects that petroleum compounds can cause in marine ecosystems. Consider the following to get an idea of the magnitude of the problem: it has been estimated that the total input of petroleum hydrocarbons to the oceans is six million metric tons per year (Thacher and Meith, 1978). Of these, about two million metric tons are due to problems related to the transportation of petroleum by sea, an amount that was predicted to increase to six million metric tons by 1980 (Thacher and Meith, 1978).

There are three major sources of petroleum hydrocarbons in the oceans (Thacher and Meith, 1978; Farrington et al, 1976; Farrington and Meyer, 1975): 1) man-generated compounds; mainly crude oil and refined products; 2) geochemically originated hydrocarbons; such as those from

seepages through the sea floor and diagenesis of organic matter; 3) biosynthetic hydrocarbons; which are the metabolic products of marine organisms. From now on, the first two classes of petroleum hydrocarbons will be referred to as either "petroleum hydrocarbons" or "crude oils."

In assessing the environmental impact of oil pollution it is necessary to differentiate between petroleum and biosynthetic hydrocarbons, but due to the extreme complexity of crude oils (Farrington et al., 1976) it is very difficult to do so. At least some general guidelines are available (Farrington et al., 1976; Farrington and Meyer, 1975): a) the n-alkane fraction of crude oils is a 50-50% mixture of odd and even numbers of carbon atom chains, whereas biosynthetic hydrocarbons always contain chains with an odd number of carbon atoms; b) alkenes are generally absent in crude oils, but they are often a major portion of the hydrocarbons found in marine organisms; c) crude oils contain a complex mixture of cycloalkanes, polycyclic aromatic hydrocarbons (PAH'S), as well as heterocyclic compounds, none of which have been found in marine organisms.

#### Physical States of Hydrocarbons in Seawater

Hydrocarbon molecules in water can be found in any of the following forms (Thacher and Meith, 1978; Shaw, 1977):  
1) Dissolved, in the thermodynamic sense (in 1975, the National Academy of Science estimated the amount of

dissolved petroleum in the oceans at 400 million tons.); 2) Colloids, defined as aggregates of less than one um in diameter (no estimates of the amounts of hydrocarbons present in this form are available, but Shaw (1977) estimates that the amount of colloidal hydrocarbons should greatly exceed that of hydrocarbons in solution.); 3) Tar Balls. These are defined as particles bigger than one um. Butler (1975) estimated the amount of tar present in surface waters in 1975 at 0.7 million tons. The total amount of petroleum hydrocarbons in the oceans was estimated to be 14,000 million tons in 1976 (Thacher and Meith, 1978).

#### Environmental Pathways for Hydrocarbon Loss in the Ocean

Once petroleum hydrocarbons enter the marine environment several pathways for the loss of hydrocarbons are possible (Thacher and Meith, 1978;): Evaporation. McAuliffe (1977) and McAuliffe et al. (1980) have presented experimental evidence, from intentional oil spills, that low molecular weight hydrocarbons (i.e. up to 12 carbon atoms) evaporate very fast, with the result that this fraction was no longer detectable in surface waters after two days. Harrison et al. (1975) predicted that the evaporation of aromatic hydrocarbons would be 100 times faster than dissolution, and that the rate of evaporation for alkanes would be 10,000 times faster than that for dissolution. Regnier (1975) and Mackay et al. (1975) measured the rate constants of evaporation of n-alkanes, the results ranging from  $3.44 \times 10^{-3} \text{ min}^{-1}$  for n-C<sub>10</sub> to  $4.00 \times 10^{-5} \text{ min}^{-1}$  for n-

C<sub>18</sub> at 20°C. More recently, Atlas et al. (1981) measured the mass transfer coefficient for high molecular weight compounds and compared their results with theoretical models, finding good agreement.

Emulsification. There is evidence (Shaw, 1977) that colloidal-size hydrocarbon particles are formed under turbulent mixing conditions in the ocean. McAuliffe et al. (1980) have also reported that the addition of emulsifiers speeds up the physical weathering of oil.

Sedimentation. Sorption of petroleum hydrocarbons on sediments can accelerate deposition on the sea floor (Means et al., 1980), where biodegradation is slower due to the lack of oxygen. The loss of volatile components can increase the density of an oil enough to produce sedimentation (McAuliffe, 1977). Another mechanism that can speed up the rate of sedimentation is by ingestion and incorporation into fecal pellets by marine copepods (Prahl and Carpenter, 1979), this being the major route of removal in some areas.

Microbial Degradation. More than 90 species of bacteria have been identified which can metabolize many constituents of oils (Thacher and Meith, 1978). Some organisms will grow at the expense of aromatic hydrocarbons, whereas others will grow only if an additional substrate is present, a phenomenon called cooxidation (Gibson, 1977). The usual route is to oxidize the aromatic hydrocarbon to a cis-dihydrodiol, and from there to form the ortho-dihydroxy

derivatives (catechols), the last step being the enzymatic cleavage of the aromatic ring (Gibson, 1977; Lehr et al., 1980). At least three species of the genus Pseudomonas can oxidize naphthalene (Jeffrey et al., 1975), and some species of the genera Flavobacterium and Beijerinckia can oxidize phenanthrene, anthracene, and benzo(a)pyrene (Gibson, 1977).

Oxidation. The photo-oxidation of polynuclear aromatic hydrocarbons in aqueous systems has been reported (Zepp and Schlotzhauer, 1979; Korfmacher et al., 1979; Katz et al., 1979). The photoreactivity of PAH's in aqueous solutions has been reported to be 10 to 100 times higher in aqueous solutions than in organic solvents (Zepp and Schlotzhauer, 1979). The necessity of the presence of oxygen is still open to discussion (Katz et al., 1979). From simulation studies of natural conditions it was reported that the photo-oxidation of PAH's adsorbed on sediments is four times higher than for dissolved PAH's (Korfmacher et al., 1979) and that the rate of photo-degradation decreases logarithmically with increasing depth (Zepp and Schlotzhauer, 1979).

Biological Incorporation. It is a well known fact that aquatic organisms accumulate organic pollutants from their environment. This is called "bioconcentration" (Albers, 1980; Hinga et al, 1980). If it is assumed that the biotic phase is approaching thermodynamic equilibrium with its medium, then it is possible to correlate the potential

bioconcentration (i.e. the total biotic accumulation under ideal conditions) of organic compounds to their physical properties (Dexter and Pavlou, 1978 and 1978a; Chiou et al., 1977). These studies were done following a method developed by Neely et al. (1974), which correlates the potential bioconcentration to the partition coefficient (defined as the dimensionless ratio of the solubility in 1-octanol to that in water) of the compound. Mackay (1982) extended the method by developing a one-constant correlation between aqueous solubility to bioconcentration. The correlation holds for bioconcentration in the range 10 to  $10^6$ . These methods have been applied to bioconcentration in marine organisms in artificial ecosystems (Hinga et al, 1980), rainbow trout (Dexter and Pavlou, 1978a; Chiou et al, 1977), fathead minnow (Southworth et al., 1980), marine zooplankton (Clayton et al., 1977), organisms in estuaries (Pavlou and Dexter, 1979), freshwater fishes (Mackay, 1982), and even in marine bird eggs (Albers, 1980).

Solution. The solubilities in seawater of both low and high molecular weight n-alkanes as well as those of some aromatic hydrocarbons have been measured (Sutton and Calder, 1974; Eganhouse and Calder, 1976). In general it has been found that the solubilities of hydrocarbons in seawater are 60 to 70% of that in pure water. Several attempts have been made to relate the solubility of a hydrocarbon to physical parameters (Shaw, 1977), like molar volume (Bohon and Clausen, 1951; McAuliffe, 1966), the number of carbon or

hydrogen atoms in the hydrocarbon molecule (Tanford, 1980), and the size of the cavity in the solvent holding the hydrocarbon solute (Hermann, 1972; Harris et al., 1973; Reynolds et al., 1974). Only a couple of workers have studied the influence of one hydrocarbon solute upon the solubility of another one (Eganhouse and Calder, 1976; Mackay, 1978) and the effect of dissolved organic matter upon the solubility of hydrocarbons in seawater (Boehm and Quinn, 1973).

Dissolved hydrocarbons are important from a practical point of view; they are the most readily available to marine organisms and therefore the most likely to have toxic effects (Hutchinson et al., 1980). This is especially true of the polynuclear aromatic hydrocarbons (Collier et al., 1980).

From a theoretical point of view, solubility data can provide information about the structure of liquid water and aqueous solutions (Frank and Evans, 1945; Nemethy and Scheraga, 1962; Shinoda, 1977). On the other hand, solubility can be related to partition coefficients, allowing the calculation of potential bioconcentration (Hansch et al., 1968; Banerjee et al., 1980; Mackay, 1982).

These aspects will be further elaborated in the next two sections.



### Water as a Solvent

Liquid water shows several anomalies when compared to similar compounds (like the hydrides of the group VI elements): its very high melting and boiling points, the increase of density on melting, the density minimum at 4°C, the large molar heat capacity, and the minimum of the viscosity as a function of pressure at about 1000 atm, to name just a few (Franks, 1972; Dahl and Andersen, 1983; Stanley and Batten, 1969).

As a solvent, water has also an anomalous behavior in solution, especially when the solute is nonpolar in which case a positive change in Gibbs free energy, and a negative enthalpy change are observed (Hvidt, 1983). There is universal agreement that the anomalous properties of water are due to its ability to form up to four strong, directional hydrogen bonds, with tetrahedral symmetry around the central oxygen atom (Frank, 1972). This high degree of association is thought to be the cause of the abnormal properties of water.

Any attempt to rationalize or to predict the solubility of nonelectrolytes in general, and of petroleum hydrocarbons in particular, should be based upon a thorough knowledge of the structure of water. Following Eisenberg and Kauzmann (1969), we will refer to "structure" as being the "relative positions and motions of the molecules", averaged over times

that are longer than the hindered translational mode at  $200 \text{ cm}^{-1}$  (about  $2 \times 10^{-13} \text{ s}$ ), but shorter than the dielectric relaxation time (about  $10^{-11} \text{ s}$ ). In this way, we will be talking about the vibrationally-averaged structure, or "V-structure" of liquid water.

There are two general types of models of liquid water: the mixture models postulate that liquid water is a mixture of several different "species", namely monomeric and polymeric water molecules in different degrees of association. On the other hand, continuum models consider that all the liquid water in a container consists of one giant "molecule" whose hydrogen-bonded structure gets more and more distorted as the temperature increases.

### Theoretical Models of Liquid water

#### a) Mixture Models.

The first step in relating the degree of structure of water to its properties as a solvent was given by Frank and Evans (1945). They explained the entropy decrease upon dissolving a nonpolar solute by assuming that an 'iceberg' forms around a solute, leading to a more ordered state. Later on, Nemethy and Scheraga (1962 and 1962a), in the first of a long series of papers, proposed that liquid water is a mixture of molecules with five different coordination numbers, ranging from zero (monomeric water) up to four. The water molecules whose coordination number is different from zero are considered to be forming ice-like clusters. Since

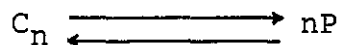
the clusters are formed and destroyed continuously, they are called "flickering clusters". The concept of "flickering clusters" was developed by Frank and Wen (Nemethy and Scheraga, 1962), but Nemethy and Scheraga were the first to develop a statistical mechanical analysis of the model. They were able to formulate a canonical partition function, and from that to calculate the number and size of the clusters as a function of temperature. The thermodynamic functions (Helmholtz free energy, internal energy, entropy, and heat capacity at constant volume) were calculated from the partition function in the usual way.

Nemethy and Scheraga (1962) considered that the structure of dilute solutions of nonelectrolytes is basically the same as above, with the main difference being that "the energy levels and hence the distribution of water molecules in the water layer next to the hydrocarbon are shifted due to the different interactions between the water and hydrocarbon molecules" (Nemethy and Scheraga, 1962). They assumed that the probability of finding a cluster is higher in the vicinity of a solute than in the bulk of pure water. The calculated values of the thermodynamic functions of solution for nonelectrolytes are in good agreement with the experimental values.

Several improvements have been made to the model (Hagler, Scheraga, and Nemethy, 1972 and 1973; Lentz, Hagler and Scheraga, 1974; Scheraga, 1977 and 1982), like using better expressions for the partition function, taking into

account the cooperativity of hydrogen bonds, etc. Curiously, as the model was improved they concluded more and more that the results are inconsistent with a mixture model (see below).

Another contribution to mixture models was made by Ben Naim (1965), who assumed that liquid water is a mixture of two kinds of molecules in chemical equilibrium with each other: monomeric water molecules (P molecules), and water molecules tetrahedrally bonded to other water molecules to form spherical clusters (C molecules). The equilibrium is



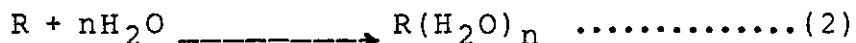
where  $n$  is the number of water molecules in the cluster. The presence of a nonelectrolyte shifts the equilibrium to the left, that is to a more ordered state. In this model any partial molecular quantity  $E_S$  can be divided in two parts:

$$E_S = E_S^* + E_S^r \dots\dots\dots(1)$$

where  $E_S^*$  is the static contribution arising from the equilibrium between C and P, and  $E_S^r$  is the relaxation term, which arises from the shift in the equilibrium between C and P. The difference between Ben Naim's model and the other models discussed before is that it does not place any constraints on the position of the new order induced by the presence of the nonelectrolyte, that is, the more structured

form does not have to surround the solute molecule totally as Frank and Evans (1945) postulated, or even partially surround it, as is the case with Nemethy and Scheraga's (1962) model. Another difference is that Ben Naim does not assume the formation of a new kind of structure due to the presence of the solute (as is the case with Frank and Evans' "icebergs"), because he merely postulates a shift in an already existing equilibrium.

Frank and Evans (1945) were the first to propose an increase in the degree of structure of water molecules around a nonpolar solute as an explanation for the entropy decrease when the solute is dissolved. The currently accepted view is that the low solubility of nonpolar compounds is due to the increased structure they introduce in the solvent. However, a group of workers have proposed the opposite explanation, namely, that the "icebergs" around a nonpolar solute promote the solubility of such compounds. These authors (Shinoda, 1977 and 1978; Hvidt, 1983, 1983a). Hvidt (1983) consider the dissolution of a nonpolar molecule as a two step process: 1) the mixing of the components, which is considered similar to the formation of a "regular" solution, and 2) the structural relaxation to the equilibrium state, considered to be a hydrophobic solvation. The "chemical" equation describing this process is (Hvidt, 1983):



where R is a nonpolar solute, and  $R(H_2O)_n$  is the solute surrounded by a solvation sphere of n molecules. The change in the free energy of the dissolution can be given as the sum of two terms

$$\Delta G = \Delta G_{\text{mix}} + \Delta G_{\text{solv}} \dots\dots\dots (3)$$

where  $G_{\text{mix}}$  is the change in the Gibbs free energy for the formation of a regular solution, and  $G_{\text{solv}}$  is the free energy change when n moles of water are transferred from pure water to the solvation spheres of one mole of nonpolar solutes. For methane and ethane, Hvidt (1983) estimates  $G_{\text{solv}}$  to be -2.7 and -2.0 kJ mole<sup>-1</sup>, respectively. It can be concluded, then, that the formation of a clathrate-like structure around a nonpolar solute increases the solubility of the solute.

#### b) Continuum Models

Continuum models of liquid water consider all the water molecules in a container to be tetrahedrally bonded by hydrogen bonds, forming a single unit. The effect of temperature is not to break the ice-like clusters, as in the mixture models, but rather to distort the tetrahedral bond angles away from their normal value of 109°.

A continuum model of water was first proposed by Bernal and Fowler (1933) in their classical work. They were the first ones to propose a continuous, disordered network of

tetrahedrally bonded molecules as a model for the structure of water. In his sequel to this work, Pople (1951) estimated the average distortion of the hydrogen bonds by assuming that the orientation of two water molecules depends only on the energy required to bend the hydrogen bond between them. This energy was approximated by a hydrogen bond binding force constant,  $K_{\theta}$  which depends only on the hydrogen bond angle  $\theta$ . This model can account for the temperature dependence of the static dielectric constant, and for the observed oxygen-oxygen pair correlation function.

Recently, a new continuum model has been developed, namely, the Random Network Model (RNM) (Rice and Sceats, 1981; Sceats and Rice, 1982). The main difference between the RNM and Pople's model is the separation of the time scales for the various classes of molecular motions in liquid water. For the V-structure of water they propose a continuous distorted hydrogen bond network, which has the following characteristics (Rice and Sceats, 1981): a) the intermolecular separation is essentially constant, and centered about the value in a crystalline phase; b) the bonding is irregular, so that there are different odd- and even-numbered rings in the network; and c) the distribution of values for the hydrogen bond angle has a nonzero width. Sceats and Rice (1982) introduced a Random Network Potential (RNP), which depends only on the average oxygen-oxygen separation and the deviation of the hydrogen bond from linearity. The RNP incorporates several quantum mechanical

corrections, such as the dependence of the zero-point energy on the hydrogen bonding, and the proper weighting of thermal motions.

The RNM is an intermediate stage theory, in the sense that it does not start with a given water-water intermolecular interaction potential, predicting all the properties of the liquid from such a potential. Instead, the intermolecular potential is replaced by a potential due to the whole hydrogen bonded network, the RNP. The effective water-water interaction potential, the molecular motions, and other properties are expressed only as functions of the distribution of intermolecular distances and distortions of the hydrogen bonds. Properties such as the temperature dependence of the width of the Raman peaks for ice Ih (the form of ice stable at one atmosphere and temperatures lower than 273 K), liquid water and D<sub>2</sub>O; the O-O-O angle distribution functions, oxygen-oxygen pair correlation functions, and the thermodynamic functions are all well predicted by the RNM.

c) The Current View, A Consensus.

Over the years a consensus appears to have been reached among the different positions. As Nemethy, Peer and Scheraga (1981) wrote in a recent review paper:

"The overall structure consists of extensive three dimensional random networks of mostly nonlinearly hydrogen-bonded molecules. The local structure tends to be tetrahedral. This



description is similar to Pople's model of liquid water and its recent extension in the random network model of Sceats et al. These results rule out any model of water wherein a small number of species that consist of a specific number of water molecules with fixed intermolecular geometries are assumed to exist; two-state interstitial models specially are not realistic."

Computer simulation techniques, employing either Monte Carlo or molecular dynamics simulations, have shown that the inclusion of a nonpolar solute increases the order of the water molecules surrounding it, forming a clathrate-like structure (Nemethy, Peer and Scheraga, 1981; Scheraga, 1982). The number of nearest neighbors has also been shown to increase, from 5 for a water molecule in the pure liquid, to 15 for a nonpolar solute of the same size (Rapaport and Scheraga, 1982). The increase in structure around a nonpolar solute does not imply the presence of permanent structures around the solute, as Nemethy, Peer and Scheraga (1981) point out:

"This does not imply the presence of long-lived or solid-like structures, but merely a slightly increased correlation time and lessened irregularity."

The aggregation of nonpolar solutes in aqueous solutions remains a point in dispute. Scheraga (1982) cites several computer simulations of the potential of mean force (defined as the solvent-induced pair potential between two solutes (Nemethy, Peer and Scheraga, 1981)) between two Lennard-Jones solutes, which shows two stable configurations. One in which the two solutes are in contact,

and one in which the two solutes are separated by one water molecule. However, Rapaport and Scheraga (1982) made a very long molecular dynamics simulation of four solute molecules "dissolved" in 339 water molecules, lasting for about 70 ps, which showed no tendency for the solutes to aggregate, even when they were placed together at the beginning of the run.

In the next chapter the effect of an electrolyte on the activity coefficient of a dissolved nonpolar solute will be discussed, as it is necessary to understand the solubility of petroleum hydrocarbons in sea water.

### Solubility in Electrolyte Solutions

The presence of an electrolyte changes the activity coefficient of a dissolved nonelectrolyte, hence changing its solubility. For many electrolyte-nonelectrolyte systems the experimental results can be described by the empirical Setchenov equation:

$$\log f/f^0 = \log S^0/S = k_s C_s \dots\dots\dots (4)$$

where  $f$ ,  $S$ ,  $f^0$  and  $S^0$  are the activity coefficient and solubility of the nonelectrolyte in pure water and in an aqueous electrolyte solution, respectively;  $C_s$  is the concentration of the nonelectrolyte, and  $k_s$  is the salting constant, also called the Setchenov parameter. If  $k_s > 0$  the solubility of the nonelectrolyte decreases in the presence of the electrolyte, and the process is referred to as "salting-out". If  $k_s < 0$ , then the solubility increases, and the nonelectrolyte is said to be "salted-in".

It can be shown that equation (4) is a special case of the following equation (Long and McDevit, 1951):

$$\log f/f^0 = \log S^0/S = k_s C_s + k_i (S - S^0) \dots\dots\dots (5)$$

when both  $S$  and  $S^0$  are small, even if  $k_i$  is of the same

order of magnitude as  $k_s$ . For polar solutes the term containing  $k_i$  must be taken into account, even if eq. (4) holds, because in such cases the experimentally measured  $k_s$  would not be the theoretically significant salting constant.

When results for different electrolytes, but for the same nonelectrolyte are reviewed several generalizations can be made (Long and McDevit, 1952; Gordon, 1975): a) the order of values for  $k_s$  is constant, with very few inversions; b) the single-ion contributions to  $k_s$  are, to a very good approximation additive; c) the contribution of the anions to  $k_s$  becomes more negative with increasing ionic radius; d) the cationic contributions to  $k_s$  do not follow either crystal or hydrated ion radii (these contributions are in the order  $\text{Na}^+ > \text{K}^+ > \text{Li}^+, \text{Rb}^+ > \text{NH}_4^+ > \text{C}_s^+ > \text{H}^+$ ); and e) for organic ions  $k_s$  becomes more negative with the presence of aromatic rings, or with increasing chain length in aliphatic organic ions. In general, it has been found that large ions with low charge will "salt-in" a nonpolar nonelectrolyte; such is the case of the tetraalkylammonium salts, the perchlorates, and straight chain carboxylic acids.

### Theoretical Models.

Many different models have been proposed to predict the magnitude of  $k_s$  for any given pair of electrolyte - nonelectrolyte cosolutes. In general, these models can be divided into three categories: electrostatic, thermodynamic and statistical mechanical. Since this review does not

pretend to be exhaustive only a few examples in each category will be discussed.

### Electrostatic Models.

In general, electrostatic models of salting-out explain the decrease of the solubility in terms of two different processes (Bockris and Reddy, 1970). The first contribution is due to the decrease in the number of "free" water molecules left to dissolve the nonelectrolyte, because many water molecules are tied up in the primary solvation shell of the electrolyte. If  $n_s$  is the number of water molecules in the first hydration shell of the ion, then the number of "free" molecules will be

$$n_f = 55.5 - C_s n_s \dots\dots\dots (6)$$

and the decrease in solubility will be given by

$$S = S_0 - S_0 C_s n_s / 55.5 \dots\dots\dots (7)$$

The second contribution arises from the secondary hydration shell of the ion, and it is related to the work done when one mole of water molecules around an ion are replaced by one mole of nonelectrolyte molecules. This effect arises from the differences in the ion-dipole, or ion-induced dipole, interactions between the nonelectrolyte and water. The decrease in the nonelectrolyte's solubility due to this factor is given by:

$$S = S_0 N C_s [4\pi (Ze)^2 (\epsilon_w - \epsilon_{ne}) / 1000 \epsilon^2 k T r_h] \dots\dots\dots (8)$$

where  $Z$  and  $e$  are the charge on the ion and on the electron respectively;  $\alpha_w$  and  $\alpha_{ne}$  are the orientation polarizabilities of water and nonelectrolyte,  $\epsilon$  is the dielectric constant of water,  $k$  is Boltzmann's constant, and  $r_h$  is the radius of the primary solvation shell.

By combining equations 7 and 8 one obtains

$$S_o - S/S_o = n_s C_s / 55.5 + N C_s [4\pi (Ze)^2 (\alpha_w - \alpha_{ne}) / 1000^2 k T r_h] \dots (9)$$

Equation (9) correctly predicts salting-out for many nonelectrolytes; however, the only possibility to predict salting-in is when the the nonelectrolyte has a dipole moment greater than that of water. Experimentally, salting-in has been observed for many systems in which the nonelectrolyte was nonpolar, and the electrolyte was big and with a low charge. The only way out is to introduce a correction term which takes into account dispersion forces (instantaneous dipole-instantaneous dipole interactions, which are attractive). This term is of the form

$$\alpha_{di} \alpha_{dne} / Z r^6 \dots (10)$$

where  $\alpha_{di}$  and  $\alpha_{dne}$  are the distortion polarizabilities of the ion and nonelectrolyte, respectively. By taking into account dispersion forces electrostatic theory predicts that salting-in will occur if dispersion forces overcome the ion-dipole interactions, that is, if both the ion and the

nonelectrolyte are big enough, so that the product  $d_i d_{ne}$  is big (the distortion polarizability of a molecule is roughly proportional to the cube of the molecular radius).

Electrostatic equations usually predict  $k_s$  values that are very similar for all 1:1 electrolytes, and salting-in if  $\alpha_{ne} > \alpha_w$  for all salts, which is not usually the case. The theory has been criticized also as not being convincing because the input parameters are very flexible (Gordon, 1975). In the recent literature electrostatic theories of salt effects have received very little attention.

#### Thermodynamic Models.

These models, developed in their original form by McDevit and Long (1952), are based on the Tamman-Tait-Gibson (T-T-G) equation for electrolyte solutions (Leyendekkers, 1976):

$$B^P V^P = 0.4343 X_1 C / (B + P_e + P) - X_2 d\psi_2 / dP \dots \dots \dots (11)$$

where  $B^P$  is the isothermal compressibility of water at an applied pressure  $P$ ,  $V^P$  is the volume of the solution at pressure  $P$ ,  $X_1$  is the number of grams of water per gram of solution,  $C$  is equal to  $0.315 V_w$ ,  $V_w$  being the specific volume of water,  $B$  is a parameter related to the internal pressure of liquid water,  $\psi_2$  is the apparent specific volume of the electrolyte in solution, and  $P_e$  is the effective pressure exerted by the electrolyte. The terms containing  $\psi_2$  are negligible at moderate pressures ( $P < 1000$  bar).

The T-T-G model assumes that the properties of an aqueous electrolyte are the same than those of pure water under an additional pressure,  $P_e$ , exerted by the electrolyte. The T-T-G model has been succesfully applied to the prediction of properties such as the refractive index (Leyendekkers and Hunter, 1977 and 1977a), viscosity (Leyendekkers, 1979), and the heat capacity (Leyendekkers, 1980) of aqueous electrolyte solutions and seawater.

McDevit and Long (1952) assumed that the only significant interaction in the process of dissolving a nonelectrolyte is the work necessary to create a cavity in the solvent, large enough to accommodate the solute. The nonideal work of transferring one mole of solute molecules from pure water to an electrolyte solution is given by

$$W = V_1^0 P_e \dots\dots\dots (12)$$

where  $V_1^0$  is the partial molar volume of the nonelectrolyte solute. No other interaction, like solute-cavity interaction is considered.

McDevit and Long (1952) derived a limiting equation for  $k_s$  by using a Taylor's expansion of the Helmholtz free energy of the solution around  $V_0 = n_w V_w + n_s V_s$ , where  $V_s$  and  $V_w$  are the molar volume of the pure liquid salt and pure water, respectively;  $n_w$  and  $n_s$  are the number of moles of water and salt. For very small concentrations of both salt



and nonelectrolyte they found

$$k_s = V_1^0(V_s - V_s^0)/2.3B_0RT \dots \dots \dots (13)$$

where  $V_s$  and  $V_s^0$  are the "liquid" volume and partial molar volume of the salt, respectively;  $B_0$  is the isothermal compressibility of water;  $R$  and  $T$  have their usual meaning.

An equivalent expression for  $k_s$  is

$$k_s = \lim_{C_s \rightarrow 0} V_1^0/2.3RT \frac{dP_e}{dC_s} \dots \dots \dots (14)$$

This equation contains explicitly the pressure exerted by the electrolyte,  $P_e$ , instead of the "liquid volume" of the salt,  $V_s$ , which is somewhat vaguely defined.

Equations (13) and (14) correctly predict the relative change of  $k_s$  for different salts, and are in good quantitative agreement for small nonelectrolytes, such as  $O_2$ ,  $H_2$ , and the noble gases (Long and McDevit, 1952). It also correctly predicts salting-in for the five organic salts for which  $V_s$  values are known (Gordon, 1975). However, for larger nonelectrolytes such as benzene or naphthalene the estimated values of  $k_s$  are usually off by a factor of two to three. McDevit and Long (1952) proposed that a correction factor needs to be added to their equation, to take into account the nonzero distance of closest approach of the nonelectrolyte to the ions. This was attempted by

Deno and Spink (1963), who estimated the correction factor to be 0.3, finding good agreement for their measured values for tetralin, diphenylmethane and 2,4-diphenyl-2-methyl-2-pentene in sodium sulphate solutions.

Cross (1975) modified the McDevit and Long's equation to take into account the change in the nonelectrolyte's activity coefficient with respect to a change in the concentration of salt, and corrected explicitly for the nonzero distance of closest approach. His corrected equation is

$$\lim_{N_n \rightarrow 0} \log f = V_i^0 C_s (V_s - V_s^0) / 2.3RTB [1 - C_s (V_s - V_s^0) / 2] r_h / (r_h + r_n) - \log (1 + 2 \times 10^{-3} m_s M_s) \dots \dots \dots (15)$$

where  $m_s$  and  $M_s$  are the molality and molecular weight of the salt,  $r_h$  is the average hydrated ionic radius,  $r_n$  is the van der Waals radius of the nonelectrolyte,  $V_s$  is the apparent molar volume of the salt in a solution of molality  $m_s$ ,  $B$  is the isothermal compressibility of the solution and  $N_n$  is the number of moles of nonelectrolyte. The other symbols have been defined before. This equation has been very successful in predicting the activity coefficient of nonpolar compounds up to fairly high concentrations of salt (up to 16 m in the case of oxygen dissolved in KOH) (Cross, 1975), and even of the polar alkyl acetates in solutions that were up to 7 m in electrolyte concentration (Cross and McTigue, 1976). In both

cases, the agreement between measured and predicted values was excellent.

Recently Aveyard (1982) used a slightly different approach, which resulted from his work on the salt effect for alcohols (Aveyard and Heselden, 1974 and 1975) by assuming that the nonideal work of transfer  $W$  (eq. 12) depends not on  $P_e$ , but on the change of surface tension of the aqueous solution when the salt is added. This means that it has been assumed that: a) the surface tension of a microscopic cavity is the same as the macroscopic value, and b) the solute-solvent interactions are the same in pure water and in the aqueous electrolyte solution as assumed by McDevit and Long (1952). Aveyard (1982) also assumed that the work of transfer depends on the surface area of the cavity, not on the volume, as McDevit and Long (1952) did.

After noting that in many cases the surface tension of an electrolyte solution is a linear function of  $m_s \phi_s$ , where  $\phi_s$  is the osmotic coefficient at molality  $m_s$ , Aveyard arrived at the following expression for  $k_s$ :

$$k_s = (\pi N)^{1/3} (4.44 V_i)^{2/3} \nu (r_H^+ - r_X^+) \phi_s / 2.3 \dots \dots \dots (16)$$

where  $\nu$  is the number of ions per mole of salt,  $r_H^+$  is the radius of the hydrated cation,  $r_X^+$  is the crystallographic cationic radius, and  $\phi_s$  is the osmotic coefficient for a one molal salt solution.

Assuming that  $(r_H^+ - r_X^+)$  is equal to the molecular diameter of the solvent, and that the pure solvent consists of close-packed spherical molecules, then for an aqueous solution of a 1:1 electrolyte equation (16) reduces to

$$k_S = 3.86V_w^{1/3}V_i^{2/3}\phi_S \dots \dots \dots (17)$$

where  $V_w$  is the molar volume of pure water. Agreement with experiment was found to be very good for nonpolar compounds ranging from methane to diphenyl, except for the salts containing the sulphate anion, but if  $(r_H^+ - r_X^+)$  is assumed to be 1.0 nm instead of 0.56 nm the agreement is excellent.

In agreement with both equations (16) and (17), a linear relation was found between  $V_i^{2/3}$  and  $k_S$ , in contrast to the McDevit-Long equation (13), which predicts a linear relationship between  $V_i$  and  $k_S$ .

### Scaled-Particle theory.

For a long time it has been considered that the dissolution of a solute in a liquid is a two-step process: 1) the creation of a cavity in the solvent, large enough to accommodate the solute, and 2) the introduction of a solute molecule into the cavity, that is, the energy of interaction of the solute with the cavity (Clever and Battino, 1975). At present the best approach to calculate the free energy change associated with these processes is the statistical mechanical theory of Reiss (Clever and Battino, 1975;

Desrosier and Morel, 1981), the Scaled Particle Theory (SPT).

SPT considers liquids as composed of particles with spherical symmetry and hard cores repelling each other with infinite force. The theory is based upon the properties of the exact radial distribution function, and from that an approximate expression for the reversible work required to add a spherical particle into a liquid composed of spherical particles is derived. The particles are assumed to obey a pairwise additive potential, and an additional particle obeying the same potential is introduced into the liquid by the procedure of distance scaling (Pierotti, 1976; Desrosiers and Morel, 1981).

For dilute solutions of gases it can be shown that

$$RT \ln H_{2,1} = \bar{G}_c + \bar{G}_i + RT \ln RT/V_1^0 \dots\dots\dots (18)$$

where  $\bar{G}_c$  and  $\bar{G}_i$  are the partial molar free energies for cavity formation and interaction, respectively;  $V_1^0$  is the pure solvent molar volume, and  $H_{2,1}$  is the Henry's law coefficient. Pierotti (1963, 1965, and 1976) applied SPT to the solubility of gases in real liquids, and calculated the molecular parameters of water that are needed in the calculations (hard-sphere molecular diameter, work function, and polarizability). These values are in good agreement with the values calculated using other methods (Pierotti, 1976).

For a complete compilation of all the necessary equations see the review by Pierotti (1976).

Shoor and Gubbins (1969) applied SPT to the solubility of gases in concentrated electrolyte solutions, and from their results they found a general expression for  $k_s$ . After assuming that the water-salt-nonelectrolyte system consists of  $m$  components, and that the solvent is a mixture of  $m-1$  components they obtained

$$\ln H_{2,1} = \bar{g}_1^h/kT + \bar{g}_1^s/kT + \ln (kT d_j) \dots \dots \dots (19)$$

where  $d_j$  is the number density of component  $j$ ,  $\bar{g}_1^h$  and  $\bar{g}_1^s$  are the free energies of creating a cavity in the electrolyte solution and of introducing the solute in the cavity, respectively.

Masterton and Lee (1970) extended the derivation of Shoor and Gubbins (1969) to obtain a general expression for  $k_s$ . They obtained

$$k_s = k_a + k_b + k_g \dots \dots \dots (20)$$

where  $k_a$  is the contribution from the cavity formation,  $k_b$  is the term containing the solute-cavity interaction, and  $k_g$  is a statistical term which disappears when the solubility is expressed in either mole liter<sup>-1</sup> or Bunsen coefficients (Masterton, 1975). Full expressions for all the terms in eq. (20) are given in Appendix A. The term  $k_a$  always leads to

salting-out, and it increases as the molecular diameter of the solute increases. It becomes smaller with increasing temperature. The term  $k_p$  always leads to salting-in, and its magnitude decreases with increasing temperature. Masterton (1975) recalculated equation (20) for seawater in the temperature range from  $0^\circ$  to  $40^\circ\text{C}$ . At  $25^\circ\text{C}$  the calculated values agree very well with the experimental values, but the temperature coefficient is about half the experimental one. For bigger solutes, such as cyclohexane and benzene the agreement is not so good (Tien Chang et al., 1974).

A further elaboration to SPT is the "Perturbation Theory" of Tiepel and Gubbins (1973). Full equations are given in Appendix A. The main differences between the SPT and perturbation theory are that Tiepel and Gubbins do not assume that  $g^i = e^i$ , where  $e^i$  is the internal energy contribution to the solute-cavity interaction term; and that Tiepel and Gubbins (1973) assume that a real liquid behaves as a hard sphere fluid only in the high-temperature limit, so that their theory involves an expansion around  $T = \infty$ . The agreement of the perturbation theory with experiment is slightly better for big solutes than it is for SPT. However, both theories have been criticized on the basis that pairwise additivity seems unlikely in aqueous solutions, and that the assumption of a random distribution of particles breaks down for big solutes and for polar solutes (Cross, 1975). Another criticism is that the thermodynamic functions for cavity formation are very sensitive to the solvent

molecular diameter. A change of only 0.1 Å in the diameter of water produces a 30% change in  $\bar{G}_C$ , which is well within the differences of the different estimates available (Desrosier and Morel, 1981).



### OBJECTIVES.

From the discussion above, it can be seen that the study of the solubility of hydrocarbons is very important from both theoretical and practical points of view. A review of the literature reveals that very little is known about the solubility of hydrocarbons in seawater at 25°C and one atmosphere and even less is known at other temperatures or pressures. Only two papers deal with solubilities in seawater at temperatures other than 25°C, and then only for a very limited range of temperatures and salt concentrations. The results of this review are summarized in table I.

To the best of our knowledge only two papers so far have dealt with the effect of pressure on Setchenov parameters (Suzuki et al., 1974; Gerth, 1983), and neither of them was done in seawater. All that is known about Setchenov parameters in seawater is at 25°C and 1 atm, which is equivalent to the specific conditions found in a very shallow tropical sea while the average temperature and pressure in the ocean are 5°C and 400 atm (the oceans' average depth is 3,800m).

It is the purpose of this work to study the solubility of naphthalene, the simplest polycyclic aromatic hydrocarbon as

a function of the salt content and the temperature, in ranges that span those likely to be found in natural ecosystems. Another goal is to set up a high-pressure generator, to study the effect of pressure on the solubility of hydrocarbons.

Table I. Setchenov coefficients for hydrocarbons in sea water.

Compound	temp.	$k_s$	reference
Naphthalene	25°C	0.256	Gordon and Thorne, 1967
Benzene		a	Brown and Wasik, 1974
Toluene	0 - 20°C		
Ethylbenzene			
Dodecane		0.22	Sutton and Calder, 1974
Tetradecane		0.25	
Hexadecane		0.68	
Octadecane	25°C	0.95	
Eicosane		0.68	
Hexacosane		2.23	
Toluene		0.206	Sutton and Calder, 1975
Ethylbenzene		0.224	
o-Xylene		0.165	
p-Xylene		0.192	
Isopropylbenzene		0.258	
1,2,4-Trimethylbenzene		0.239	
1,2,3-Trimethylbenzene		0.262	
1,3,5-Trimethylbenzene		0.259	
n-Butylbenzene		0.306	
s-Butylbenzene		0.235	
t-Butylbenzene		0.198	

Table I. Continued.

Compound	temp.	$k_s$	reference
Naphthalene		0.3031	Eganhouse and Calder, 1976
Biphenyl	25°C	0.4119	
Phenanthrene		0.3871	
Toluene		0.166	Rossi and Thomas, 1981
Acenaphthene	25°C	0.238	
Pyrene		0.319	

<sup>a</sup>the  $k_s$  values change with temperature. A plot of  $k_s$  as a function of temperature is given in the Discussion.

Solid polycyclic aromatic hydrocarbons were chosen because they are the most toxic fraction of crude oils, their metabolic products have been shown to be carcinogenic, and because they present fewer complications due to colloid formation, or to "accomodation" in the structure of the solvent.

### EXPERIMENTAL

Naphthalene was zone refined (James Hinton, Valparaiso, IA), phenanthrene and anthracene were scintillation grade (Eastman). The salts NaCl, KCl,  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{Na}_2\text{SO}_4$  were from Alpha (Ultra Pure grade).  $\text{NaHCO}_3$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  were from Baker (reagent grade). Hexane and pentane were obtained from Malinckrodt (reagent grade), and methylene chloride was supplied by Aldrich (Spectro Quality, Gold Label). All these reagents were used as received, without further purification. The water used throughout this work was deionized and then distilled from an all glass still (Corning model AG-2).

Natural seawater was IAPSO standard seawater (Institute of Oceanographic Sciences, Surrey, England), which is used as a salinity standard and therefore is provided with a very accurate value of its salt content.

All absorption spectra were recorded with a Cary 219 double-beam uv-vis spectrophotometer with a nominal slit of 0.5 nm. Matched one centimeter quartz cuvettes were used, and a baseline was recorded by running a spectrum with distilled water in both the reference and sample beams. The temperature of the solutions was controlled by running water and propylene glycol from a thermoregulated bath (Lauda

D8/25) through the cuvette holder.

In order to accommodate the high pressure cell (see below), the cuvette holder was removed and replaced by a custom made holder, that aligned the optical axis of the high pressure cell with the sample beam of the instrument. In the reference beam a block of plastic, painted black to minimize stray light, was placed. This block of plastic had a hole of the same diameter as the opening of the optical axis of the cell. This was done to approximately match the reference and sample light intensities, thus keeping the baselines in a low range of absorbances. The whole sample compartment was covered with a light tight wooden box, painted black to minimize scattered light.

Luminescence measurements were done on a Perkin-Elmer LS-5 spectrofluorimeter. One centimeter quartz fluorescence cuvettes were used. The cell holder was kept at the same temperature as the solution to be analyzed by circulating water from a Lauda B-1 thermoregulator. A nominal slit of 3 nanometers was used for the excitation and emission monochromators. The excitation and emission wavelengths for phenanthrene and anthracene were 300, 365, 258, and 401 nanometers, respectively.

All temperature measurements were done with a digital telethermometer (Bailey model BAT-12).

The electrolyte solutions were prepared gravimetrically

in the range 0 to 0.5 molal, except for the NaCl and KCl solutions, for which the range was 0 to 1 molal. The concentration of the electrolyte solutions are in the molality scale (moles of solute per kilogram of solvent), which is independent of both temperature and pressure; therefore no corrections for volume changes are needed. However, due to the method of measurement used here, it is necessary to correct the hydrocarbon concentration for temperature and pressure induced volume changes, even if it is expressed in the molal scale. The calibration plots were done at 25°C, so if the same solution were to be measured at a lower temperature or higher pressure, then more hydrocarbon molecules would be in the light path of the instrument, leading to an erroneously higher concentration value.

Artificial seawater solutions were prepared following the recipe given by Lyman and Fleming (1940). Only the six most important electrolytes were used because, as shown by Gordon and Thorne (1967), the contributions of the other salts to  $k_s$  is negligible. A stock solution with a salinity of about 70 parts per thousand (ppt) was prepared (the average salinity for oceanic waters is 35±2 ppt), and from it dilutions were prepared with distilled water. Natural seawater was prepared by gravimetric dilutions of natural standard seawater with distilled water. Some samples of standard seawater were irradiated with ultraviolet light from a medium-pressure mercury vapor lamp overnight in order



to oxidize any dissolved organic matter that might have been present.

### One Atmosphere Work

In one part of the work the solubilities of naphthalene in water and electrolyte solutions were determined by equilibrating an excess of this aromatic compound in 100 ml flasks containing the solvent under study. These flasks were placed in a thermostatically controlled water bath (Haake model E52). Typically, the temperatures were 8, 15, 20, 25, 30, and 35°C. Given that a reliable and consistent method was needed to remove the excess undissolved naphthalene from the saturated solutions, different filtration methods were tested. A known amount of naphthalene was dissolved in methanol first to make sure that no crystals would be present in the solutions. An aliquot of the methanolic solution was diluted in water in such a way that the final concentration of methanol in water was less than 0.05% v/v, and the final concentration of naphthalene was about half the saturation solubility. A 5 ml glass syringe was filled with the solution to be analyzed, and fitting with different filters placed at the tip of the syringe. In the case of the glass wool filter, it was placed between the barrel of the syringe and the needle. The concentration of naphthalene in the filtrate was calculated from the absorbance at 276 nm and the absorptivity value given by Gordon and Thorne (1967). The results are given in Table II as the percent naphthalene

that passed through the filter. The rest of the naphthalene was probably adsorbed on the filter, or evaporated during the filtration. Each value given is the average of at least seven trials. Based on these results the glass wool filter method was chosen.

In another parts of the work a different approach was tried to obtain saturated solutions of hydrocarbons. In this method, developed at the U.S. National Bureau of Standards (DeVoe et al., 1981; Wasik et al., 1983; May et al., 1983; Tewari et al., 1981; Tewari et al., 1982), the surface area of contact between the hydrocarbon and the solvent is greatly increased, thereby leading to decreased saturation times. Typically, the hydrocarbon of interest is deposited on 60-80 mesh glass beads (Alltech Associates) by adding 20 g of the beads to 200 ml of a 0.1% w/w solution of the hydrocarbon in methylene chloride, and then evaporating the solvent in a rotary evaporator. A 60 X 0.6 cm polypropylene tube was filled with the dry beads and placed inside a one meter water jacket connected to a thermoregulated bath (Lauda model B-1). For equilibration between 200 and 500 ml of water at 50°C were pumped through the column using a Bodine NSI-34RH pump. Then, water or seawater at the appropriate temperature was pumped through the column. The effluent from the column was collected in a one centimeter quartz cuvette, and the concentration of the hydrocarbon measured by emission or absorption spectroscopy. Calibration curves were done by emission spectroscopy for phenanthrene

Table II. Comparison of several filters for transmission of aqueous solutions of naphthalene.

filter	efficiency <sup>a</sup>
Unfiltered	100.0 %
Glass-wool	98.5 %
Glass-fiber	97.9 %
Needle filter (5) <sup>b</sup>	97.8 %
Millipore AH (0.45)	83.0 %
Polycarbonate (1.0)	94.0 %
Whatman 3	91.9 %
Cellulose (0.45)	79.5 %

<sup>a</sup>Referred to an unfiltered, unsaturated solution.

<sup>b</sup>The number in parenthesis refers to the nominal pore size in microns.

and anthracene in water. These plots were linear up to saturation. (See figures 1 and 2).

### High-Pressure Work

The high pressure work was done with a custom built high pressure generator assembled according to our specifications by the Stanford University machine shop.

A block diagram of the high pressure generator is shown in figure (3). It consists of an air driven high pressure pump (Haaskel Eng. and Supply Co., model DHE-302), which converts the compressed air input (about 30 psig) provided by a one HP air compressor (Sears model 919-176210) into high hydraulic pressure by means of a large area piston of nominal ratio 302:1. The high pressure so obtained is further increased by a 1:10 high pressure intensifier (Haaskel model 15770-1). All connections between the different components are made with seamless stainless steel super pressure tubing (1/4 inch, rated at 100,000 psi) provided by Aminco (Silver Springs, Maryland).

Non-rotating stem three-way cross valves (Aminco 44-19155, 100,000 psi) (A, B, C and D in fig. 3) were used to separate different sections of the generator and the high pressure cell. For the study of aqueous solutions the pressure transmitting fluid was distilled water. However, pentane and hexane were used in some other experiments. Thus, with these valves shut, the optical high pressure cell

Figure 1

Calibration plot for phenanthrene in water, by emission spectroscopy.

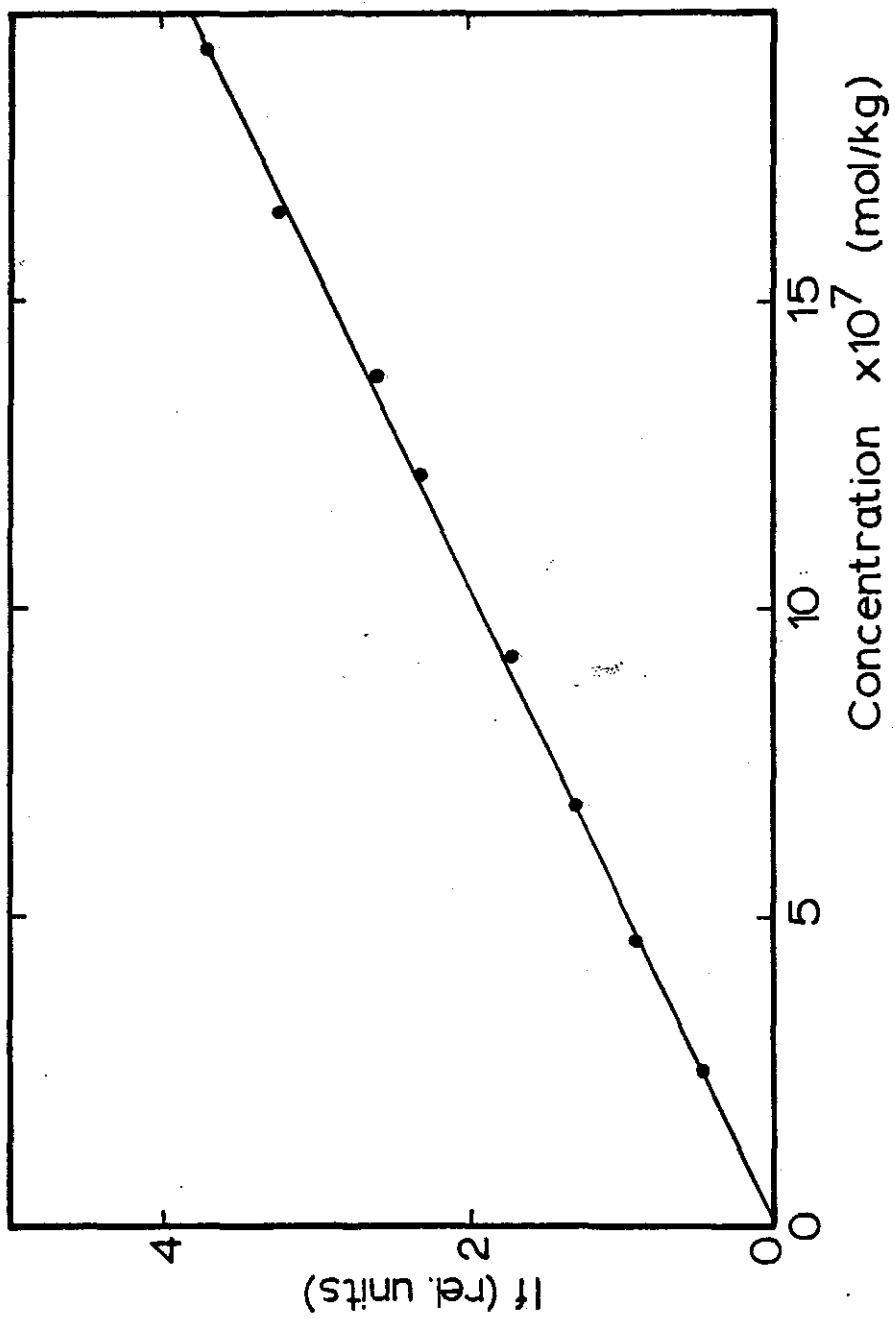


Figure 2

Calibration plot for anthracene in water, by emission spectroscopy.

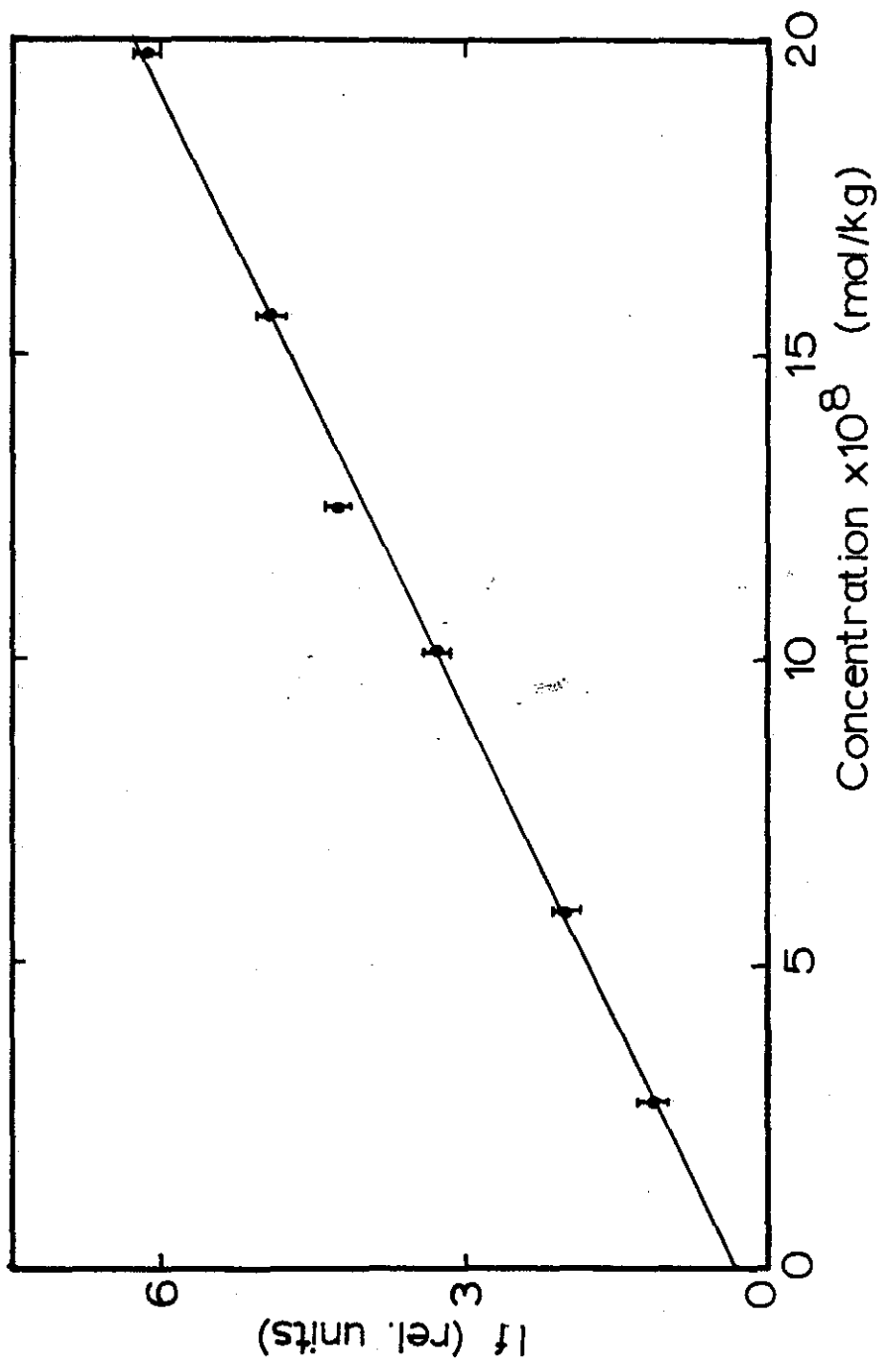
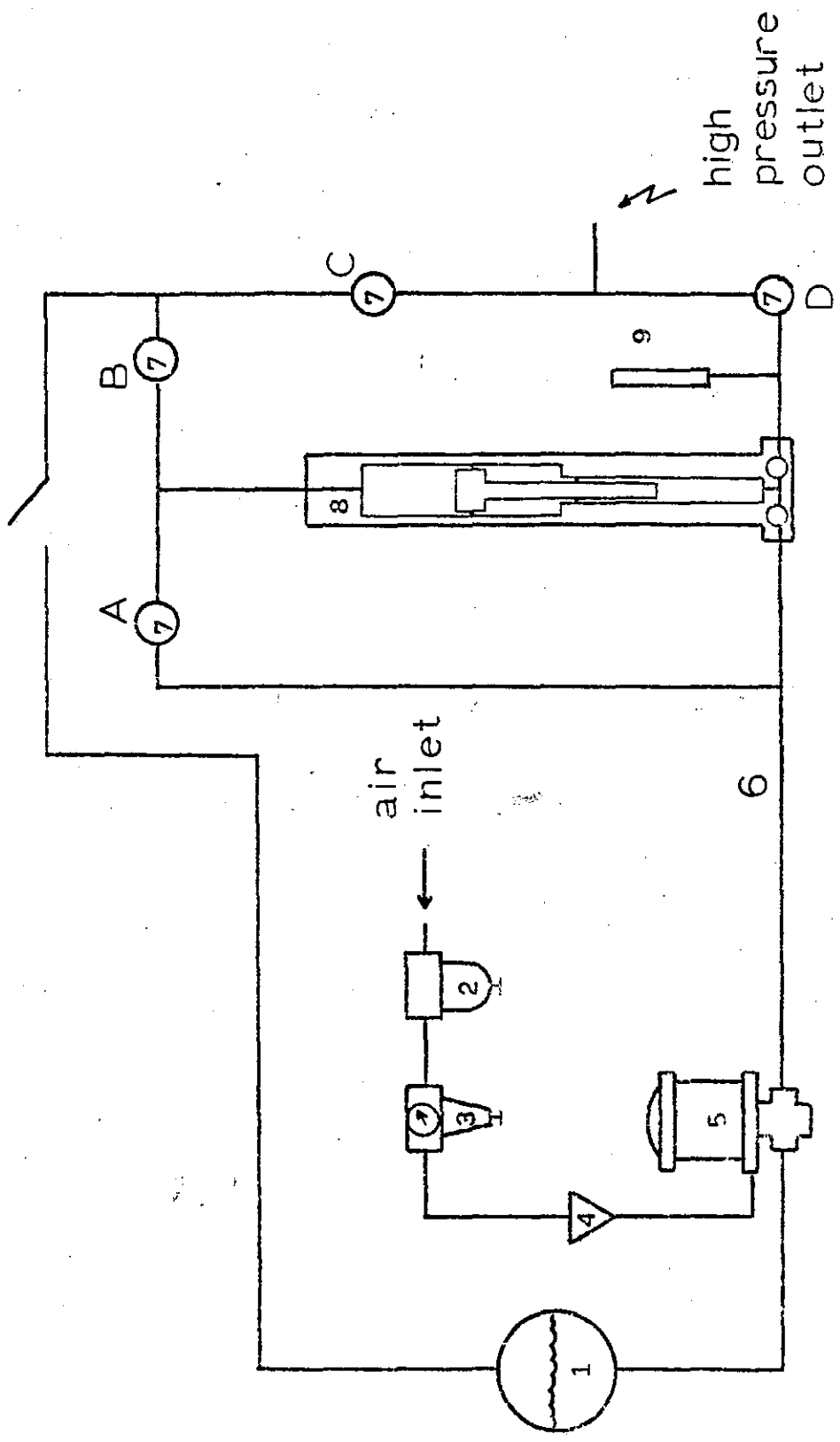




Figure 3

Block diagram of the high pressure generator. (1) is the fluid reservoir; (2) is a filter; (3) pressure gauge; (4) is a shut-off valve; (5) high pressure pump; (6) high-pressure tubing; (7) three-way cross valves; (8) high pressure intensifier; (9) high pressure transducer.



can be carried under pressure to the Cary 219 Spectrophotometer.

Pressures are measured with a pressure transducer (Precision Sensors model 6550-100). A 9.8 V DC excitation potential was applied to the high pressure transducer by a custom built power supply. The output potential was measured with Keithley 169 multimeter. The pressure was then calculated from a calibration table provided by the manufacturer. See table III. Since this component is connected to the high pressure generator via a 60,000psi rated coupler (Autoclave Engineers) the cells can be used safely to pressures up to 4 kilobars.

Typically, in a high pressure experiment the air compressor is started, taking it to a pressure of 30 to 40 psi. The air-liquid pump is started by opening its shut-off valve. If valves A through C are closed and D is open, it is possible to get an exit pressure of up to 9000 to 12,000 psi by increasing the outlet pressure of the compressor, without using the high pressure intensifier.

For higher pressures, it is necessary to use the pressure intensifier, and make sure that the piston in the intensifier is up. In order to raise the piston, valve B is open and the other three-way valves shut. This causes the pressure to increase only in the lower arm of the generator, pushing the piston up. Normally no more than seven strokes of the pump are needed to take the piston up. Once the

Table III. Calibration table for the high pressure transducer, based on values obtained with N.B.S. traceable laboratory standards.

pressure (psi)	output (mV)	
	increasing	decreasing
0	0.00	0.008
10,000	1.713	1.694
20,000	3.430	3.384
40,000	6.855	6.773
60,000	10.277	10.190
80,000	13.668	13.617
100,000	17.050	17.050

piston is up, valve B is shut and the high pressure cell is connected to the outlet port of the generator. To increase the pressure valves A and D are opened, thus allowing the compressed water coming from the pump to get into the upper arm of the generator. The compressed water in the upper arm pushes the piston down, increasing the pressure in the lower arm of the generator by a factor of ten, which in turn increases the pressure in the high pressure cell through valve D. Once the desired pressure has been reached, as indicated by the reading in the multimeter, both valves D and the one connected to the cell are closed, and the cell disconnected from the generator and taken to the spectrophotometer.

To release the pressure the pump's shut-off valve must be closed, and all the three-way valves must be open. When the pressure inside the generator is one atmosphere again, as indicated by a reading of zero in the multimeter, valves A through D are closed again and the generator is ready for another experiment.

The high pressure optical cell is shown in Figure 4; its outside dimensions are 5.69 cm in diameter and 3.71 cm high and it fits the sample compartment of the Cary 219 Spectrophotometer and the Perkin-Elmer LS-5 Spectrofluorimeter. The cell geometry is a modification of the original design by Fichten (Rodriguez, 1978), which allows the use of the cell at low pressures without leaks.

Several cells were built from this design at the Stanford University machine shop, and were heat treated for hardness to a Rockwell C scale value of 50-55.

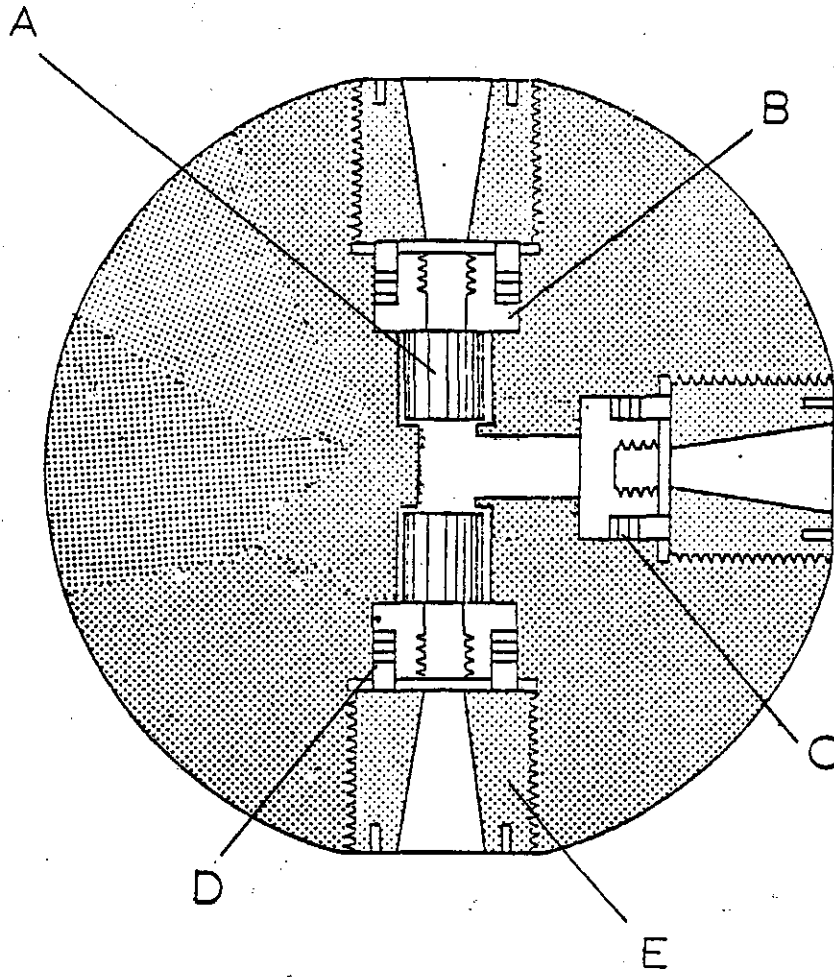
The optical windows are  $60^\circ$  taper Lynde synthetic sapphires (A) made by Union Carbide. The windows are 0.635 cm in diameter by 0.635 cm in length, ground optically flat on both ends. Sapphires were ordered with a  $3.81 \times 10^{-2}$  cm radius on both edges to help prevent cracking under high pressure. The sapphires are sitting on 'O' rings, and held in place by two mushroom plugs (B), which in turn are supported by thin packing rings made of copper, indium, Teflon and brass (C), prevented from extruding by two small beryllium-copper rings of triangular cross-section (D) which rest against the face of a hardened support ring of the same material. The support ring is held in place by a threaded plug (E) with a  $10^\circ$  tapered aperture hole to minimize shadowing; this plug can be screwed in, flush with the cell body. The stem of the mushroom plug is backed up by this threaded plug in case it should suffer "pinch off" from the high pressures at the packing rings.

A three-way valve was attached to the high pressure cell, thus allowing us to seal the contents of the cell without pressure drops.

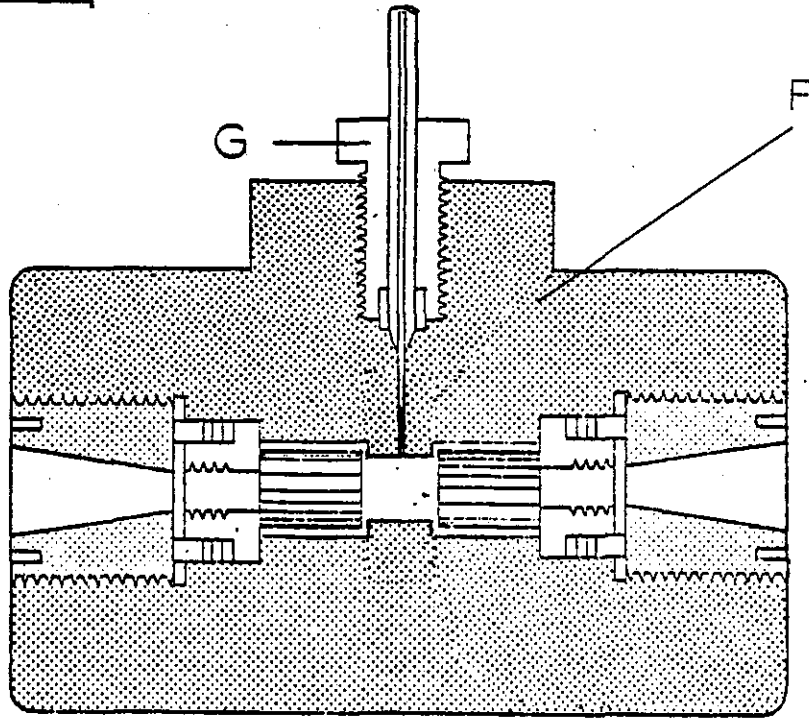
The light path of the high pressure cell is variable, depending on how tight the threaded plugs are, therefore, before each high pressure experiment it is necessary to

Figure 4

Top and side cross sectional views of the high pressure cell for absorption spectroscopy. (A) sapphire windows; (B) mushroom plugs; (C) copper, indium, teflon and brass packing rings; (D) beryllium-copper rings; (E) threaded plug; (F) stainless steel jacket; (G) Aminco hgh pressure nut and connecting tube;



1 cm

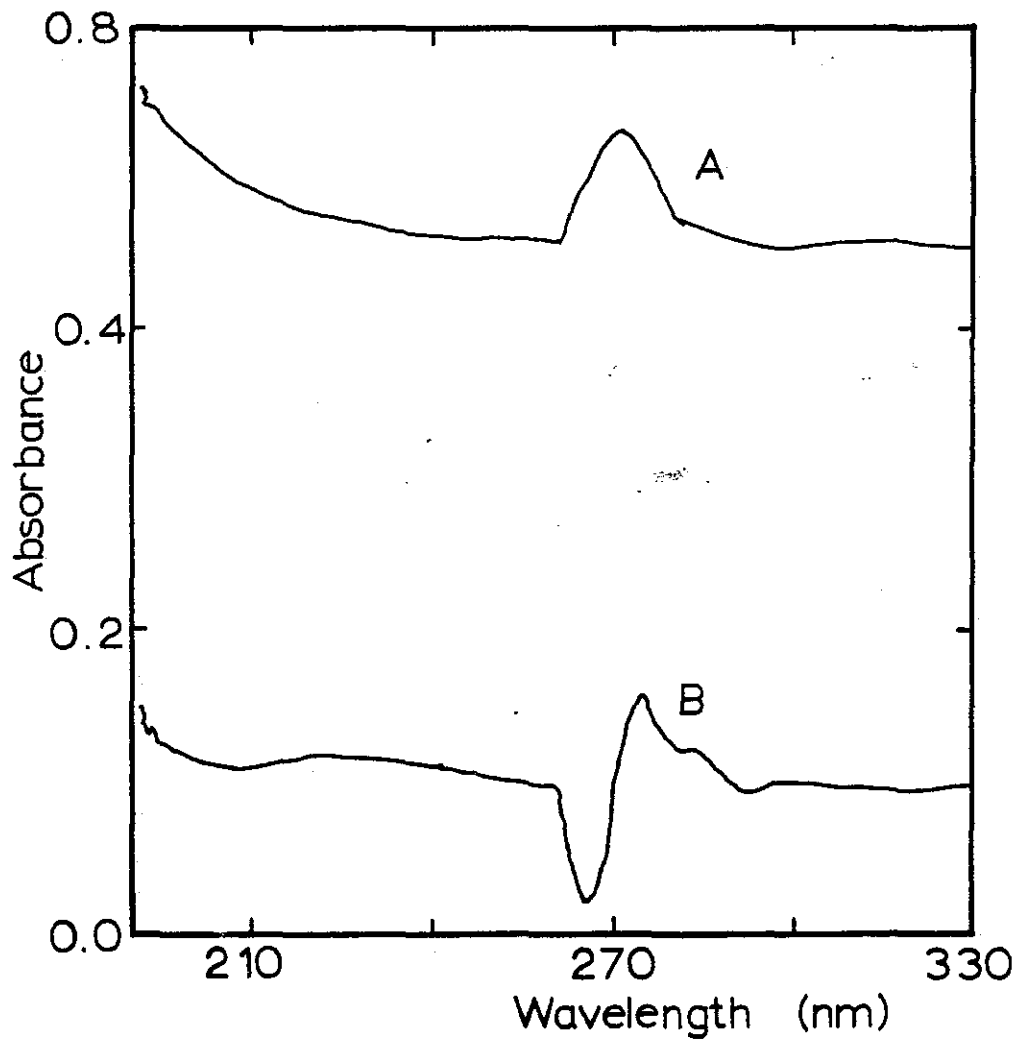




measure the one-atmosphere spectrum of naphthalene in both a one centimeter quartz cuvette and the high pressure cell to calculate the light path. Also, it is necessary to subtract the baseline produced by the cell filled with distilled water, because it produces a spectrum that cannot be removed by the AUTOBASELINE mode of the Cary 219 Spectrophotometer. As mentioned above, this effect is somewhat reduced by placing in the reference beam a block of opaque plastic with a small diameter hole . See Figure 5.

Figure 5

"Spectrum" produced by the high pressure cell filled with distilled water. (A) versus air in the reference beam; (B) versus an opaque block of plastic.



## RESULTS

### a) Shake-Flask Method

The solubility of naphthalene in NaCl, KCl, MgCl<sub>2</sub>, and Na<sub>2</sub>SO<sub>4</sub> by the shake-flask technique is given in Table IV in the temperature range 8° to 30°C, and in CaCl<sub>2</sub> and NaHCO<sub>3</sub> solutions in the range 8° to 35°C. The solubilities were calculated from the absorbance at 276 nm and the absorptivity value given by Gordon and Thorne (1967) of 4946 ± 36 kg/(mol cm). These values were corrected for temperature induced volume changes by multiplying by a correction factor R:

$$R = D_{25}/D_t \dots\dots\dots(21)$$

where D<sub>25</sub> is the density of the electrolyte solution at 25°C, and D<sub>t</sub> is the density at the experimental temperature t. The densities for the NaCl, Na<sub>2</sub>SO<sub>4</sub> and MgCl<sub>2</sub> solutions as a function of temperature were calculated from an equation given by Lo Surdo et al. (1982), and the densities for NaHCO<sub>3</sub> were calculated from the equation given by Hershey et al. (1983). These equations are of the form

$$10^3(D-D^*) = \sum_{i=1} \sum_{j=0} A_{ij} t^{j_m(i+1)/2} \dots\dots\dots(22)$$

where D and D\* are the densities of the electrolyte solution of molality m and the density of pure water, respectively;

$A_{ij}$  is the matrix containing the coefficients for the equation, and  $t$  is the temperature in degrees Celsius. The values of  $D^*$  were calculated from

$$D^* = 0.9998395 + 6.7914 \times 10^{-5} t - 9.0894 \times 10^{-6} t^2 + 1.0171 \times 10^{-7} t^3 - 1.2846 \times 10^{-9} t^4 + 1.1592 \times 10^{-11} t^5 - 5.0125 \times 10^{-14} t^6 \dots \dots \dots (23)$$

The estimated standard error of eq.(22) for the range 0 molal to saturation in salt concentration, and 0 to 50°C in temperature is less than 25 parts per million for all the salts studied (Lo Surdo et al., 1982). Since no high accuracy density data are available for KCl and CaCl<sub>2</sub> solutions, the corrections were taken to be the same as those for NaCl and MgCl<sub>2</sub>, respectively. This approximation does not cause a large error, because, as can be seen from Table IV, the corrections are small. While this thesis was being written, a paper containing density data for MgCl<sub>2</sub> and CaCl<sub>2</sub> solutions, was published Ikono (1983). Ikono shows that the difference in density between a 0.5 m solution of these electrolytes is less than 0.6 % in the range 15° to 45°C, and even smaller for more dilute solutions, confirming our earlier assumption.

The corrected solubility values were then converted to the mole fraction scale by using the equation

$$X = S / (S + m_S + m_W) \dots \dots \dots (24)$$

where X is the solubility in the mol fraction scale, S is the solubility in moles per kilogram, and  $m_s$  and  $m_w$  are the molalities of the electrolyte and water, respectively (Whitefield, 1979 ). Eq. (24) was modified, so that the molality of water in water,  $m_w$ , can be made temperature dependent:

$$m_w = D^* \times 1000 / 18.01534 \dots\dots\dots (25)$$

where  $D^*$  was calculated from eq. (22).

The uncertainties in the solubilities were estimated assuming that the error in the absorbance measurements is 1% full scale (the commonly accepted value of 0.5% was not used because the Cary 219 was used in the AUTO BASELINE mode and therefore the total uncertainty is twice 0.5%). This uncertainty was propagated through all the calculations using standard statistical techniques (Bevington, 1967).

The solubilities were then fitted to the Setchenov equation in its equivalent form

$$\log S = \log S_0 - k_s C_s \dots\dots\dots (26)$$

by the least-squares method. The results are given in Table V, along with the estimated standard errors for the fit, the

estimated uncertainty in  $k_s$ , and the coefficient of determination. The value of  $r^2$  is used instead of  $r$ , because  $r^2$  is an estimate of the fraction of the variance due to random variations of the results. Table VI gives the Setchenov parameters for each salt at 25°C, and literature values when available. Considering that different techniques were used, the agreement with the published values is very good, with the exception of KCl, which seems too high compared with the literature values.

The values for the Setchenov parameter for each salt were used to calculate the salting-out of naphthalene in seawater, by taking a weighed mean for the six salts at each temperature, the mole fraction for each salt in seawater as given by Gordon and Thorne (1967) being the weights. The values of the mole fraction for each salt are given in Table VII, and the calculated values for the Setchenov parameter in seawater are given in table VIII along with the value obtained by Gordon and Thorne (1967) at 25°C, for comparison. The agreement with their value at 25°C is excellent. This is the only one we can compare with, because this work represents the first attempt to measure the salting-out of naphthalene as a function of temperature.

The solubility values were also fitted to the integrated form of the van't Hoff equation

$$\log X = -\Delta H^{\circ}/2.303RT + C \dots\dots\dots(27)$$

where  $\Delta H^\circ$  is the enthalpy change for the process: solid naphthalene - aqueous naphthalene, C is an integration constant, and the other symbols have their usual meanings. The results for this fit are given in Table IX along with the estimated standard errors of the fit, the uncertainty in  $H^\circ$ , and the coefficient of determination. The enthalpy change for solution in water is 25 kJ/mol, the average values for the different electrolytes being 23 kJ/mol for NaCl, 25 kJ/mol for KCl, 25 kJ/mol for  $MgCl_2$ , 22 kJ/mol for  $CaCl_2$ , 25 kJ/mol for  $Na_2SO_4$ , and 25.5 kJ/mol for  $NaHCO_3$ .

The values for  $k_s$  in Table V show no trend as a function of temperature, with the exception of the results for NaCl, which show a minimum around 25°C. However, the results for NaCl and all the other salts are the same within the experimental uncertainty, the average values being 0.233 for NaCl, 0.216 for KCl, 0.282 for  $MgCl_2$ , 0.326 for  $CaCl_2$ , 0.655 for  $Na_2SO_4$ , and 0.276 for  $NaHCO_3$ . The "shake-flask" technique, because of its inherently large experimental uncertainty, seems to indicate that the Setchenov parameters for each salt are equal in the temperature range studied, a result which appears arroneous in view of our subsequent work.

The enthalpy change for the dissolution of naphthalene in the electrolyte solutions shows no systematic trend, all the values being the same within the experimental error. However, the internal consistency of the data must be



stressed, as shown both by the high values for the coefficient of determination ( $r^2$ ) for the Setchenov parameter calculations and the enthalpy change calculations, and by the very good agreement found with the  $k_s$  value of Gordon and Thorne (1967) at 25°C.

The comparison of the values reported here for the enthalpy change for the dissolution of naphthalene in water with the values in the literature shows very good agreement. May et al., (1983) recalculated some of the experimental enthalpy change values reported in the literature, and obtained values of 29.9 kJ/mol for the data of Bohon and Claussen (1951), 21.8 kJ/mol for the results of Schwartz, (1977), and 23.8 kJ/mol from the results of Wauchope and Getzen, (1972). These results compare well with the value of 25 kJ/mol obtained in this work.

Table IV. Solubility of naphthalene in aqueous electrolyte solutions, expressed in the molal and mole fraction scale.  $S$  is the uncorrected solubility, and  $S_c$  is the solubility corrected for temperature-induced volume changes. The values in parenthesis are the estimated experimental errors.

Table IV. Solubility of naphthalene in aqueous electrolyte solutions, by the shake-flask technique.

$t/(^{\circ}\text{C})$	$S \times 10^4 / (\text{mol/kg})$	$S_c \times 10^4 / (\text{mol/kg})$	Mol Fraction $\times 10^6$
water			
35	3.78	3.79 (0.05)	6.85 (0.13)
30	3.25	3.26 (0.05)	5.88 (0.12)
25	2.63	2.63 (0.05)	4.75 (0.11)
20	2.27	2.27 (0.04)	4.10 (0.11)
15	1.78	1.78 (0.02)	3.22 (0.06)
8	1.54	1.53 (0.02)	2.77 (0.06)
NaCl, $m=0.1955$			
30	2.74	2.75 (0.05)	4.95 (0.12)
25	2.33	2.33 (0.04)	4.19 (0.11)
20	2.02	2.02 (0.02)	3.63 (0.06)
15	1.68	1.68 (0.02)	3.01 (0.06)
8	1.37	1.36 (0.02)	2.45 (0.06)
$m=0.4055$			
30	2.52	2.53 (0.04)	4.53 (0.11)
25	2.16	2.16 (0.04)	3.88 (0.11)
20	1.92	1.92 (0.03)	3.44 (0.06)
15	1.57	1.57 (0.02)	2.81 (0.06)
8	1.25	1.25 (0.02)	2.24 (0.06)

Table IV. Continued.

$t/ (^{\circ}\text{C})$	$S \times 10^4 / (\text{mol/kg})$	$S_c \times 10^4 / (\text{mol/kg})$	Mol Fraction $\times 10^6$
m=0.6043			
30	2.21	2.22 (0.04)	3.97 (0.11)
25	1.90	1.90 (0.01)	3.29 (0.03)
20	1.63	1.62 (0.02)	2.90 (0.06)
15	1.37	1.37 (0.02)	2.44 (0.06)
8	1.10	1.09 (0.02)	1.95 (0.04)
m=0.8395			
30	1.94	1.94 (0.03)	3.46 (0.06)
25	1.71	1.71 (0.02)	3.05 (0.06)
20	1.45	1.45 (0.02)	2.58 (0.06)
15	1.23	1.22 (0.02)	2.17 (0.06)
8	0.971	0.967 (0.01)	1.72 (0.03)
m=1.029			
30	1.83	1.84 (0.02)	3.26 (0.06)
25	1.56	1.56 (0.02)	2.77 (0.06)
20	1.37	1.37 (0.02)	2.42 (0.06)
15	1.11	1.10 (0.01)	1.19 (0.02)
8	0.876	0.872 (0.01)	1.54 (0.03)
KCl, m=0.2023			
30	2.75	2.75 (0.05)	4.97 (0.12)
25	2.53	2.52 (0.04)	4.55 (0.11)
20	2.08	2.07 (0.04)	3.73 (0.11)

Table IV. Continued.

$t/(^{\circ}\text{C})$	$S \times 10^4 / (\text{mol/kg})$	$S_c \times 10^4 / (\text{mol/kg})$	Mol Fraction $\times 10^6$
15	1.67	1.67(0.02)	3.00(0.06)
8	1.33	1.32(0.02)	2.37(0.06)
m=0.4338			
30	2.53	2.53(0.05)	4.55(0.11)
25	2.07	2.07(0.04)	3.71(0.11)
20	1.74	1.74(0.02)	3.11(0.06)
15	1.45	1.45(0.02)	2.59(0.06)
8	1.15	1.15(0.02)	2.05(0.06)
m=0.6196			
30	2.30	2.30(0.04)	4.12(0.11)
25	2.05	2.05(0.04)	3.66(0.11)
20	1.64	1.64(0.02)	2.92(0.06)
15	1.35	1.35(0.02)	2.41(0.06)
8	1.08	1.08(0.02)	1.92(0.05)
m=0.8348			
30	2.11	2.11(0.04)	3.77(0.11)
25	1.87	1.87(0.02)	3.32(0.06)
20	1.51	1.51(0.02)	2.68(0.06)
15	1.24	1.24(0.02)	2.20(0.06)
m=1.030			
30	1.88	1.88(0.02)	3.34(0.06)
25	1.53	1.53(0.02)	2.77(0.06)
20	1.39	1.38(0.02)	2.45(0.06)

Table IV. Continued.

$t/ (^{\circ}\text{C})$	$S \times 10^4 / (\text{mol/kg})$	$S_C \times 10^4 / (\text{mol/kg})$	Mol Fraction $\times 10^4$
15	1.15	1.14 (0.02)	2.03 (0.06)
8	0.905	0.901 (0.01)	1.59 (0.03)
MgCl <sub>2</sub> , m=0.1085			
30	2.96	2.96 (0.05)	5.35 (0.12)
20	2.07	2.07 (0.04)	3.73 (0.11)
15	1.72	1.72 (0.02)	3.09 (0.06)
8	1.36	1.35 (0.02)	2.43 (0.06)
m=0.2043			
30	2.84	2.85 (0.05)	5.13 (0.12)
25	2.26	2.26 (0.04)	4.08 (0.11)
20	1.89	1.89 (0.02)	3.40 (0.06)
15	1.61	1.60 (0.02)	2.88 (0.06)
8	1.29	1.29 (0.02)	2.32 (0.06)
m=0.3174			
30	2.67	2.67 (0.05)	4.81 (0.11)
25	2.19	2.19 (0.04)	3.93 (0.11)
20	1.81	1.81 (0.02)	3.25 (0.06)
15	1.51	1.51 (0.02)	2.70 (0.06)
8	1.23	1.22 (0.02)	2.19 (0.06)
m=0.4150			
30	2.50	2.50 (0.04)	4.49 (0.11)
25	2.02	2.02 (0.04)	3.62 (0.11)

Table IV. Continued.

$t/(^{\circ}\text{C})$	$S \times 10^4 / (\text{mol/kg})$	$S_c \times 10^4 / (\text{mol/kg})$	Mol Fraction $\times 10^6$
20	1.77	1.77 (0.02)	3.17 (0.06)
15	1.41	1.40 (0.02)	2.51 (0.06)
8	1.15	1.14 (0.02)	2.04 (0.06)
m=0.5219			
30	2.29	2.29 (0.04)	4.11 (0.11)
25	1.83	1.83 (0.02)	3.27 (0.06)
20	1.60	1.59 (0.02)	2.85 (0.06)
15	1.29	1.29 (0.02)	2.30 (0.06)
8	1.06	1.05 (0.02)	1.88 (0.05)
CaCl <sub>2</sub> , m=0.07978			
35	3.99	4.00 (0.07)	7.23 (0.17)
30	3.38	3.39 (0.05)	6.12 (0.12)
25	2.79	2.79 (0.05)	5.03 (0.12)
20	2.45	2.45 (0.04)	4.41 (0.11)
15	2.03	2.03 (0.04)	3.66 (0.11)
8	1.72	1.72 (0.02)	3.09 (0.06)
m=0.1696			
35	3.81	3.82 (0.05)	6.91 (0.13)
30	3.21	3.21 (0.05)	5.79 (0.12)
25	2.60	2.60 (0.05)	4.69 (0.11)
20	2.39	2.39 (0.04)	4.30 (0.11)
15	1.94	1.93 (0.04)	3.47 (0.11)

TABLE IV. CONTINUED.

$t/ (^{\circ}\text{C})$	$S \times 10^4 / (\text{mol/kg})$	$S_c \times 10^4 / (\text{mol/kg})$	Mol Fraction $\times 10^6$
8	1.66	1.65 (0.02)	2.97 (0.06)
m=0.2905			
35	3.41	3.43 (0.05)	6.17 (0.12)
30	2.93	2.93 (0.05)	5.27 (0.12)
25	2.37	2.37 (0.04)	4.26 (0.11)
20	2.07	2.07 (0.04)	3.71 (0.11)
15	1.74	1.73 (0.02)	3.11 (0.06)
8	1.47	1.46 (0.02)	2.62 (0.06)
m=0.4213			
35	3.13	3.14 (0.05)	5.65 (0.12)
30	2.78	2.78 (0.05)	4.99 (0.12)
25	2.18	2.18 (0.04)	3.91 (0.11)
20	1.90	1.90 (0.02)	3.40 (0.06)
15	1.61	1.60 (0.02)	2.87 (0.06)
8	1.37	1.37 (0.02)	2.45 (0.06)
m=0.5401			
35	3.96	3.97 (0.07)	7.13 (0.17)
30	2.44	2.45 (0.04)	4.38 (0.11)
25	2.04	2.04 (0.04)	3.65 (0.11)
20	1.73	1.73 (0.02)	3.09 (0.06)
15	1.45	1.44 (0.03)	2.58 (0.06)
8	1.21	1.21 (0.02)	2.15 (0.06)



Table IV. Continued.

$t/(^{\circ}\text{C})$	$S \times 10^4 / (\text{mol/kg})$	$S_c \times 10^4 / (\text{mol/kg})$	Mol Fraction $\times 10^6$
$\text{Na}_2\text{SO}_4, m=0.1085$			
30	2.49	2.49 (0.04)	4.50 (0.11)
25	2.23	2.23 (0.04)	4.02 (0.11)
20	1.87	1.87 (0.02)	3.36 (0.06)
15	1.54	1.53 (0.02)	2.77 (0.06)
8	1.20	1.20 (0.02)	2.15 (0.06)
$m=0.1934$			
30	2.19	2.19 (0.04)	3.95 (0.11)
25	2.01	2.01 (0.03)	3.49 (0.04)
20	1.74	1.74 (0.02)	3.13 (0.06)
15	1.38	1.38 (0.02)	2.47 (0.06)
8	1.10	1.09 (0.02)	1.97 (0.05)
$m=0.3072$			
30	2.05	2.05 (0.04)	3.69 (0.11)
25	1.69	1.69 (0.02)	3.04 (0.06)
20	1.41	1.41 (0.02)	2.53 (0.06)
15	1.14	1.14 (0.02)	2.04 (0.06)
8	0.902	0.898 (0.01)	1.61 (0.03)
$m=0.4215$			
30	1.57	1.52 (0.02)	2.82 (0.06)
25	1.43	1.43 (0.02)	2.56 (0.02)
20	1.19	1.19 (0.02)	2.13 (0.06)
15	0.982	0.979 (0.01)	1.75 (0.03)

Table IV. Continued.

$t/(^{\circ}\text{C})$	$S \times 10^4 / (\text{mol/kg})$	$S_c \times 10^4 / (\text{mol/kg})$	Mol Fraction $\times 10^6$
8	0.756	0.753 (0.01)	1.35 (0.03)
m=0.5171			
30	1.39	1.39 (0.02)	2.50 (0.06)
25	1.19	1.19 (0.02)	2.13 (0.06)
20	1.01	1.01 (0.02)	1.80 (0.05)
15	0.842	0.839 (0.01)	1.50 (0.03)
8	0.664	0.661 (0.01)	1.18 (0.03)
NaHCO <sub>3</sub> , m=0.09821			
35	3.47	3.48 (0.05)	6.30 (0.13)
30	3.01	3.01 (0.05)	5.44 (0.12)
25	2.44	2.44 (0.04)	4.40 (0.11)
20	2.05	2.05 (0.02)	3.69 (0.06)
15	1.70	1.70 (0.02)	3.05 (0.06)
8	1.38	1.38 (0.02)	2.48 (0.06)
m=0.1963			
35	3.30	3.31 (0.05)	5.98 (0.12)
30	2.84	2.84 (0.05)	5.12 (0.12)
25	2.27	2.27 (0.04)	4.09 (0.11)
20	1.93	1.93 (0.02)	3.46 (0.06)
15	1.62	1.61 (0.02)	2.90 (0.06)
8	1.28	1.28 (0.02)	2.29 (0.06)
m=0.3163			

Table IV. Continued

$t/(^{\circ}\text{C})$	$S \times 10^4 / (\text{mol/kg})$	$S_c \times 10^4 / (\text{mol/kg})$	Mol Fraction $\times 10^6$
35	3.07	3.06 (0.05)	5.53 (0.12)
30	2.60	2.60 (0.04)	4.68 (0.11)
25	2.12	2.12 (0.04)	3.81 (0.11)
20	1.79	1.79 (0.02)	3.22 (0.06)
15	1.49	1.49 (0.02)	2.66 (0.06)
8	1.20	1.20 (0.02)	2.15 (0.06)
m=0.3967			
35	2.93	2.94 (0.05)	5.28 (0.12)
30	2.45	2.45 (0.04)	4.41 (0.11)
25	1.98	1.98 (0.02)	3.55 (0.06)
20	1.69	1.69 (0.02)	3.02 (0.06)
15	1.42	1.41 (0.02)	2.53 (0.06)
8	1.14	1.14 (0.02)	2.03 (0.06)
m=0.5270			
35	2.63	2.64 (0.05)	4.74 (0.12)
30	2.31	2.32 (0.04)	4.15 (0.11)
25	1.86	1.86 (0.03)	3.33 (0.06)
20	1.60	1.60 (0.02)	2.86 (0.06)
15	1.31	1.31 (0.02)	2.34 (0.06)
8	1.08	1.07 (0.02)	1.91 (0.04)

Table V. Setchenov parameters for the salting-out of naphthalene in different electrolytes as a function of temperature.

$t/(^{\circ}\text{C})$	$k_s/(\text{kg/mol})$	$(\text{Std. Error})^2 \times 10^5$	$r^2$
NaCl			
30	0.229(0.013)	7.8	0.9899
25	0.220(0.018)	13.8	0.9811
20	0.227(0.021)	20.1	0.9742
15	0.241(0.014)	9.0	0.9896
8	0.247(0.086)	3.3	0.9964
KCl			
30	0.207(0.010)	4.0	0.9935
25	0.258(0.031)	37.1	0.9713
20	0.210(0.020)	17.4	0.9728
15	0.200(0.012)	6.1	0.9893
8	0.205(0.013)	6.6	0.9915
MgCl <sub>2</sub>			
30	0.277(0.019)	3.9	0.9862
25	0.307(0.047)	12.0	0.9562
20	0.254(0.033)	11.4	0.9531
15	0.305(0.011)	12.9	0.9962
8	0.269(0.017)	3.0	0.9886
CaCl <sub>2</sub>			
35	0.325(0.022)	3.2	0.9910

Table V. Continued.

$t/(^{\circ}\text{C})$	$k_s/(\text{kg/mol})$	$(\text{Std. Error})^2 \times 10^5$	$r^2$
30	0.303(0.024)	8.0	0.9814
25	0.304(0.012)	1.8	0.9957
20	0.352(0.027)	9.9	0.9828
15	0.330(0.012)	2.1	0.9958
8	0.341(0.025)	8.7	0.9839
$\text{Na}_2\text{SO}_4$			
30	0.630(0.064)	45.3	0.9696
25	0.655(0.028)	8.6	0.9945
20	0.681(0.035)	13.4	0.9921
15	0.653(0.013)	1.8	0.9989
8	0.657(0.024)	6.1	0.9961
$\text{NaHCO}_3$			
35	0.286(0.014)	2.2	0.9928
30	0.283(0.014)	2.3	0.9923
25	0.286(0.013)	1.9	0.9937
20	0.264(0.014)	2.1	0.9919
15	0.276(0.007)	0.5	0.9981
8	0.263(0.014)	2.3	0.9911

Table VI. Literature values for the Setchenov parameters of naphthalene at 25°C.

Salt	This Work	Gordon and Thorne <sup>a</sup>	M. Paul <sup>b</sup>	Vesala <sup>c</sup>
NaCl	0.220	0.220	0.260	-----
KCl	0.258	0.186	0.204	0.207
Na <sub>2</sub> SO <sub>4</sub>	0.655	0.696	0.716	-----
MgCl <sub>2</sub>	0.307	0.301	-----	-----
CaCl <sub>2</sub>	0.303	0.322	-----	-----
NaHCO <sub>3</sub>	0.286	0.319	-----	-----

<sup>a</sup>Gordon, J.E. and Thorne, R.L., (1967).

<sup>b</sup>Paul, M., (1952).

<sup>c</sup>Vesala, A. and Lonnberg, B., (1980).

Table VII. Mole fractions of the six most important constituents of seawater.

Salt	Mole Fraction <sup>a</sup>
NaCl	0.79914
MgCl <sub>2</sub>	0.10407
Na <sub>2</sub> SO <sub>4</sub>	0.05476
CaCl <sub>2</sub>	0.01976
KCl	0.01771
NaHCO <sub>3</sub>	0.00456

<sup>a</sup> Taken from Gordon and Thorne, (1967).

Table VIII. Setchenov parameters for the salting-out of naphthalene in seawater as a function of temperature, calculated as the weighted mean of the six salts.

$t / (^{\circ}\text{C})$	$k_s / (\text{kg/mol})$
30	0.257
25	0.256
25	0.256 <sup>a</sup>
20	0.260
15	0.271
8	0.273

<sup>a</sup>Value calculated by Gordon and Thorne, (1967).



Table IX. Enthalpy change for the process solid naphthalene-aqueous naphthalene at 25°C.

molality	$\Delta H^\circ / (\text{kJ/mol})$	(Std. Error) $^2 \times 10^5$	$r^2$
0	25.1 (5.2)	34.9	0.9877
NaCl			
0.1955	22.7 (3.4)	4.1	0.9979
0.4055	22.8 (3.8)	6.5	0.9966
0.6043	22.6 (3.6)	5.3	0.9972
0.8395	22.9 (3.0)	2.5	0.9987
1.029	24.6 (4.5)	12.6	0.9943
KCl			
0.2023	25.0 (5.3)	24.4	0.9895
0.4338	24.6 (4.1)	8.2	0.9966
0.6196	25.5 (4.8)	15.8	0.9934
0.8348	26.6 (5.7)	13.0	0.9919
1.030	23.4 (4.5)	12.0	0.9941
MgCl <sub>2</sub>			
0.1085	25.4 (3.5)	4.1	0.9987
0.2043	25.2 (5.4)	25.7	0.9891
0.3174	25.4 (4.9)	17.0	0.9929
0.4150	25.4 (5.0)	19.3	0.9919
0.5219	25.0 (5.3)	23.1	0.9900

Table IX. Continued.

molality	$\Delta H^\circ / (\text{kJ/mol})$	(Std. Error) $^2 \times 10^5$	$r^2$
<b>CaCl<sub>2</sub></b>			
0.07978	21.4 (5.5)	27.0	0.9842
0.1696	21.3 (5.7)	32.6	0.9809
0.2905	23.2 (4.8)	25.8	0.9894
0.4213	23.1 (5.4)	40.9	0.9831
0.5401	23.1 (4.7)	15.1	0.9923
<b>Na<sub>2</sub>SO<sub>4</sub></b>			
0.1085	24.4 (4.2)	9.2	0.9958
0.1934	22.9 (5.3)	24.6	0.9874
0.3072	26.9 (3.9)	6.9	0.9974
0.4215	24.5 (4.8)	16.4	0.9926
0.5171	24.3 (2.1)	0.6	0.9997
<b>NaHCO<sub>3</sub></b>			
0.09821	25.5 (4.1)	14.2	0.9951
0.1963	25.9 (3.9)	11.7	0.9961
0.3163	25.5 (4.0)	12.8	0.9956
0.3967	25.6 (4.4)	17.3	0.9941
0.5270	24.9 (4.2)	15.1	0.9946

b) Generator Column Method.

The solubility measurements of naphthalene in water and seawater obtained with the column generator were similarly corrected for temperature induced volume changes. The density of seawater as a function of temperature and salinity was calculated from the equation given by Wang and Millero (1973):

$$V_{SW} = 1.000027 / (1 + s_t 10^{-3}) \dots \dots \dots (28)$$

where  $V_{SW}$  is the specific volume of seawater, and  $s_t$  is given by

$$s_t = A_t + B_t s_o + C_t s_o^2 \dots \dots \dots (29)$$

where the coefficients are functions of both temperature and salinity. The solubilities were transformed to the mole fraction scale using the same equations given above. The results given in Table X are the averages of at least three experimental determinations.

The solubilities were fitted to the Setchenov equation, and the results are given in Table XI. The electrolyte concentration in seawater was calculated taking advantage of the well known fact that the proportion between the major constituents of seawater is constant, irrespective of what the salinity is. If the major constituents are present in

constant proportions, then a weighted average molecular weight can be calculated for "seasalt". This value will depend upon the recipe used to mimic the composition of natural seawater (Leyendekkers, 1976). For the recipe used in this work the weighted average molecular weight has a value of 68.0811 g/"mole". Once this value is known, the "molality" of seasalt can be calculated from (Leyendekkers, 1976)

$$m_s = S / (M_t (1 - S/1000)) \dots\dots\dots (30)$$

where  $m_s$  is the "molality" of seasalt,  $S$  is the salinity in parts per thousand, and  $M_t$  is the "molecular weight" of sea salt.

As the results obtained with the generator column are considered to be of higher accuracy, the Clarke and Glew equation

$$R \ln X = -\Delta G^\circ / \theta + \Delta H^\circ (1/\theta - 1/T) + \Delta C_p^\circ (\theta/T - 1 + \ln(T/\theta)) \dots (31)$$

(where  $\theta$  is a reference temperature (298.15 K) and the other symbols have their usual thermodynamic meanings) was used to calculate the thermodynamic functions for the process solid hydrocarbon-aqueous hydrocarbon (Clarke and Glew, 1966; May et al., 1983; Blandamer et al., 1982). In contrast to the integrated van't Hoff equation, the equation proposed by Clarke and Glew does not assume the change in heat capacity

to be equal to zero in the temperature range of interest. Also, this equation has the advantage that the adjustable coefficients are not correlated, and that the adjustable parameters are the desired thermodynamic functions.

The solubilities of naphthalene were fitted to the Clarke and Glew equation by a multivariable linear least-squares fit program from the Statistical Package for the Social Sciences (SPSS) (Version H, Release 9.1). The results are given in Table XII, along with the values obtained by May et al., (1983).

From the results in Table XII it can be seen that the more positive value (less favorable) for the Gibbs free energy of dissolution of naphthalene in seawater, as compared to the value in pure water, is due entirely to an entropic contribution. From the discussion in the introduction, these results seem to indicate that the solute creates less order in seawater than it does in pure water.

As can be seen from the results given in Tables XI and XII, the accuracy of the generator column method is better than that obtained with the "shake-flask" technique. The estimated uncertainties for the Setchenov parameter are much smaller; the same is true for the errors in the thermodynamic functions, as can be seen from Table XII, where the solubility values obtained with the "shake-flask" method were also fitted to the Clarke and Glew equation. The error in the Gibbs free energy is five times smaller for the

data obtained using the generator column, and the error in the enthalpy change is ten times smaller. The agreement with the thermodynamic functions calculated by May et al., (1983), who also used the Generator Column Method, is excellent. Furthermore, the error in the thermodynamic functions is smaller for the results obtained in this work, probably due to the more extended temperature range used.

Using the Generator Column Method, the Setchenov parameters as a function of temperature show a minimum around 25°C, as can be seen from Figure (6). This result was unexpected because minima of the salting-out coefficient have been reported only for gases at temperatures higher than 100°C (Clever and Holland, 1968), but never around room temperature. This result made it desirable to have values for the salting-out of other aromatic hydrocarbons as a function of temperature in order to ascertain that the behavior shown by naphthalene was not anomalous.

Table X. Solubility of naphthalene in water and seawater by the generator column method.

$t/(^{\circ}\text{C})$	$S \times 10^4 / (\text{mol/kg})$	$S_C \times 10^4 / (\text{mol/kg})$	Mol Fraction $\times 10^6$
water			
43.7	5.35	5.38(0.07)	9.79(0.19)
34.6	3.77	3.78(0.05)	6.85(0.13)
24.8	2.59	2.59(0.05)	4.67(0.11)
13.5	1.69	1.68(0.02)	3.03(0.06)
3.5	1.18	1.18(0.02)	2.12(0.06)
seawater, $m=0.2679$			
43.6	4.52	4.55(0.05)	8.23(0.13)
34.7	3.22	3.23(0.05)	5.82(0.13)
24.8	2.20	2.20(0.04)	3.96(0.11)
13.2	1.41	1.41(0.02)	2.53(0.06)
3.5	1.00	1.00(0.02)	1.79(0.05)
$m=0.3587$			
43.7	4.29	4.32(0.07)	7.80(0.18)
34.6	3.03	3.05(0.05)	5.48(0.12)
24.8	2.10	2.10(0.04)	3.77(0.11)
13.2	1.35	1.34(0.02)	2.41(0.05)
3.5	0.953	0.981(0.01)	1.70(0.03)
$m=0.5329$			
43.6	3.89	3.92(0.05)	7.06(0.13)
34.6	2.79	2.80(0.05)	5.03(0.12)
24.8	1.91	1.91(0.03)	3.43(0.06)
13.2	1.23	1.23(0.02)	2.20(0.06)
3.5	0.857	0.854(0.01)	1.52(0.03)

Table XI. Setchenov parameters for the salting-out of naphthalene in sea water as a function of temperature.

$t/ (^{\circ}\text{C})$	$k_s / (\text{kg/mol})$	$(\text{Std. Error})^2 \times 10^5$	$r^2$
43.6	0.267(0.007)	0.12	0.9988
34.6	0.254(0.009)	1.5	0.9969
24.8	0.252(0.007)	0.67	0.9993
13.2	0.262(0.014)	2.7	0.9947
3.5	0.270(0.003)	0.12	0.9998



Figure 6

Setchenov parameter for the salting-out of naphthalene in seawater as a function of temperature.

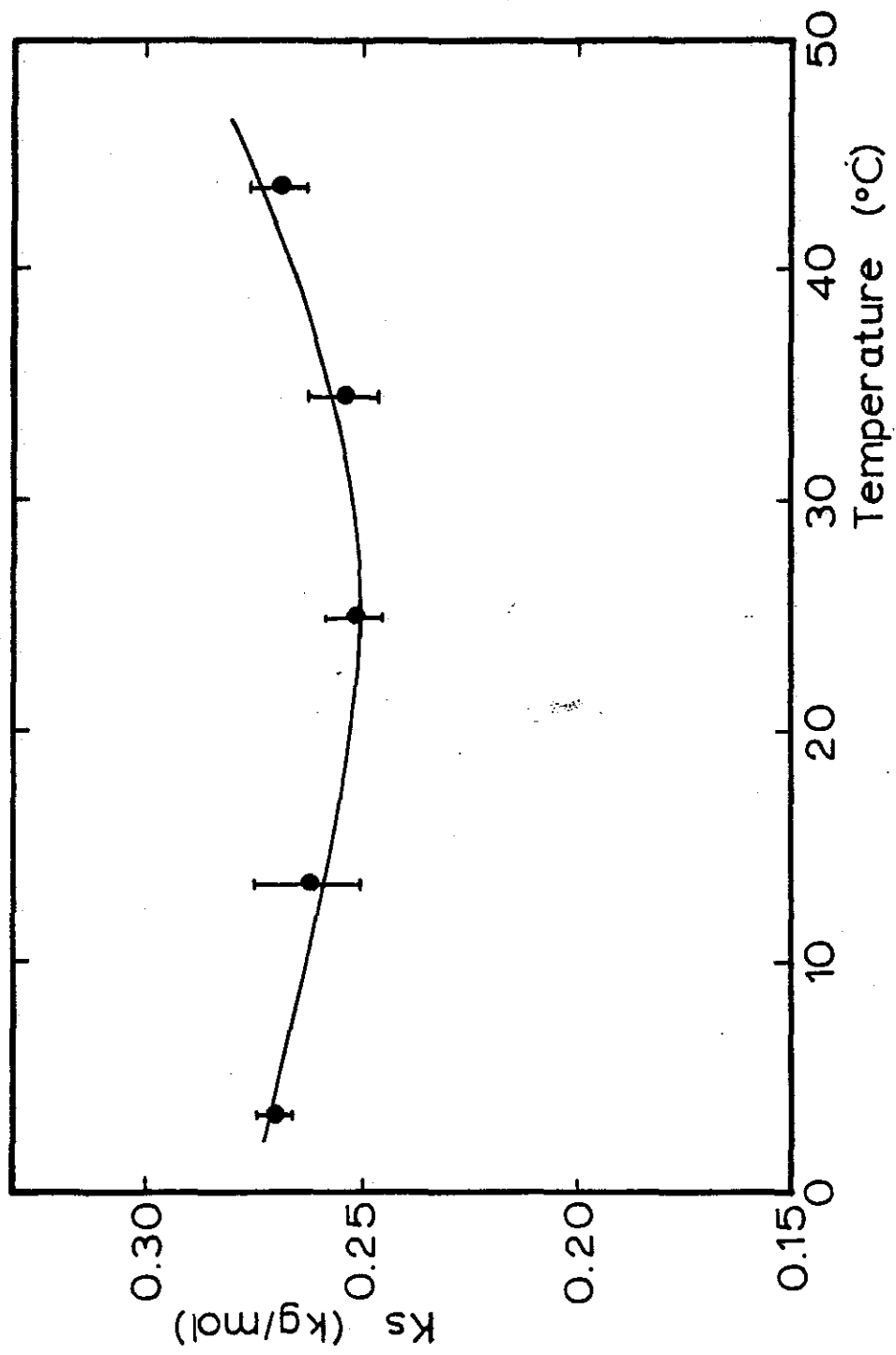


Table XII. Thermodynamic functions for the process solid naphthalene-aqueous naphthalene.

solution	$\Delta G/(\text{kJ/mol})$	$\Delta H/(\text{kJ/mol})$	$T\Delta S/(\text{kJ/mol})$	$\Delta C_p/(\text{kJ/molK})$
water	30.41(0.019)	28.4(0.1)	-2.01	0.26(0.02)
water <sup>a</sup>	30.55(0.032)	28.6(1.3)	-1.95	0.31(0.17)
water <sup>b</sup>	30.32(0.094)	27.57(1.19)	-2.75	-0.29(0.40)
seawater	31.16(0.014)	28.4(0.09)	-2.76	0.19(0.02)

<sup>a</sup>calculated from the experimental results of May et al., (1983).

<sup>b</sup>calculated with the results obtained in this work using the "shake-flask" technique.

In order to compare with the values obtained with naphthalene, the solubilities of anthracene and phenanthrene in natural seawater were measured using the Generator Column technique. The concentrations were calculated from a calibration plot of the fluorescence of these compounds. The solubility of phenanthrene in water is approximately 100 times less than that of naphthalene, and the solubility of anthracene is about 1000 times less than the solubility of naphthalene. This low solubility makes the use of absorption spectroscopy very difficult, so the more sensitive technique of emission spectroscopy was chosen. The calibration plot was calculated by a weighted linear least-squares program (program L/B, written by Dr. Richard P. Dodge), the weights being the instrumental uncertainties. The resulting equations are:

$$[A] = I_f - 0.31451(0.057)/2.9584 \times 10^7 (8.83 \times 10^5) \quad \dots\dots(32)$$

for anthracene, where  $I_f$  is the measured fluorescence intensity, and the other numbers are the intercept and slope of the calibration plot and their estimated uncertainties. The equation for phenanthrene is:

$$[Ph] = I_f - 0.007631(0.013)/1.9258 \times 10^6 (1.4 \times 10^4) \quad \dots\dots(33)$$

The results were processed in the same manner described above for naphthalene. The solubility values are given in

Tables XIII and XIV. The calculated Setchenov coefficients for both compounds as a function of temperature are given in Tables XV and XVI and are shown in Figures (7) and (8). The thermodynamic functions for the process solid hydrocarbon-aqueous hydrocarbon are given in Tables XVII and XVIII.

The solubility of phenanthrene  $9.92 \times 10^{-8}$  at  $25^{\circ}\text{C}$  is in very good agreement with the value obtained by May et al., (1983) of  $9.65 \times 10^{-8}$ , but the solubility of anthracene of  $7.98 \times 10^{-9}$  is higher than their value of  $3.82 \times 10^{-9}$ . The agreement of the calculated thermodynamic functions is very good in the case of the Gibbs free energy change for both phenanthrene and anthracene, but the values for the enthalpy change are so different that the entropy term for the dissolution of phenanthrene becomes negative ( $-0.67$  kJ/mol), while the value reported by May et al., (1983) is positive:  $+3.28$  kJ/mol.

As can be seen from Tables XV and XVI, and Figures (7) and (8), the Setchenov parameters for the salting-out of these compounds in seawater show a minimum also, but at a lower temperature in the case of anthracene. These results are consistent with the minimum obtained with naphthalene.

Table XIII. Solubility of anthracene in natural seawater by the generator column method.

$t/(^{\circ}\text{C})$	$S \times 10^7 / (\text{mol/kg})$	$S_c \times 10^7 / (\text{mol/kg})$	Mol Fraction $\times 10^9$
water			
5.0	1.51	1.51 (0.05)	2.73 (0.14)
13.1	2.15	2.15 (0.03)	3.88 (0.09)
25.1	4.42	4.42 (0.06)	7.98 (0.14)
34.9	8.04	8.07 (0.09)	14.6 (0.20)
44.3	14.8	14.9 (0.02)	26.9 (0.38)
m=0.2013			
5.0	1.38	1.38 (0.03)	2.48 (0.01)
13.0	1.98	1.97 (0.04)	3.59 (0.09)
25.1	4.04	4.04 (0.05)	7.27 (0.10)
34.9	7.66	7.69 (0.09)	13.8 (0.3)
44.0	12.9	13.0 (0.2)	23.5 (0.5)
m=0.3261			
13.0	1.71	1.71 (0.03)	3.07 (0.07)
25.5	3.66	3.66 (0.05)	6.57 (0.10)
34.8	6.78	6.80 (0.07)	12.2 (0.20)
44.0	10.3	10.3 (0.11)	18.58 (0.30)
m=0.5328			
5.0	1.14	1.14 (0.04)	2.04 (0.09)
13.1	1.70	1.69 (0.03)	3.03 (0.07)

Table XIII. Continued.

$t(^{\circ}\text{C})$	$S \times 10^7 / (\text{mol/kg})$	$S_c \times 10^7 / (\text{mol/kg})$	Mol Fraction $\times 10^9$
24.9	3.33	3.33 (0.05)	5.96 (0.10)
35.0	6.00	6.02 (0.09)	10.8 (0.20)
44.0	10.7	10.8 (0.20)	19.3 (0.60)

Table XIV. Solubility of phenanthrene in natural seawater by the generator column method.

$t/(^{\circ}\text{C})$	$S \times 10^6 / (\text{mol/kg})$	$S_c \times 10^6 / (\text{mol/kg})$	Mol Fraction $\times 10^8$
water			
3.10	1.84	1.84 (0.02)	3.31 (0.04)
13.8	3.36	3.35 (0.02)	6.04 (0.05)
24.9	5.49	5.49 (0.07)	9.92 (0.2)
34.7	10.1	10.1 (0.2)	18.3 (0.4)
43.6	16.5	16.6 (0.1)	30.1 (0.2)
m=0.5329			
2.6	1.28	1.27 (0.01)	2.27 (0.03)
13.8	2.61	2.60 (0.03)	4.64 (0.07)
24.9	5.04	5.04 (0.06)	9.01 (0.2)
34.8	8.91	8.94 (0.08)	16.1 (0.2)
43.6	13.5	13.6 (0.10)	24.6 (0.03)
m=0.1658			
14.0	3.08	3.07 (0.003)	5.52 (0.007)
24.9	5.77	5.77 (0.009)	10.4 (0.002)
43.9	16.4	16.5 (0.17)	29.8 (0.04)



Table XV. Setchenov parameters for the salting-out of anthracene in natural seawater.

$t/ (^{\circ}\text{C})$	$k_s/ (\text{kg/mol})$	Std. Error <sup>2</sup> $\times 10^5$	$r^2$
5	0.239(0.004)	2.2	0.9973
13	0.202(0.004)	0.2	0.9997
25	0.244(0.020)	4.7	0.9896
34.9	0.245(0.008)	0.8	0.9990
44	0.268(0.010)	1.6	0.9985

Table XVI. Setchenov parameters for the salting-out of phenanthrene in natural seawater.

$t / (^{\circ}\text{C})$	$k_s / (\text{kg/mol})$	Std. Error <sup>2</sup> $\times 10^5$	$r^2$
2.6	0.300	---	-----
13.8	0.213 (0.007)	0.8	0.9989
24.9	0.0784	---	-----
34.7	0.104	---	-----
43.6	0.174 (0.04)	29.3	0.9391

Figure 7

Setchenov parameter for the salting-out of anthracene in seawater as a function of temperature.

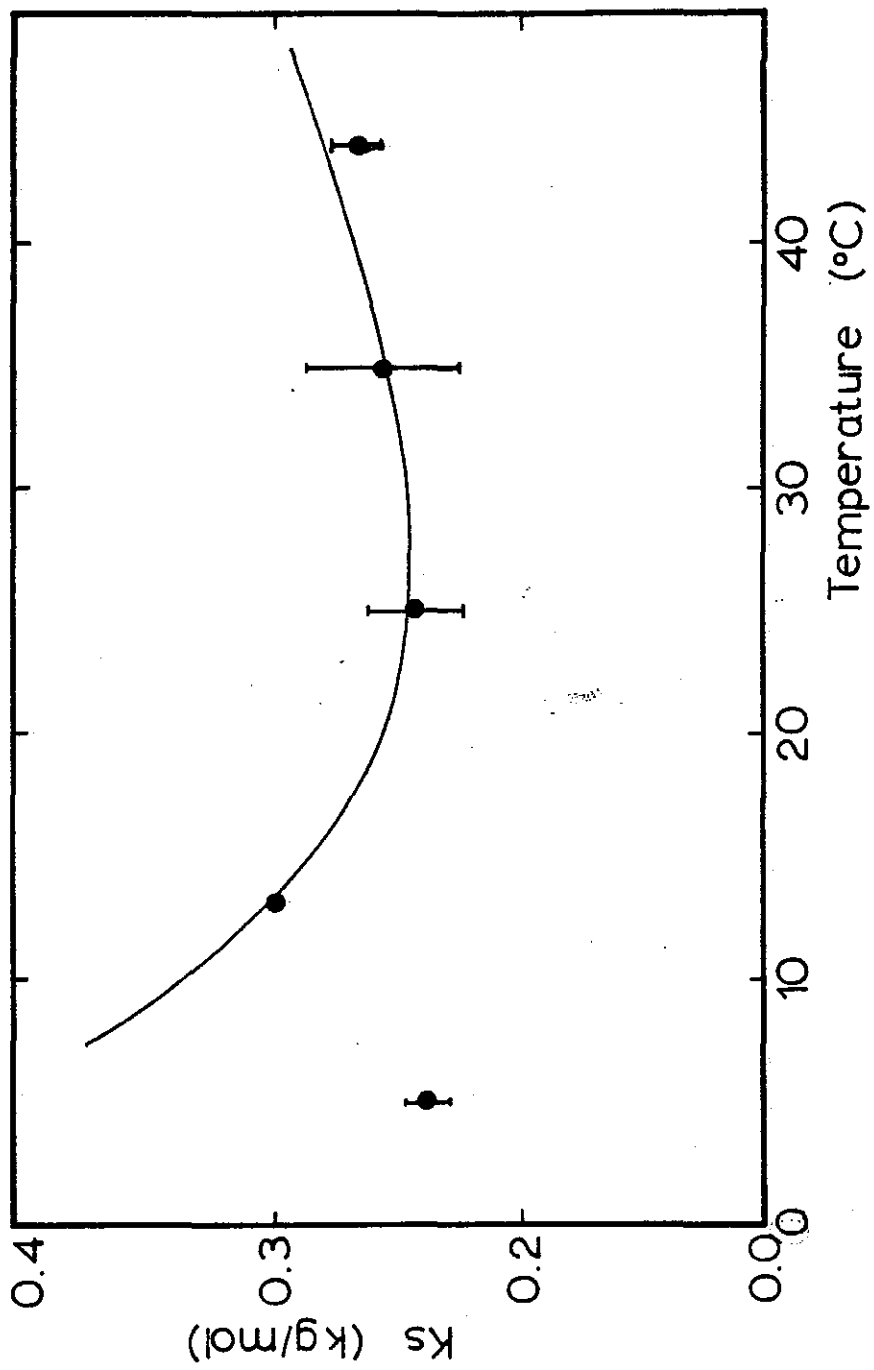


Figure 8

Setchenov parameter for the salting-out of phenanthrene in seawater as a function of temperature.

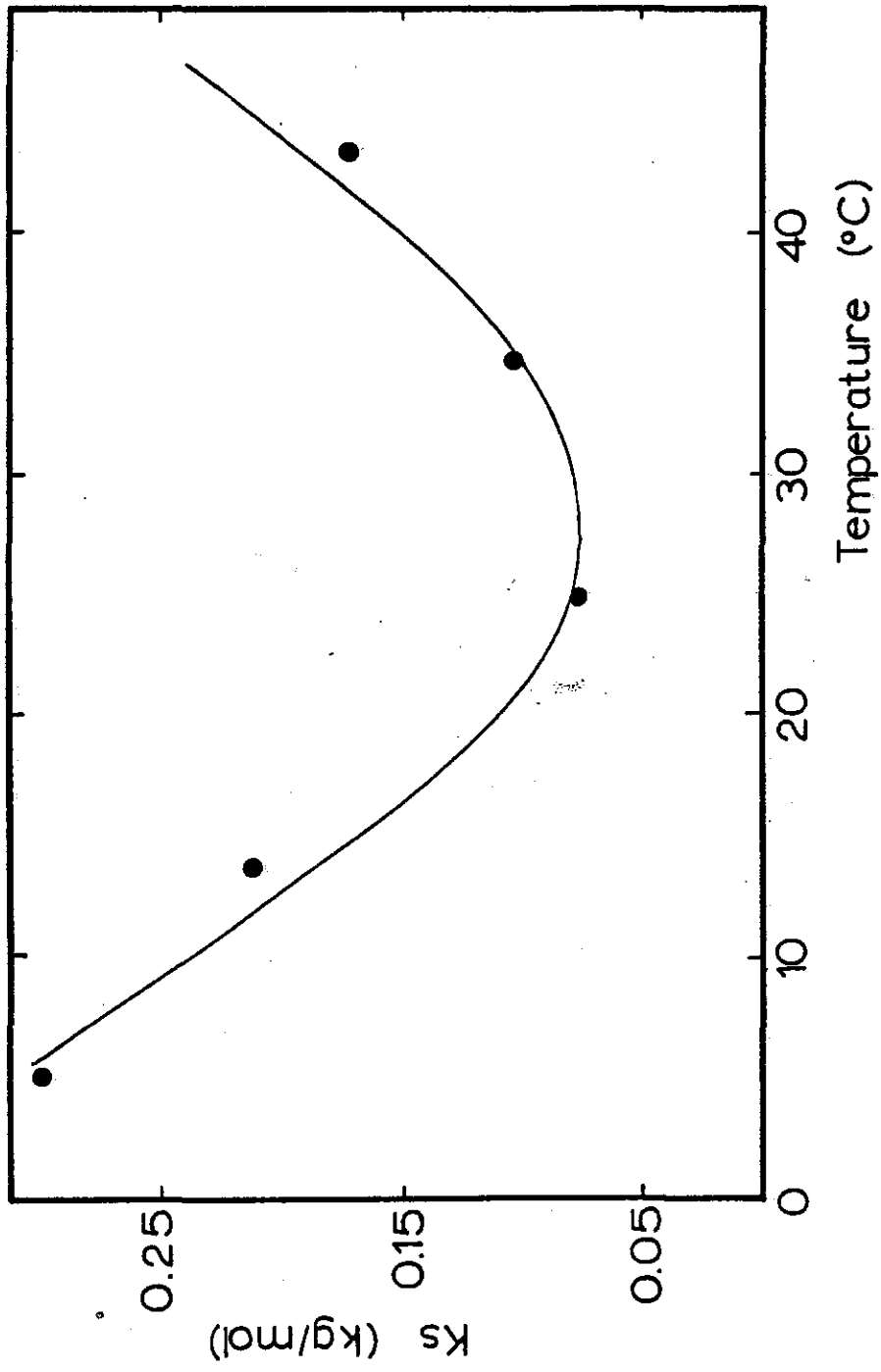


Table XVII. Thermodynamic functions for the process  
solid phenanthrene-aqueous phenanthrene.

solution	$\Delta G$ /(kJ/mol)	$\Delta H$ (kJ/mol)	TAS/(kJ/mol)	$\Delta C_p$ (kJ/mol K)
water	39.83(0.19)	40.50(1.26)	-0.67	0.44(0.20)
water <sup>a</sup>	39.98(0.03)	36.70(1.90)	3.28	0.29(0.21)
seawater	40.17(0.08)	42.47(0.50)	-2.30	-0.018(0.08)

<sup>a</sup>May et al., (1983).

Table XVIII. Thermodynamic functions for the process  
solid anthracene-aqueous anthracene.

solution	$\Delta G$ /(kJ/mol)	$\Delta H$ /(kJ/mol)	TAS/(kJ/mol)	$\Delta C_p$ /(kJ/molK)
water	46.28(0.11)	44.03(0.70)	-2.25	0.71(0.12)
water <sup>a</sup>	47.69(0.02)	47.2 (1.5)	-0.49	0.41(0.18)
seawater	46.96(0.04)	43.13(0.28)	-3.83	0.61(0.05)

<sup>a</sup>values of May et al., (1983).



c) High pressure results.

The experimental method used in this work assumes that the solubility of the solute will decrease with an increase in pressure. In cases where there is an increase in the solubility of the solute this method cannot be used because there is no more solid solute available to be dissolved. In that case what would be observed is a constant solubility as a function of pressure. Previous work has shown that the solubility of naphthalene decreases in aqueous solutions upon compression (Suzuki et al., 1974; Rodriguez, 1979).

Given that the high pressure transducer is not connected directly to the optical cell it is necessary to relate the pressure in the high pressure generator, (as measured with the pressure transducer) with the actual pressure inside the cell. One way of doing this is by studying the shift in the absorption spectrum of a hydrocarbon molecule dissolved in a nonpolar solvent, such as pentane. It is a well known fact that the dielectric constant of the solvent affects the spectra of dissolved molecules, and that increasing the pressure changes the dielectric constant of the solvent, thus shifting the position of the absorption bands of the solute.

Robertson and co-workers (1957), studied the effect of applied pressure on the absorption spectra of aromatic hydrocarbons dissolved in pentane, finding a linear relationship between the shift of the maxima and the

dielectric constant of the solvent. Therefore it is possible to determine the actual pressure of the sample if the magnitude of the shift is known.

The  ${}^1L_a$  band of anthracene dissolved in n-pentane at 374 nm was selected for comparison with Robertson's values. A typical example of the pressure-induced red shift in the absorption spectra is shown in Figure (9). If Robertson's value of 161 for the ratio  $\Delta\lambda/\lambda\epsilon$  (where  $\lambda$  is the wavelength and  $\epsilon$  is the dielectric constant), is considered to be correct, then the change in the dielectric constant of n-pentane can be calculated from the observed shifts of the  ${}^1L_a$  transition of anthracene. The dielectric constant of n-pentane as a function of pressure have been measured by Danforth (1931), and therefore measurements of pressure-induced spectral shifts can be used to compute the actual pressure exerted on the sample.

Our results show that at pressures between 2500 and 3500 atm the readings of the pressure transducer were on the average 15% higher than the actual pressure in the high pressure optical cell.

For the measurement of solubility, a saturated aqueous solution of naphthalene was placed inside the high pressure cell, and the pressure increased. The cell was taken to the spectrophotometer and readings of the absorbance were automatically taken every fifteen minutes, until a constant value was obtained. Typical results are shown in Figures

(10) and (11). Figure (10) shows the absorption spectrum of a saturated solution of naphthalene in water at 25°C, at one atmosphere and 1771 atm. Figure (11) shows the absorbance of a solution of naphthalene as a function of time. In general, the higher the pressure the faster equilibrium was reached. Most runs took from two to three days to equilibrate. Table XX gives the experimental result for the solubility of naphthalene in water as a function of pressure at 25°C. The solubility of naphthalene decreases with pressure. However, no precise values could be obtained. This problem, and the long equilibration times made impractical the determination of Setchenov parameters as a function of pressure in a reasonable time.

Figure 9

Pressure-induced red shift of the absorption spectrum of anthracene in n-pentane. A, spectrum at one atmosphere; B, spectrum at 2300 atm.

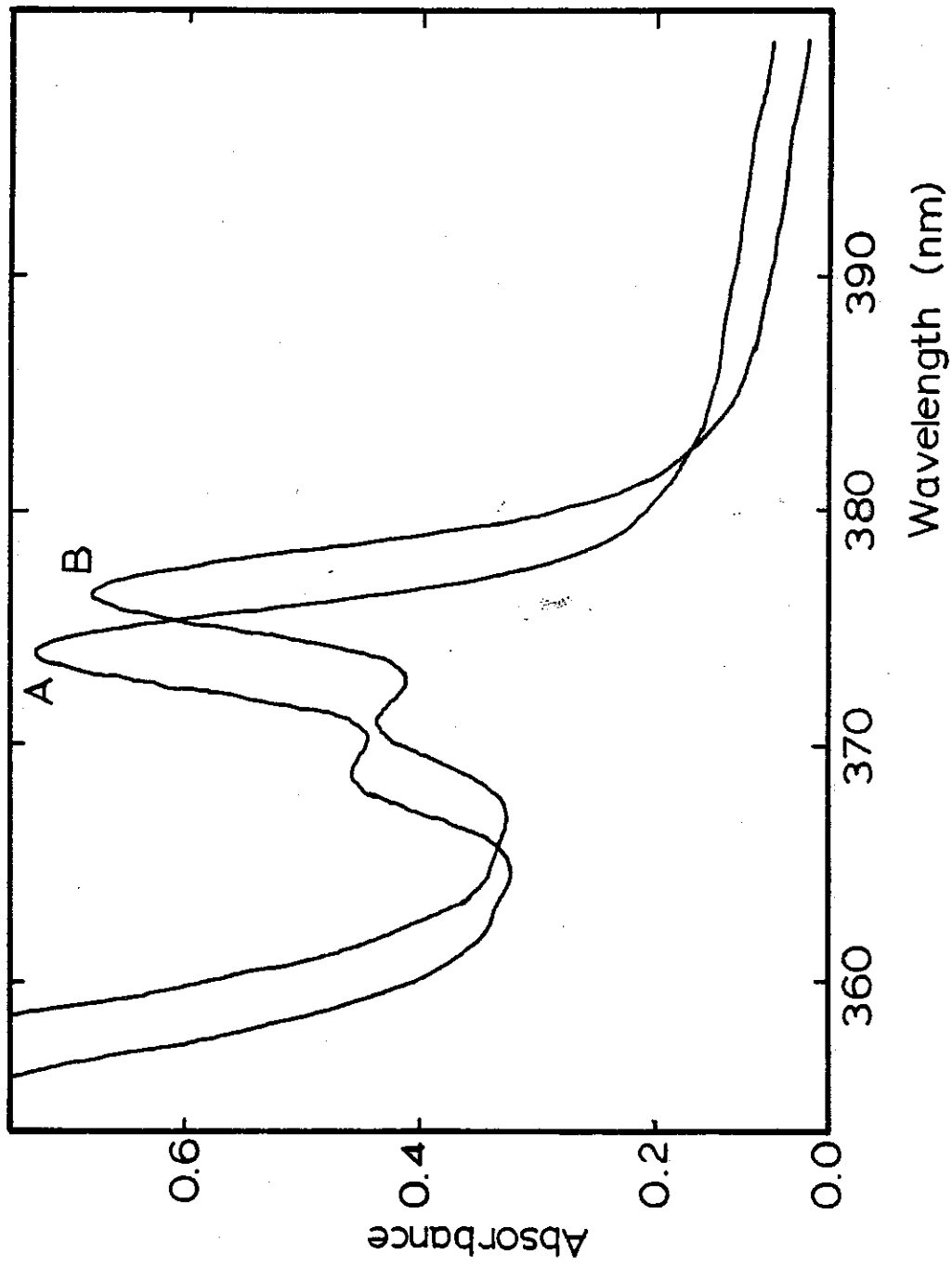


Figure 10

Absorption spectrum of naphthalene in water at: A, one atmosphere and B, 1771 atmospheres.

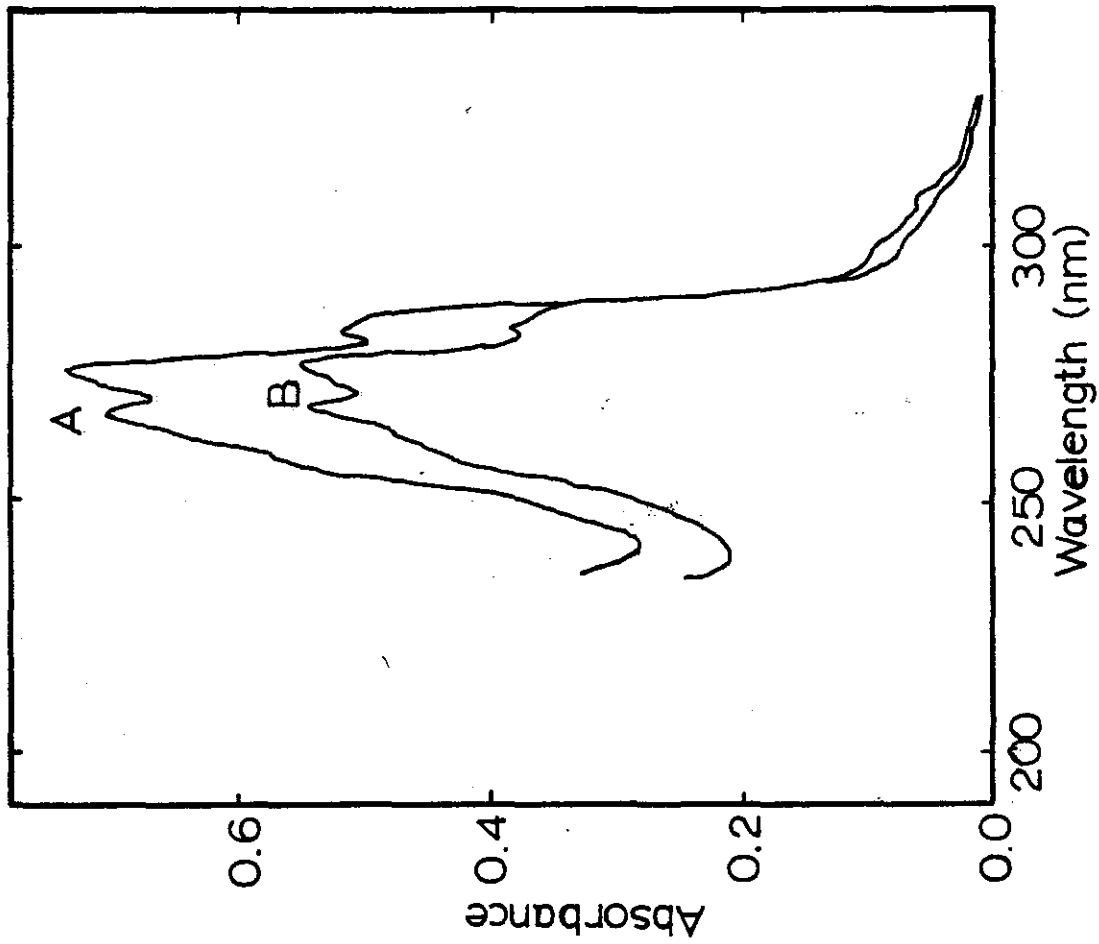


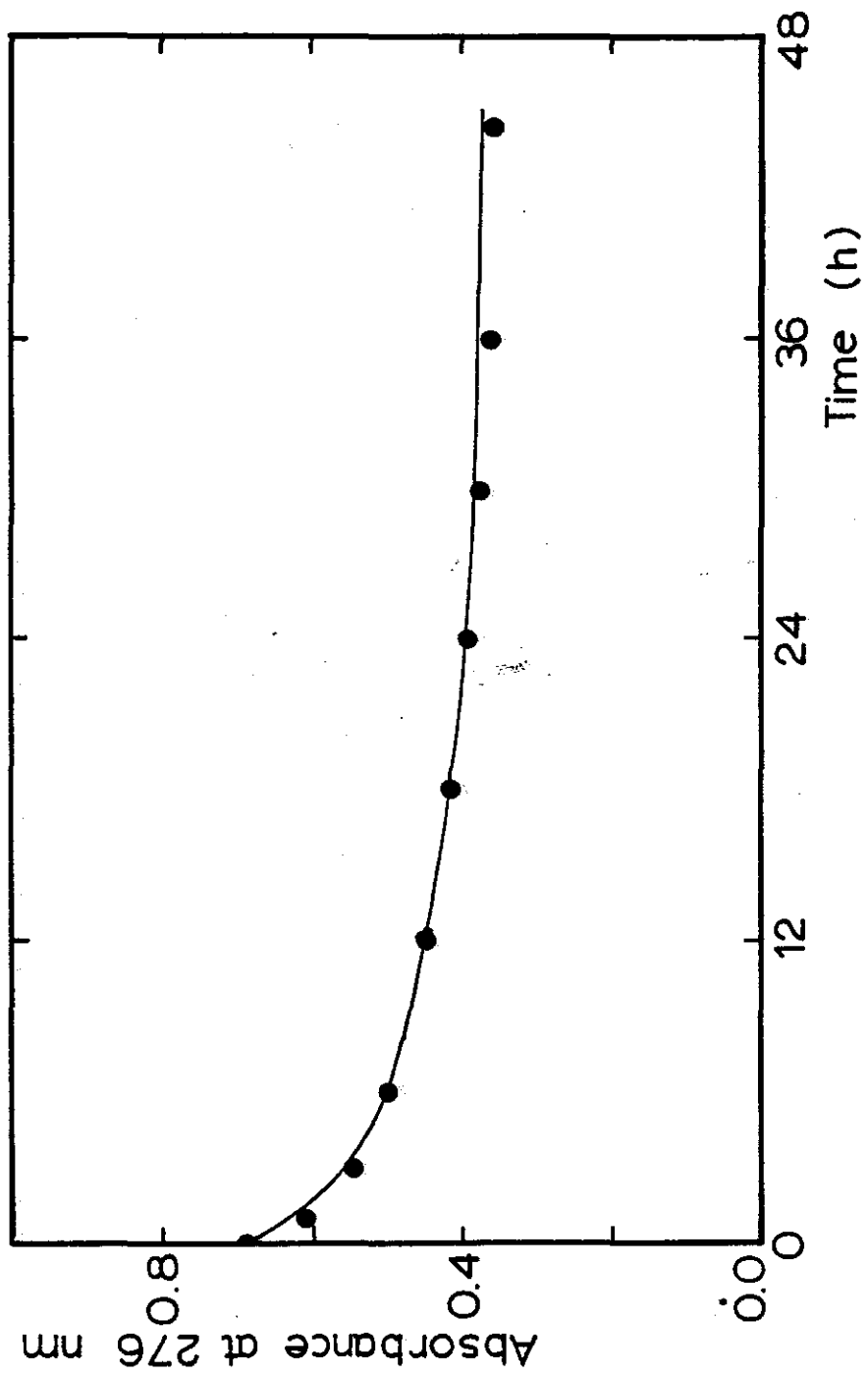
Table XIX. Solubility of naphthalene in water as a function of pressure at room temperature.

Pressure/atm	Solubility x 10 <sup>4</sup> /(mole/kg)
334	0.735(0.02)
535	1.59(0.04)
1503	1.92(0.05)
1771	1.56(0.04)



Figure 11 .

Absorbance of naphthalene in water as a function of time.



## DISCUSSION

The solubility of naphthalene in water and in aqueous electrolyte solutions behaved as expected. The solubility of naphthalene decreases in the presence of all the salts studied in this work, that is, naphthalene was salted-out at all the temperatures investigated. This was expected from the results reported previously in the literature at 25°C for naphthalene and other hydrocarbons, which were also salted-out by these salts and sea salt. The solubility of naphthalene increased with increasing temperature in all the electrolyte solutions studied. The solubility of naphthalene as a function of temperature had been investigated in water only, but there were no theoretical reasons to expect a different behavior in seawater, or in the other electrolyte solutions.

The thermodynamic functions for the process: solid hydrocarbon-aqueous hydrocarbon presented in this work are in good agreement with the values reported in the literature. The entropy change reported here is always negative, in agreement with the values reported by May et al., (1983), except for the positive value for the entropy change of solution for phenanthrene reported by them. For the three hydrocarbons studied in this work the Gibbs free energy change on going from water to seawater is positive, a

result to be expected from the lower solubility of these hydrocarbons in seawater with respect to pure water. This change is due to a negative entropy term which, considering that the initial state is the hydrocarbon dissolved in pure water, means that the hydrocarbon solute induces less ordering in seawater than it does in water. This effect might be due to the electrostriction caused by the ions dissolved in seawater. The major ionic components of seawater are known to "break" the structure of water by forming strongly attached primary hydration shells. This effect can explain the decreased order created by the aromatic solute in seawater, as compared with water. The disruption of the structure of water caused by the ions makes it more difficult for the nonpolar solute to form its own hydration shell.

Although minima have been reported for the salting-out of gases at temperatures above room temperature (Clever and Holland, 1968; Masterton, 1975b), the unexpected result of the presence of a minimum for the salting-out of aromatics below room temperature, makes it necessary examine the theoretical models to find out if the minimum can be predicted.

We have shown before (Gold and Rodriguez, 1983) that the Tamman-Tait-Gibson (TTG) model can be used to predict the salting-out of gases in seawater. In order to use the TTG model it is necessary to know the value of  $dP_e/dm_s$  as a

function of temperature. The effective pressures exerted by seasalt as a function of both seasalt concentration and temperature were calculated from (Leyendekkers, 1977):

$$B^P V^P = 0.4343 X_1 (0.315 V_W) / (B_t + P_e + P) \dots\dots\dots (34)$$

where  $B^P$  is the isothermal compressibility at pressure  $P$ ,  $V^P$  and  $V_W$  are the volume of the solution at pressure  $P$  and the volume of pure water at atmospheric pressure, and  $X_1$  is the number of grams of water per gram of solution. The other terms have been defined before.

The values of  $B^P$  and  $V^P$  for seawater in the range 0 to 40 ppt of salinity, and 0 to 40°C in temperature were calculated from the high pressure equation of state of Millero et al (1980):

$$K = P v^O / (v^O - v^P) = K^O + AP + BP^2 \dots\dots\dots (35)$$

where  $v^O$  and  $v^P$  are the specific volumes at zero and  $P$  applied pressure, and  $K$  is the second degree secant modulus ( $K^O = 1/B_O$ ). The parameters  $K^O$ ,  $A$ , and  $B$  are given by

$$K^O = K_W^O + aS + bS^{3/2} \dots\dots\dots (36)$$

$$A = A_W + cS + dS^{3/2} \dots\dots\dots (37)$$

$$B = B_W + eS \dots\dots\dots (38)$$

where S is the salinity, the coefficients  $K_W^O$ ,  $A_W$ , and  $B_W$  for pure water are polynomial functions of the temperature, and the coefficients a to e are functions of the temperature. The values of  $P_e$  were calculated from 0 to 40 ppt every 5 ppt for every five degrees temperature from 0° to 40°C using the computer program "Seawater", listed in the appendix. The results were then fitted to a polynomial in the concentration at every temperature, using a modified version of the program "Nth Order Regression" (Poole and Borchers, 1981):

$$P_e = a + bm_s + cm_s^2 + \dots \dots \dots (39)$$

so that the term

$$\lim_{m_s \rightarrow 0} dP_e/dm_s$$

is just b. Then the b values were fitted to a polynomial in the temperature, the result being:

$$\lim_{m_s \rightarrow 0} P_e/dm_s = 485.916 - 6.3129t + 0.099051t^2 - 6.3853 \times 10^{-4}t^3 \dots (40)$$

with a standard error of one part per thousand. This equation was used to calculate the  $k_s$  values predicted by the TTG model as a function of temperature. The results are shown in Figure (12). The temperature dependence of the

predicted values for  $k_s$  is of the same form as that of the gases dissolved in seawater (Gold and Rodriguez, 1983), the predicted temperature coefficient being better than the values predicted by the scaled particle theory. However, in the case of naphthalene the TTG model predicts values for  $k_s$  which are bigger than the experimental values by a factor of three (see Table XIX), and it does not predict the presence of a minimum around 25°C.

The values for  $k_s$  predicted by the Scaled Particle Theory were calculated from the equations given by Masterton (1975) and listed in the Appendix. This equations are written for  $k_s$  in the ionic strength scale, so the values from Table X were recalculated using the equation (Leyendekkers, 1976):

$$I_w = 0.01994S/(1-S/1000) \dots\dots\dots(41)$$

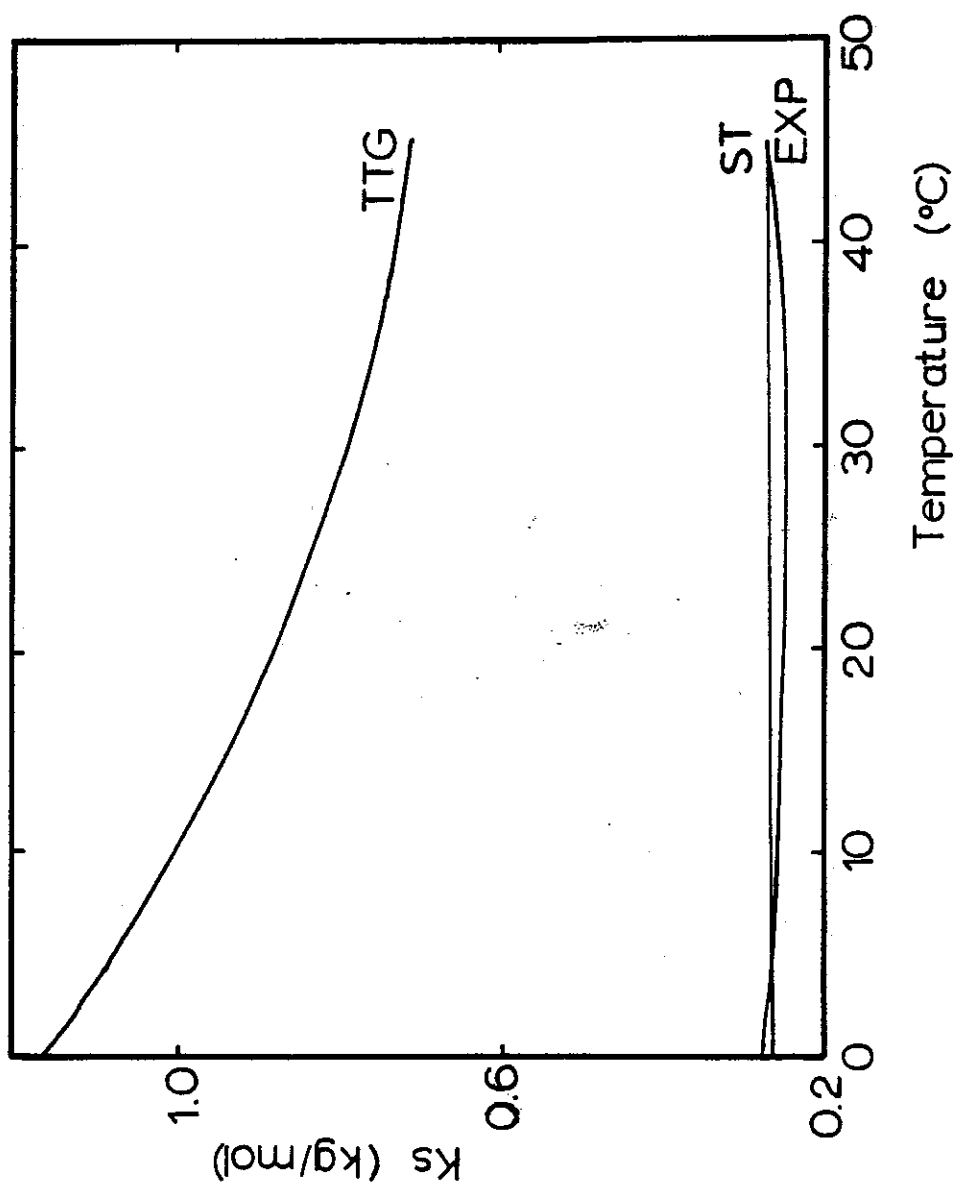
where S is the salinity in parts per thousand.

The calculation of  $k_s$  from  $k_a$  and  $k_b$  requires the knowledge of the Lennard-Jones parameters for the solutes. These parameters, which to the best of our knowledge have not been published for naphthalene, were calculated using two approaches. The first approach uses an empirical relationship between the critical properties of a compound and the Lennard-Jones constants (Stiel and Thodos, 1962; Sen Tee, Gotoh, and Stewart, 1966):

Figure 12

Comparison of the experimental values for the Setchenov parameter of naphthalene in seawater as a function of temperature, with the values predicted by the Tamman-Tait-Gibson and the Surface Tension models.





$$\xi/k = 65.3 T_C Z_C^{18/5} \dots\dots\dots(42)$$

and

$$\sigma_1 = 0.812 (T_C/P_C)^{-13/5} \dots\dots\dots(43)$$

where  $T_C$  is the critical temperature,  $P_C$  is the critical pressure, and  $Z_C$  is the critical compressibility ( $=P_C V_C/T_C$ ). The critical constants for naphthalene were taken from the compilations by Kudchadker et al., (1978) and Dreisbach, (1955). Using this method, the work function was calculated to be 394.1 K, and the intermolecular distance as 6.89 Å. The calculated value for  $k_s$  using these parameters is 0.546 kg/mol, which is three times higher than the experimental result of 0.186 kg/mol.

In the second approach the work function was calculated using the Mavroyannis-Stephen equation (Balon et al., 1983):

$$\xi/k = 2.28 \times 10^{-8} (\alpha^{3/2} E^{1/2} / \sigma^6) \dots\dots\dots(44)$$

where  $\alpha$  is the molecular polarizability,  $E$  is the total number of electrons, and  $\sigma$  is the intermolecular distance. The molecular polarizability ( $17.48 \times 10^{-24} \text{ cm}^3$ ) was taken from the compilation by Miller and Savchik (1979), and the intermolecular distance was taken to be equal to the crystallographic diameter (Balon et al., 1983), which was calculated from the bond lengths and angles determined from

X-ray diffraction by Ponomarev et al. (1976), and Sellers and Boggs, (1981). The calculated value for  $\epsilon_1/k$  is 169.3 K, which compares well with the value calculated by Balon et al., (1983) for 1-naphthol of 123.3 K. The value for  $\sigma$  is  $6.58 \times 10^{-8}$  cm. The calculated values for  $k_s$  using these parameters are in better agreement with the experimental values than the values calculated using the first set of parameters, as can be seen from Table XIX. The results for  $k_a$ ,  $k_b$  and  $k_s$  as a function of temperature were fitted to a polynomial in the temperature

$$k_b = -0.2062 - 0.002417t + 3.6023 \times 10^{-5}t^2 - 3.1179 \times 10^{-7}t^3 \quad \dots\dots (45)$$

$$k_a = 0.61402 - 0.0037816t + 6.6317 \times 10^{-8}t^2 - 6.3879 \times 10^{-7}t^3 \quad \dots\dots (46)$$

$$k_s = 0.35378 - 0.0013407t + 2.9163 \times 10^{-5}t^2 - 3.1246 \times 10^{-7}t^3 \quad \dots\dots (47)$$

with a standard error smaller than  $3 \times 10^{-3}$ . These polynomials are shown in Figure (13), and the predicted value of  $k_s$  is compared with the experimental value in Figure (14). It can be seen that this model does not predict the minimum in  $k_s$  as a function of temperature, but the magnitude of the predicted values is in better agreement with the experimental values than those predicted by the TTG model.

The Surface Tension model was also used to predict the values of  $k_s$  as a function of temperature. The osmotic coefficients of seawater with a seasalt concentration equal

to one molal as a function of temperature were calculated from the equation given by Millero (1976):

$$1-\phi = 2.303SA^{1/2}(\sigma/3)+BI+CI^{3/2}+DI^2 \dots\dots\dots(48)$$

where A, B, C, D and  $\sigma$  are temperature-dependent parameters. The values obtained were fitted to a polynomial in the temperature:

$$k_s = 2.4864 \times 10^{-3} \times (0.10589 + 7.8373 \times 10^{-5}t - 8.0991 \times 10^{-7}t^2) \dots(49)$$

These results are compared with the experimental values in Table XIX and Figure (12). The best quantitative agreement with the experimental results is obtained with this model.

The temperature coefficient calculated from each model is compared to the experimental values in Table XIX. All the models, except for the Surface Tension model, predict a negative temperature coefficient at 25°C, in agreement with experiment. The failure of the Surface Tension model to predict the sign of the temperature coefficient should not be considered a drawback of the model because the reference temperature was chosen to be 25°C, just before the minimum in the  $k_s$  vs. temperature curve, when  $k_s$  is decreasing. If the reference temperature had been higher than 25°C, then the experimental value would have been positive, in agreement with the Surface Tension model, but not with

Figure 13

Setchenov parameter,  $k_s$ , and its contributions  $k_a$  and  $k_b$ , for naphthalene in seawater as a function of temperature, as predicted by the Scaled Particle Theory.

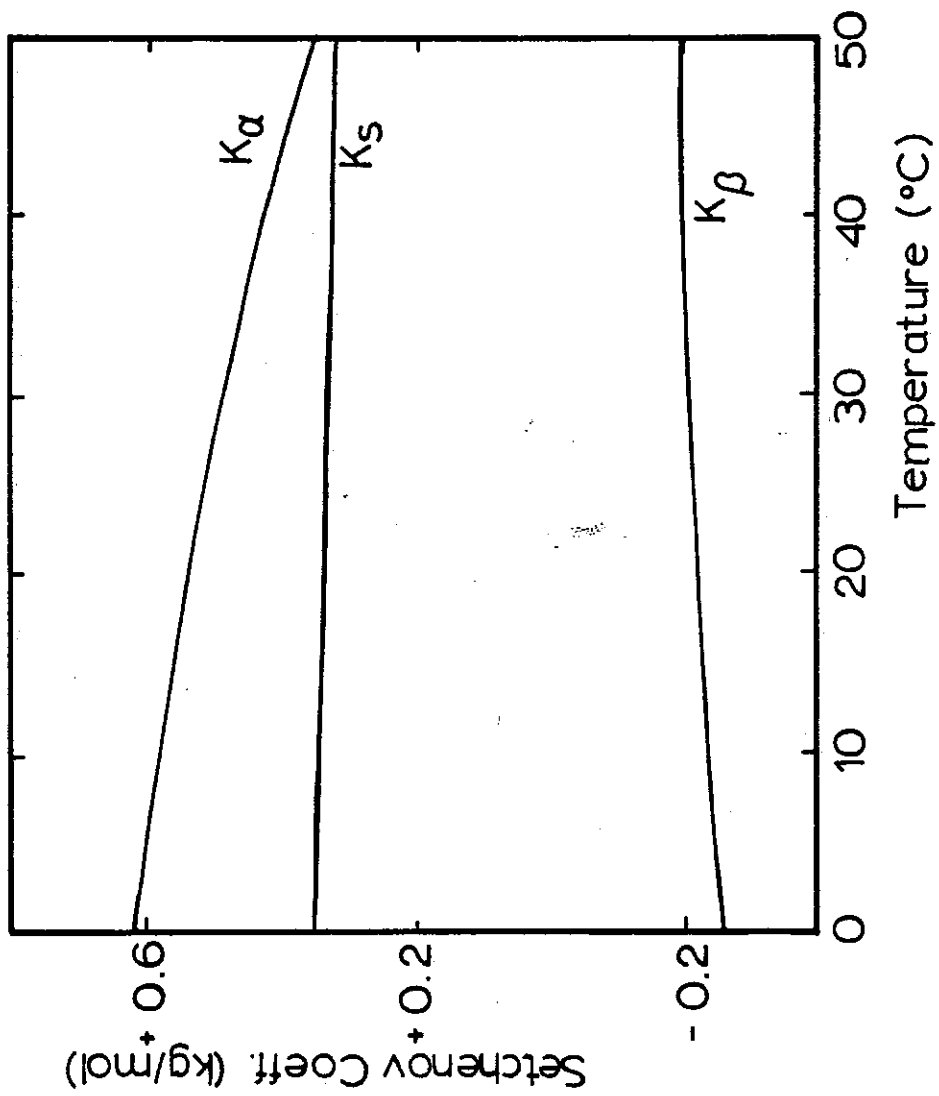
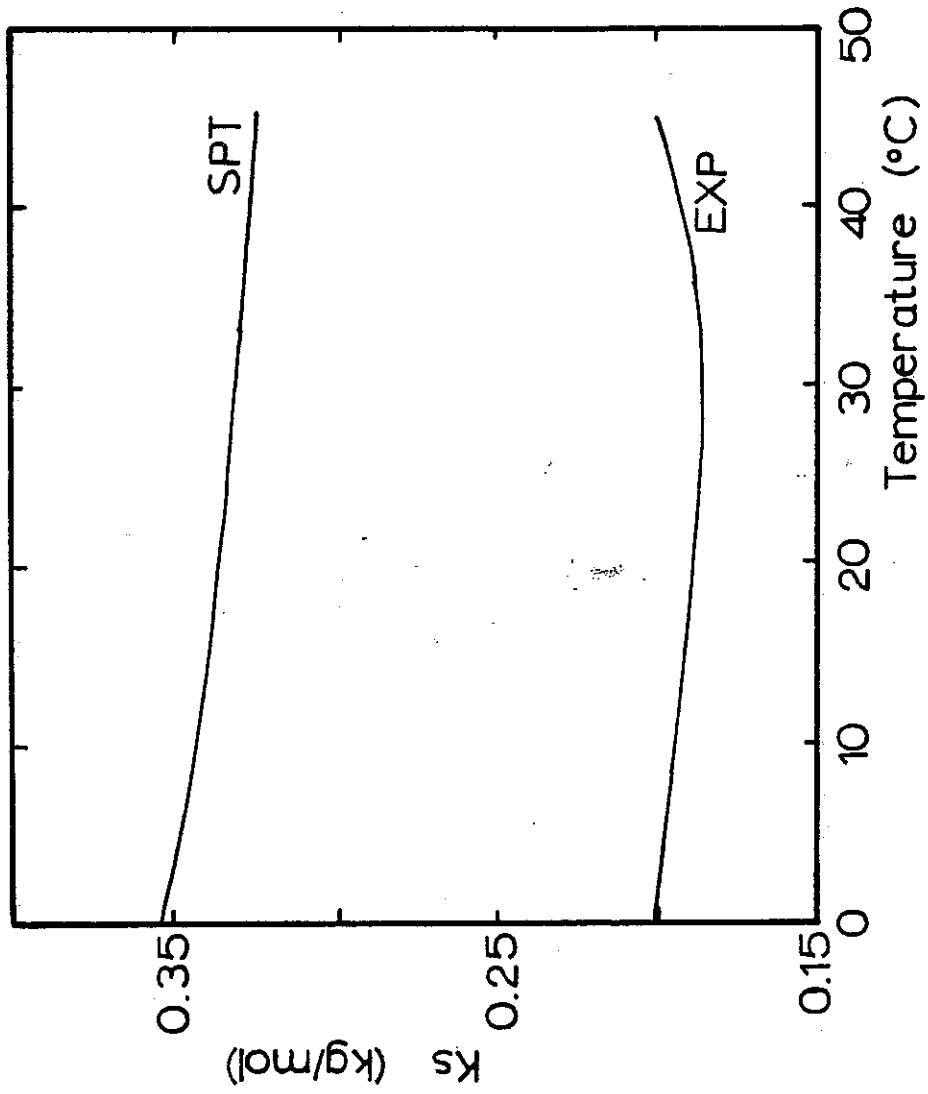


Figure 14

Comparison of the experimental value of the Setchenov parameter as a function of temperature, with the value predicted by the Scaled Particle Theory.





either the Scaled Particle Theory or the Tamman-Tait-Gibson model.

From the predicted values for  $k_s$  by the different models, it seems that the main interaction in the process of dissolving a hydrocarbon molecule is the creation of a cavity in the solvent. The good agreement of the Surface Tension model, which does not assume any interaction between the hydrocarbon and the cavity surrounding it, with our experimental values points in that direction. It also implies that the SPT model overestimates the contribution to  $k_s$  due to the creation of the cavity in the solvent, probably due to the assumption that the intermolecular potentials in liquid water are additive. The TTG model predicts values that are about three times higher than the experimental results, a result that has been observed before for other big molecules, and it is due to the neglect in the original model of the distance of closest approach between the solute and the ions in the solution.

The results presented here for anthracene and phenanthrene confirm that the observed minimum in the Setchenov parameter for naphthalene in seawater is not an anomalous behavior. This was further confirmed when the results given by Brown and Wasik, (1973), for the solubility of benzene and toluene in water and artificial seawater were used to calculate the Setchenov parameters for these compounds in the range from  $0^\circ$  to  $20^\circ\text{C}$ . the results are shown in Figure (15). A minimum is clearly visible around

10°C.

The values for the solubilities of naphthalene under pressure are calculated under the assumption that the absorptivity coefficient of the aromatic in water is pressure-independent. Two other authors have reported solubilities of aqueous naphthalene at 25°C under pressure. Suzuki et al., (1974) obtained their values by removing the solutions from the high pressure cell for external analysis via ultraviolet spectroscopy at one atmosphere. Rodriguez (1978) analyzed his solutions by measuring the absorbance of all the solutions 15 minutes after compression. As expected, the pressure dependence of the solubility is higher in Suzuki's experiment. This work represents the first attempt to reach "true" equilibrium by following the absorption of the compressed solution as a function of time.

The lack of precision of the results is probably the result of adsorption of the unsolubilized naphthalene on the sapphire windows of the high pressure optical cell. This effect made it necessary to clean with ethanol the surface of the windows in contact with the solution.

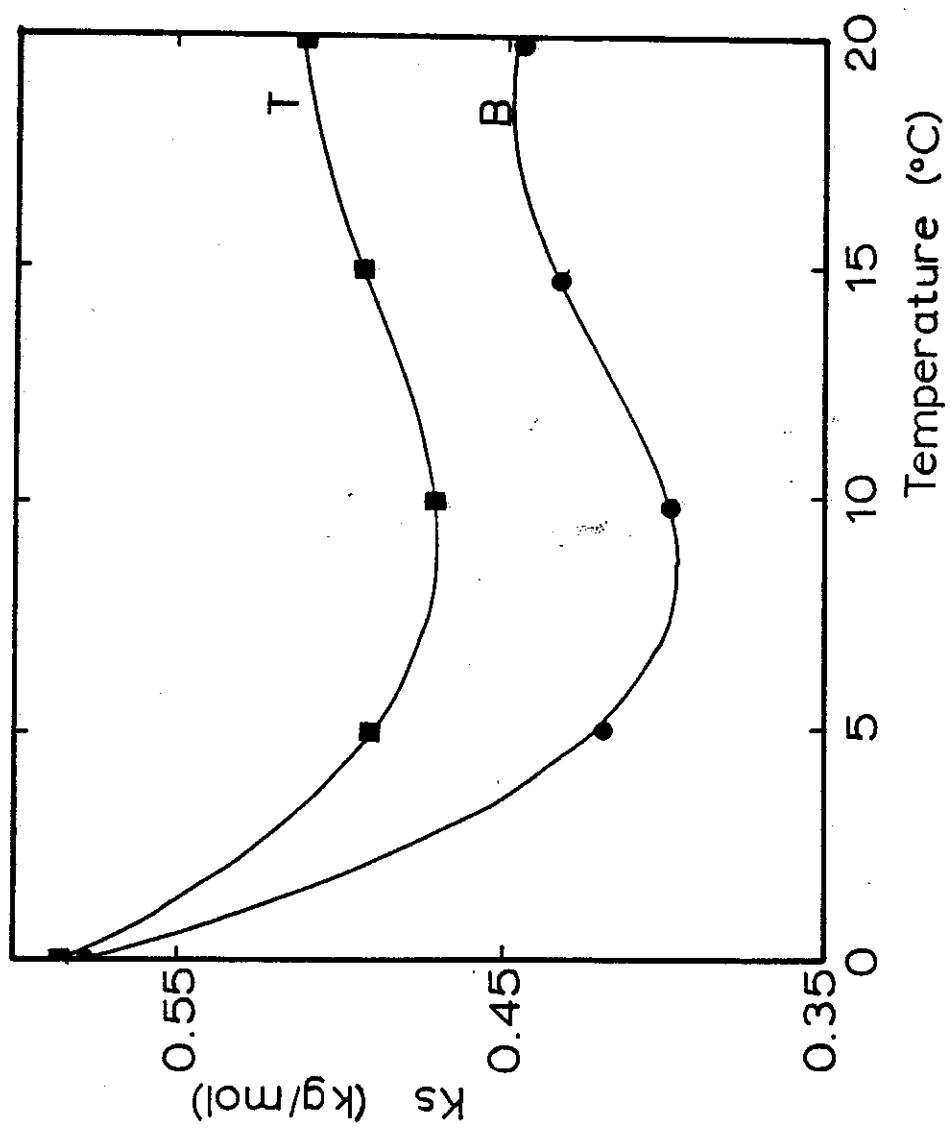
Table XX. Experimental and predicted values for the Setchenov parameter and its temperature coefficient for naphthalene in sea water at 25° C.

	Experimental	T-T-G	SPT	ST
$k_s$	0.252	0.836	-----	0.267
	0.186 <sup>a</sup>	-----	0.333	-----
$dk_s/dt$	$-4.2 \times 10^{-4}$	$-9.1 \times 10^{-3}$	-----	$9.4 \times 10^{-8}$
	$-3.2 \times 10^{-4}$	-----	$-4.7 \times 10^{-4}$	-----

<sup>a</sup> recalculated using the ionic strength scale.

Figure 15

Setchenov parameters for benzene and toluene in seawater as a function of temperature, calculated from the values given by Brown and Wasik, 1973.



## CONCLUSIONS

A comparison of the two methods used to measure solubilities in this work shows that, for work at one atmosphere, the Column Generator method is better. No changes could be found for the values of  $k_s$  as a function of temperature using the "Shake-Flask" method, and all the values were measured to be the same within experimental error. Although the values for  $r^2$  calculated for the Setchenov equation, and for the van't Hoff equation, are quite high, the "Shake-Flask" technique gives higher standard errors for the fit. On the other hand, the results obtained with the Generator Column method are much less scattered, as indicated for the lower uncertainties obtained when both the Setchenov and Clarke-Glew equations were fitted to these results.

A minimum was found for the Setchenov parameter,  $k_s$ , for the salting-out of naphthalene in seawater as a function of temperature. This result was supported when a minimum was also found for the salting-out as a function of temperature of anthracene and phenanthrene. Further confirmation was obtained when the Setchenov parameters for benzene and toluene in seawater were calculated from published solubilities, and a minimum was similarly found. Thus, it can be concluded that the simplest aromatic hydrocarbons show a minimum in the salting-out as a function of

temperature.

The transference of the hydrocarbon solute, from water to seawater at 25°C, was found to be mostly an entropy-driven process. At the temperature of the the minimum the enthalpy change for the transfer of one mole of solute from water to seawater must be zero, so at this temperature the Gibbs free energy change of transfer is entirely the result of an entropic contribution.

Of the three theoretical models used in this work, none predicts the presence of a minimum. However, the Surface Tension model is in good agreement with the experimental values over the temperature range investigated. This means that the main process in dissolving a hydrocarbon solute is the creation of a cavity, large enough to hold the solute. The interaction of a polynuclear aromatic hydrocarbon solute with the cavity is negligible. The Scaled Particle Theory and the Tamman-Tait-Gibson model tend to overestimate the contribution due to the formation of the cavity in the solvent. The T-T-G model fails for big molecules because in its original form it does not take into account the non-zero distance of closest approach between the nonpolar solute and the ions. The SPT model gives a poor correlation probably due to the non-additivity of the intermolecular potential in liquid water, which is not considered in the model. Another problem is that this model requires the input of molecular parameters for which a wide range of values, or methods to calculate them, are available in the literature.

Although the main objective of this work, i.e. to set up a high pressure system, was accomplished, measurement of solubilities were complicated by the adsorption of excess hydrocarbon. Furthermore, the long time required for equilibration made it impractical to measure Setchenov parameters as a function of pressure. In general we can say that the solubility of naphthalene decreases upon compression, but the values were not precise.

For future work, it can be suggested: a) that the sapphire windows be siliconized, to minimize adsorption of the unsolubilized solute and, b) to connect the high pressure transducer directly to the high pressure optical cell, so that the pressure inside the cell can be measured directly. Also, the design of a thermostated jacket for the high pressure cell is desirable. This would allow the measurement of the solubilities as a function of both temperature and pressure.

For work at one atmosphere, the study of the alkylbenzenes is suggested. The partial molar volume of the simplest alkylbenzenes in aqueous solutions has been measured at 25°C, as well as the enthalpy change of solution at the same temperature. These measurements can be repeated in the temperature range where these compounds show a minimum in the Setchenov parameter. Therefore, independent measurements would be available for all parameters needed in the theoretical models.



## REFERENCES

Aquan-Yuen, M.; Mackay, D., and Ying Shiu, W., "Solubility of Hexane, Phenanthrene, Chlorobenzene, and p-Dichlorobenzene in Aqueous Electrolyte Solutions", J. Chem. Eng. Data, 24(1):30-34, (1979).

Albers, P.H., "Transfer of Crude Oils from Contaminated Water to Bird Eggs", Environm. Res., 22:307-314 (1980).

Atlas, E.; Foster, R.; and Glam, C.S., "Air-Sea Exchange of High Molecular Weight Organic Pollutants: Laboratory Studies", Environm. Sci. Technol., 16(5):283-286, (1981).

Aveyard, R. and Heselden, R., "Salting-in of Alcohols by Symmetrical Tetra-Alkylammonium Bromides", J. Chem. Soc., Faraday Trans. I, 70:1953-1964, (1974).

Aveyard, R. and Heselden, R., "Salting-out of Alkanols by Inorganic Electrolytes", J. Chem. Soc., Faraday Trans. I, 71:312-321, (1975).

Aveyard, R., "A Surface Tension Approach to the Salting-Out of Nonpolar Nonelectrolytes", Can. J. Chem., 60:1317-1326, (1982).

Balon Almeida, M.; Maestre Alvarez, A.; Muñoz de Miguel, E.; and Soria del Hoyo, E., "Setchenov Coefficients for Naphthols by Distribution Method", Can. J. Chem., 61:244-248, (1983).

Banerjee, S.; Yalkowsky, S.H.; and Valvani, S.C., "Water solubility and Octanol/Water Partition Coefficients of Organics. Limitations of the Solubility-Partition Coefficient Correlation", Environm. Sci. Technol., 14(10):1227-1229, (1980).

Ben-Naim, J., "Thermodynamics of Aqueous Solutions of Noble Gases. I.", J. Phys. Chem. 69(10):3240-3245, (1965).

Bernal, J.D. and Fowler, R.H., "A Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ions", J. Chem. Phys. 1(8):515-548, (1933).

✓ Blandamer, M.J., Burgess, J., Robertson, R.E, and Scott, J.M.W., "Dependence of Equilibrium and Rate Constants on Temperature and Pressure", Chem. Rev., 82:259-286, (1982).

Bockris, J. O'M. and Reddy, A.K.N., "Modern Electrochemistry", Vol. I, Plenum/Rosetta, New York, NY, third printing 1973.

Boehm, P.D. and Quinn, J.G., "Solubilization of Hydrocarbons by the Dissolved Organic Matter in Seawater" Geochim. Cosmochim. Acta, 37:2459-2477 (1973).

Bohon, R.L. and Clausen, W.F.; "The Solubility of Aromatic Hydrocarbons in Water", J. Am. Chem. Soc., 73:1571-1578, (1951).

Brown, R.L., and Wasik, S.P.; "Method of Measuring the Solubilities of Hydrocarbons in Aqueous Solutions", J. Res. Natl. Bur. Stdrs., 78A(4):453-460, (1974).

Butler, J.N., "Pelagic Tar", Scientific American, 232:90-97 (1975)

Chiou, C.T.; Freed, V.H.; Schmedding, D.W.; and Kohnert, R.L., "partition Coefficient and Bioaccumulation of Selected Organic Chemicals", Environm. Sci. Technol., 11(5):475-478 (1977).

✓ Clarke, E.C. and Glew, D.N., "Evaluation of Thermodynamic Functions from Equilibrium Constants", Trans. Faraday Soc. 62:539-547, (1966).

Clayton Jr., J.R.; Pavlou, S.P.; and Breitner, N.F., "Polychlorinated Biphenils in Coastal Marine Zooplankton: Bioaccumulation by Equilibrium Partitioning", Environm. Sci. Technl., 11(7):676-682 (1977).

Clever, H.L. and Battino, R., "The Solubility of Gases in Liquids", In Dack, M.R.J., Ed., "Solutions and Solubilities", Techniques of Chemistry Series, Vol. 8, Part 1, Wiley, New York, 1975.

Clever, H.L. and Holland, C.J., "Solubility of Argon Gas in Aqueous Alkali Halide Solutions. Temperature Coefficient of the Salting-Out Parameter", J. Chem. Eng. Data 13(3):411-414, (1968).

Collier, T.K.; Krahn, M.M.; and Malins, D.C. "The Disposition of Naphthalene and its Metabolites in the Brain of Rainbow Trout (Salmo gairdneri)", Environm. Res., 23:35-41 (1980).

Cross, R.F., "Expansion of the McDevit and Long Theory of Nonelectrolyte Activity Coefficients to a Consideration of Concentrated Aqueous Electrolyte Solutions", J. Phys. Chem., 79(17):1822-1828, (1975).

Cross, R.F. and McTigue, P.T., "Activity Coefficients of Alkyl Acetates in Concentrated Electrolyte Solutions", J. Chem. Phys., 80(8):814-821, (1976).

Dahl, L.W. and Andersen, H.C., "Cluster Expansions for Hydrogen-Bonded fluids. III. Water", J. Chem. Phys., 78(4):1962-1979, (1983).

Dahl, L.W. and Andersen, H.C., "A Theory of the Anomalous Thermodynamic Properties of Liquid Water", J. Chem. Phys., 78(4):1980-1993, (1983a).

Danforth, W.E., "The Dielectric Constant of Liquids Under High Pressure", Phys. Rev., 38:1224-1235, (1931).

Deno, N.C. and Spink, C.H., "The McDevit-Long Equation for Salt Effects on Non-Electrolytes", J. Am. Chem. Soc., 67:1347-1349, (1963).

Desrosier, N.M. and Morel, J.P., "Evaluation of Thermodynamic Functions Relative to Cavity Formation in Liquids: Uses and Misuses of Scaled Particle Theory", Can. J. Chem. 59(1):1-7, (1981).

DeVoe, H., Miller, M.M., and Wasik, S.P., "Generator Columns and High Pressure Liquid Chromatography for Determining Aqueous Solubilities and Octanol-Water Partition Coefficients of Hydrophobic Substances", J. Res. Natl. Bur. Stands., 86(4):361-366, (1981).

Dexter, R.N. and Pavlou, S.P. "Distribution of Stable Organic Molecules in the Marine Environment: Physical Chemical Aspects. Chlorinated Hydrocarbons". Mar. Chem. 7:67-84 (1978a).

Dexter, R.N. and Pavlou, S.P. "Mass Solubility and Aqueous Activity Coefficients of Stable Organic Chemicals in the Marine Environment: Polychlorinated Biphenils". Mar. Chem. 6:41-53 (1978b).

Dreisbach, R.R., "Physical Properties of Chemical Compounds", Advances in Chemistry Series 15, American Chemical Society, 1955.

Eganhouse, R.P. and Calder, J.A. "The Solubility of Medium Molecular Weight Aromatic Hydrocarbon Co-Solutes and Salinity". Geochim. Cosmochim. Acta 37:2459-2477 (1973).

Eisenberg, D. and Kauzmann, W., "The Structure and Properties of Water", Oxford University Press, New York, NY, 1969.

Farrington, J.W. and Meyer, P.A. "Hydrocarbons in the Marine Environment" In "Environmental Chemistry", Vol. I, The Chemical Society, London, 1975.

Farrington, J.W.; Teal, J.M. and Parker, P.L. "Petroleum Hydrocarbons", In Goldberg, E.D. "Strategies for Marine Pollution Monitoring", Wiley-Interscience, New York, 1976.

Frank, H.S. and Evans, M.W., "Free Volume and Entropy in Condensed Systems. III. Partial Molal Entropy in Dilute Solutions; Structure and Thermodynamics in Aqueous Electrolytes", J. Chem. Phys. 13(11):507-532, (1945).

Frank, H.S., "Structural Models", In Franks, F., "Water: A Comprehensive Treatise", Vol. I, Plenum Press, New York, second printing 1974.

Gerth, W.A., "Effects of Dissolved Electrolytes on the Solubility and Partial Molar Volume of Helium in Water from 50 to 400 Atmospheres at 25°C", J. Solution Chem. 12(9):655-669, (1983).

Gibbs, J.H., "On the Nature of Liquid Water", Ann. N.Y. Acad. Sci., 303:10-21, (1977).

Gibson, D.J., "Biodegradation of Aromatic Petroleum Hydrocarbons", In Wolfe, D.A., Ed., "Fate and Effects of Petroleum Hydrocarbons in Marine Organisms and Ecosystems", Pergamon Press, New York, 1977.

Gold, G. and Rodriguez, S., "El Modelo TTG y el Salting-Out de Gases en Agua de Mar", paper presented to the XVIII National Meeting of the Mexican Chemical Society, Coatzacoalcos, 1983.

Gordon J.E. and Thorne, R.L., "Salt Effects on the Activity Coefficient of Naphthalene in Mixed Aqueous Electrolyte Solutions. I. Mixtures of Two Salts", J. Phys. Chem. 71(13):4390-4399, (1967).

Gordon, J.E., "The Organic Chemistry of Electrolyte Solutions", Wiley-Interscience, New York, 1975.

Hagler, A.T., Scheraga, H.A., and Nemethy, G., "Structure of Liquid Water. Statistical Thermodynamic Theory", J. Phys. Chem., 76(22):3229-3243, (1972).

Hagler, A.T. and Scheraga, H.A., "Current Status of the Water-Structure Problem; Application to Proteins", Ann. N.Y. Acad. Sci., 204:51-78, (1973).

Hansch, C.; Quinlan, J.E.; and Lawrence, G.L., "The Linear Free-Energy Relationship Between Partition Coefficients and the Aqueous Solubility of Organic Liquids", J. Org. Chem., 33(1):347-350, (1968).

Harrison, W.; Winnick, M.A.; Kwong, P.T.; and Mackay, D., "Crude Oil Spills, Environ. Sci. Technol., 9(3):231-234, (1975).

Hermann, R.B., "Theory of Hydrophobic Bonding. II. Correlation of Hydrocarbon Solubility in Water with Solvent Cavity Surface Area", J. Phys. Chem. 76(19):2754-2759, (1972).

Hershey, J.P.; Sotolongo, S.; and Millero, F.J., "Densities

and Compressibilities of Aqueous Sodium Carbonate and Bicarbonate from 0 to 45°C", J. Solution Chem. 12(4):233-254, (1983).

Heric, E.L. and Berryman, J.M., "Molar Volume of Supercooled Naphthalene at 25°C", J. Chem. Eng. Data, 14(4):486-487, (1969).

Hinga, K.R.; Pilson, M.E.Q.; Lee, R.F.; Farrington, J.W.; Tjessem, K.; and Davis, A.C., "Biogeochemistry of Benzanthracene in an Enclosed Marine Ecosystem", Environ. Sci. Technol., 14(9):1136-1144, (1980).

Hutchinson, T.C.; Hellebust, J.A.; Tam, D.; MacKay, D.; Mascarenhas, R.A.; and Shiu, W.Y., "The Correlation of the Toxicity to Algae of Hydrocarbons and Halogenated Hydrocarbons with Their Physico-Chemical Properties", Environ. Sci. Res. 16:577-586, (1980).

Hvidt, A., "The Solubility of Hydrocarbons in Water", Acta Chem. Scand., A37:99-103, (1983).

Hvidt, A., "Interactions of Water with Nonpolar Solutes", Ann. Rev. Biophys. Bioeng. 12:1-20, (1983).

Ikono, T., "Density, Viscosity, and Electrolytic Conductivity of Concentrated Aqueous Electrolyte Solutions at Several Temperatures. Alkaline-Earth Chlorides,  $\text{LaCl}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaNO}_3$ ,  $\text{NaBr}$ ,  $\text{KNO}_3$ ,  $\text{KBr}$ , and  $\text{Cd}(\text{NO}_3)_2$ ", J. Chem. Eng. Data 29(1):45-52, (1983).

Jeffrey, A.M.; Yeh, H.J.; Jerina, D.M.; Patel, J.R.; Davey, J.F.; and Gibson, D.T., "Initial Reactions in the Oxidation of Naphthalene by Pseudomonas putida", Biochemistry 14(13):575-584, (1975).

Katz, M.; Chan, C.; Tosine, H.; and Sakuma, T., "Relative Rates of Photochemical and Biological Oxidation (in vitro) of Polynuclear Aromatic Hydrocarbons", In Jones, P.W. and Leber, P., Eds., "Polynuclear Aromatic Hydrocarbons", Ann Arbor Science Publishers, Ann Arbor, 1979.

Khan, S. and Pandya, K.P., "Biochemical Studies on the Toxicity of n-Octane and n-Nonane", Environ. Res. 22:271-276, (1980).

Klevens, H.B., "Solubilization of Polycyclic Hydrocarbons", J. Phys. Colloid Chem. 54:283-298, (1950).

Korfmacher, W.A.; Natusch, D.F.S.; Taylor, D.R.; Wehry, E.L.; and Mamantov, G., "Thermal and Photochemical Decomposition of Particulate PAH", In Jones, P.W. and Leber, P., Eds., "Polynuclear Aromatic Hydrocarbons", Ann Arbor Science Publishers, Ann Arbor, 1979.

Kudchadker, A.P.; Kudchadker, S.A.; and Wilhoit, R.C., "Naphthalene", API Monograph Series, API Publication 707, 1978.

Lehr, R.E.; Taylor, C.W.; Kumar, S.; Levin, W.; Chang, R.; Wood, A.W.; Conney, A.H.; Thakker, D.R.; Yagi, H.; Mah, H.D.; and Jerina, D.M., "Differences in Metabolism Provide a Basis for the Low Mutagenicity and Carcinogenicity of Benzo(e)Pyrene Compared to Benzo(a)Pyrene", In Jones, P.W. and Leber, P., Eds., "Polynuclear Aromatic Hydrocarbons", Ann Arbor Science Publishers, Ann Arbor, 1979.

Lentz, B.R.; Hagler, A.T.; and Scheraga, H.A., "Structure of Liquid Water. II. Improved Statistical Thermodynamic Treatment and Implications of a Cluster Model", J. Phys. Chem. 78(15):1531-1550, (1974).

Leyendekkers, J.V., "Thermodynamics of Seawater", Part 1, M. Dekker, New York, 1976.

Leyendekkers, J.V. and Hunter, R.J., "Refractive Index of Aqueous Electrolyte Solutions. Extrapolations to Other Temperatures, Pressures, and Wavelengths and to Multicomponent Systems", J. Chem. Eng. Data 22(4):427-431, (1977).

Leyendekkers, J.V. and Hunter, R.J., "The Tamman-Tait-Gibson Model for Aqueous Electrolyte Solutions. Application to the Refractive Index", J. Phys. Chem. 81(17):1657-1663, (1977).

Leyendekkers, J.V., "The Viscosity of Aqueous Electrolyte Solutions and the TTG Model", J. Solution Chem. 8(12):853-869, (1979).

Leyendekkers, J.V., "The Tamman-Tait-Gibson Model. Application to the Heat Capacities of Aqueous Electrolyte

Solutions", J. Chem. Soc., Faraday Trans. I 76:1206-1217, (1980).

Long, F.A. and McDevit, W.F., "Activity Coefficient of Nonelectrolyte Solutes in Aqueous Salt Solutions", Chem. Rev. 51:119-169, (1952).

LoSurdo, A.; Alzola, E.M.; and Millero, F.J., "The (P, V, T) Properties of Concentrated Aqueous Electrolytes. I. Densities and Apparent Molar Volumes of NaCl, Na<sub>2</sub>SO<sub>4</sub>, MgCl<sub>2</sub>, and MgSO<sub>4</sub> Solutions From 0.1 mol kg<sup>-1</sup> to Saturation and from 273.15 to 323.15 K", J. Chem. Thermodynamics 14:649-662, (1982).

Lyman, J. and Fleming, R.H., "Composition of Seawater", J. Mar. Res. 3:134-146, (1940).

Mackay, D. and Leinonen, P.J., "Rate of Evaporation of Low Solubility Contaminants from Water Bodies to the Atmosphere", Environ. Sci. Technol. 9(13):1178-1180, (1975).

Mackay, D.; Ying Shiu, W.; and Sutherland, R.P., "Determination of Air-Water Henry's Law Constants for Hydrophobic Pollutants", Environ. Sci. Technol. 13(3):333-337, (1979).

Mackay, D., "Correlation of Bioconcentration Factors", Environ. Sci. Technol. 16(5):274-278, (1982).

Masterton, W.L. and Pei Lee, T., "Salting Coefficients from Scaled Particle Theory", J. Phys. Chem. 74(8):1776-1782, (1970).

Masterton, W.L., "Salting Coefficients for Gases in Seawater from Scaled Particle Theory", J. Solution Chem. 4(6):523-534, (1975).

Masterton, W.L. and Pei Lee, T., "Temperature dependence of the Salting Coefficient", In Adams, W.A. Ed., "Chemistry and Physics of Aqueous Gas Solutions", The Electrochemical Society, Princeton, N.J., 1975.

May, W.E.; Wasik, S.P.; Miller, M.M.; Tewari, Y.B.; Brown-Thomas, J.M.; and Goldberg, R.N., "Solution Thermodynamics of Some Slightly Soluble Hydrocarbons in Water", J. Chem.



Eng. Data 28(2):197-200, (1983).

McAuliffe, C.D., "Solubility in Water of Paraffin, Cycloparaffin, Olefin, Acetylene, Cycloolefin, and Aromatic Hydrocarbons", J. Phys. Chem. 70(4):1267-1275, (1966).

McAuliffe, C.D., "Dispersal and Alteration of Oil Discharged on a Water Surface", In Wolfe, D.A., "Fate and Effects of Petroleum Hydrocarbons in Marine Organisms and Ecosystems", Pergamon Press, New York, 1977.

McAuliffe, C.D.; Johnson, J.C.; Greene, S.H.; Canevari, G.P.; and Searl, T.D., "Dispersion and Weathering of Chemically Treated Crude Oils in the Ocean", Environ. Sci. Technol. 14(12):1509-1518, (1980).

McDevit, W.F. and Long, F.A., "Activity Coefficient of Benzene in Aqueous Salt Solutions", J. Am. Chem. Soc. 74:1773-1777, (1952).

Means, J.C.; Wood, S.G.; Hasset, J.J.; and Banwarth, W.L., "Sorption of Polynuclear Aromatic Hydrocarbons by Sediments and Soils", Environ. Sci. Technol. 14(12):1524-1528, (1980).

Miller, K.J. and Savchik, J.A., "A New Empirical Method to Calculate Average Molecular Polarizabilities", J. Am. Chem. Soc. 101(24):7206-7213, (1979).

Millero, F.J. and Leung, W.H., "The Thermodynamics of Seawater at One Atmosphere", Am. J. Sci. 276:1035-1077, (1976).

Millero, F.J.; Chen, C.T.; Bradshaw, A.; Schleicher, K., "A New High Pressure Equation of State for Seawater", Deep-Sea Res. 27A:255-264, (1980).

Neely, W.B.; Branson, D.R.; and Blau, G.E., "Partition Coefficient to Measure Bioconcentration Potential of Organic Chemicals in Fish", Environ. Sci. Technol. 8(3):1113-1115, (1974).

Nemethy, G. and Scheraga, H.A., "Structure of Water and Hydrophobic Bonding in Proteins. I. A Model for the Thermodynamic Properties of Liquid Water", J. Chem. Phys. 36(12):3382-3400, (1962).

Nemethy, G. and Scheraga, H.A., "Structure of Water and Hydrophobic Bonding in Proteins. II. Model for the Thermodynamic Properties of Aqueous Solutions of Hydrocarbons", J. Chem. Phys. 36(12):3401-3417, (1962).

Nemethy, G.; Peer, W.J.; and Scheraga, H.A., "Effect of Protein-Solvent Interactions on Protein Conformation", Ann. Rev. Biophys. Bioeng. 10:459-497, (1981).

Paul, M., "Solubilities of Naphthalene and Biphenyl in Aqueous Solutions of Electrolytes", J. Am. Chem. Soc. 74:5274-5277, (1952).

Pavlou, S.P. and Dexter, R.N., "Distribution of Polychlorinated Biphenyls (PCB) in Estuarine Ecosystems. Testing the Concept of Equilibrium Partitioning in the Marine Environment", Environ. Sci. Technol. 13(1):65-71, (1979).

Pierotti, R.A., "The Solubility of Gases in Liquids", J. Phys. Chem. 67:1840-1845, (1963).

Pierotti, R.A., "Aqueous Solutions of Nonpolar Gases", J. Phys. Chem. 69:281-288, (1965).

Pierotti, R.A., "A Scaled Particle Theory of Aqueous and Nonaqueous Solutions", Chem. Rev. 76(6):717-726, (1976).

Ponomarev, V.I.; Filipenko, O.S.; and Atovman, L.O., "Crystal and Molecular Structure of Naphthalene at  $-150^{\circ}\text{C}$ ", Sov. Phys. Crystallogr. 21(2):215-216, (1976).

Poole, L. and Borchers, M., "Some Common BASIC Programs", 3rd. Edition, Osborne/McGraw-Hill, New York, 1981.

Pople, J.A., "Molecular Association in Liquids. II. A Theory of the Structure of Water", Proc. Roy. Soc. (London) A205:163-178, (1951).

Prahl, F.G. and Carpenter, R., "The Role of Zooplankton Fecal Pellets in the Sedimentation of Polycyclic Aromatic Hydrocarbons in Dabob Bay, Wash.", Geochim et Cosmochim. Acta 43:1959-1972, (1979).

Rapaport, D.C. and Scheraga, H.A., "Hydration of Inert Solutes", J. Phys. Chem. 86(6):873-880, (1982).

Regnier, Z.R. and Scott, B.F., "Evaporation Rates of Oil Components", Environ. Sci. Technol. 9(5):469-472, (1975).

Reynolds, J.A.; Gilbert, D.B.; and Tanford, C., "Empirical Correlation Between Hydrophobic Free Energy and Aqueous Cavity Surface Area", Proc. Natl. Acad. Sci. U.S.A. 71(8):2925-2927, (1974).

Rice, S.A. and Sceats, M.G., "A Random Network Model for Water", J. Phys. Chem. 85(9):1108-1119, (1981).

Robertson, W.W.; Weigand, O.E.; and Matsen, F.A., "Pressure Effects on the Ultraviolet Absorption Spectra of Some Aromatic Hydrocarbons", J. Mol. Spectros. 1(1):1-10, (1957).

Rodriguez, S., Ph.D. Dissertation, University of California at Santa Barbara, 1978.

Rossi, S.S. and Thomas, W.H., "Solubility Behavior of Three Aromatic Hydrocarbons in Distilled Water and Natural Seawater", Environ. Sci. Technol. 15(6):715-716, (1981).

Sceats, M.G. and Rice, S.A., "Amorphous Solid Water and its Relationship to Liquid Water: A Random Network Model for Water", In Franks, F., "Water: A Comprehensive Treatise", Vol. 7, Plenum Press, New York, 1982.

Scheraga, H.A., "Intermolecular Potential for Water and the Hydration of Proteins", Ann. N.Y. Acad. Sci. 303:2-10, (1977).

Scheraga, H.A., "Structure and Thermodynamic Properties of Aqueous Solutions of Small Molecules and Proteins", Pure & Appl. Chem. 54(8):1495-1505, (1982).

Schwartz, F.P., "Determination of Temperature Dependence of Solubilities of Polycyclic Aromatic Hydrocarbons in Aqueous Solutions by a Fluorescence Method", J. Chem. Eng. Data 22(3):273-277, (1977).

Sellers, H. and Boggs, J.E., "The Structure of Naphthalene", J. Mol. Structure 74:137-142, (1981).

Seng Tee, L.; Gotoh, S; and Stewart, W.E., "Molecular Parameters for Normal Fluids: The Lennard-Jones 12-6 Potential", Ind. Eng. Chem. Fundam. 5(3):356-363, (1966).

Shaw, D.G., "Hydrocarbons in the Water Column", In Wolfe, D.A., "Fate and Effects of Petroleum Hydrocarbons in Marine Organisms and Ecosystems", Pergamon Press, New York, 1977.

Shinoda, K., "'Iceberg' Formation and Solubility", J. Phys. Chem. 81(13):1300-1302, (1977).

Shinoda, K., "Principles of Solution and Solubility", Dekker, New York, 1978.

Shoor, S.K. and Gubbins, K.E., "Solubility of Nonpolar Gases in Concentrated Electrolyte Solutions", J. Phys. Chem. 73(3):498-505, (1969).

Southworth, G.R., Keffer, C.C.; and Beauchamp, J.J., "Potential and Realized Bioconcentration. A Comparison of Observed and Predicted Bioconcentration of Azurenes in the Fathead Minnow", Environ. Sci. Technol. 14(12):1529-1531, (1980).

Stiel, L.I. and Thodos, G., "Lennard-Jones Force Constants Predicted from Critical Properties", J. Chem. Eng. Data 7(2):234-236, (1962).

Sutton, C. and Calder, J.A., "Solubility of Higher-Molecular-Weight n-Parafins in Distilled Water and Seawater", Environ. Sci. Technol. 8(7):654-657, (1974).

Sutton, C. and Calder, J.A., "Solubility of Alkylbenzenes in Distilled Water and Seawater at 25°C", J. Chem. Eng. Data 20(3):320-322, (1975).

✓ Suzuki, K.; Taniguchi, Y; Ishigami, T.; and Tsuchiya, M., "The Effect of Pressure on the Solubility of Naphthalene in Water and Aqueous Tetraalkylammonium Salt Solutions", In Osuyi, J. (Ed.), "Proceedings of the Fourth International Conference on High Pressure", The Physico-Chemical Society

of Japan, Kyoto, 1974.

Swinerton, J.W. and Lamontagne, R.A., "Oceanic Distribution of Low-Molecular-Weight Hydrocarbons. Baseline Measurements", Environ. Sci. Technol. 8(7):657-659, (1974).

Tanford, C., "The Hydrophobic Effect: Formation of Micelles and Biological Membranes", 2nd. Edition, Wiley, New York, N.Y., 1980.

Tewari, Y.B.; Miller, M.M.; and Wasik, S.P., "Calculation of Aqueous Solubility of Organic Compounds", J. Res. Natl. Bur. Stands. 87(2):155-158, (1981).

Tewari, Y.B.; Miller, M.M.; Wasik, S.P.; and Martire, D., "Aqueous Solubility and Octanol/Water Partition Coefficient of Organic Compounds at 25.0°C", J. Chem. Eng. Data 27(4):451-454, (1982).

Thacher, P.S. and Meith-Aucin, N., "The Oceans: Health and Prognosis", In Borgese, E.M. and Ginsburg, N., Eds. "Ocean Yearbook 1", University of Chicago Press, Chicago, 1978.

Tiepel, E.W. and Gubbins, K.E., "Thermodynamic Properties of Gases Dissolved in Electrolyte Solutions", Ind. Eng. Chem. Fundam. 12(1):18-25, (1973).

Vesala, A. and Lonngberg, B., "Salting-In Effects of Pyridinium Chlorides on Aromatic Compounds", Acta Chem. Scand. A34(3):187-192, (1980).

Wasik, S.P.; Miller, M.M.; Tewari, Y.B.; May, W.E.; Sonnefeld, W.J.; DeVoe, H.; and Zoller, W.H., "Determination of the Vapor Pressure, Aqueous Solubility, And Octanol/Water Partition Coefficients of Hydrophobic Substances by Coupled Generator/Liquid Chromatographic Methods", Res. Rev. 85:29-42, (1983).

Wauchope, R.D. and Getzen, F.W., "Temperature Dependence of Solubilities in Water and Heats of Fusion of Solid Aromatic Hydrocarbons", J. Chem. Eng. Data 17(1):38-41, (1972).

Whitefield, M., "Activity Coefficients in Natural Waters", In Pytkowicz, R.M. Ed., "Activity Coefficients in Electrolyte Solutions", Vol. II, CRC Press, Boca Raton, FA,

1979.

Zepp, R.G. and Schlotzhauer, P.F., "Photoreactivity of Selected Aromatic Hydrocarbons in Water", In Jones, P.W. and Leber, P., Eds., "Polynuclear Aromatic Hydrocarbons", Ann Arbor Science Publishers, Ann Arbor, 1979.

APPENDIX A

Scaled Particle Theory

The expressions for  $k_a$ ,  $k_b$ , and  $k_g$  for 1:1 electrolytes are (Masterton and Pei Lee, 1970):

$$\begin{aligned}
 k_a = & 2.15 \times 10^{20} (\sigma_3^3 + \sigma_4^3) - 2.47 \times 10^{-4} \phi + \alpha_1 (6.45 \times 10^{20} (\sigma_3^2 + \sigma_4^2) + \\
 & + 1.34 \times 10^{28} (\sigma_3^3 + \sigma_4^3) - 4.23 \times 10^4 \phi) + \sigma_1^2 (6.45 \times 10^{20} (\sigma_3 + \sigma_4) + \\
 & + 4.01 \times 10^{28} (\sigma_3^2 + \sigma_4^2) + 1.32 \times 10^{36} (\sigma_3^3 + \sigma_4^3) - 4.17 \times 10^{12} \phi) \dots (A1)
 \end{aligned}$$

$$\begin{aligned}
 k_b = & -1.85 \times 10^{14} (\epsilon_1/k)^{1/2} (\sigma_3^{3/4} z_3^{1/4} (\sigma_1 + \sigma_3)^3 / \sigma_3^3 + \\
 & \sigma_4^{3/4} z_4^{1/4} (\sigma_1 + \sigma_4)^3 / \sigma_4^3 + 6.26 \times 10^{17} \phi (\epsilon_1/k)^{1/2} (\sigma_1 + \sigma_2)^3 + \\
 & 4.00 \times 10^{-2} \phi \alpha_1 / (\sigma_1 + \sigma_2)^3 \dots (A2)
 \end{aligned}$$

$$k_g = 0.016 - 4.34 \times 10^{-4} \phi \dots (A3)$$

where  $\phi$  is the apparent partial molal volume of the electrolyte,  $\epsilon/k$  is the depth of the Lennard-Jones potential,  $\alpha$  is the polarizability, and  $\sigma$  is the molecular (or ionic) diameter. The subscripts refer 1 to the nonelectrolyte, 2 to the solvent (water), 3 to the cation, and 4 to the anion.

These equations were later reformulated by Masterton (1975) to predict the salting-out of nonelectrolytes in

seawater. The concentration of seasalt is expressed in the ionic strength scale. The expressions for  $k_a$  and  $k_b$  are:

$$k_a = A + Bx10^6\sigma_1 + Cx10^{14}\sigma_1^2 \dots\dots\dots (A4)$$

$$k_b = -1.498x10^{24}/T ((A_v/0.0360)-0.05040) ((\epsilon_1/k)^{1/2} \sigma_{12}^3 + 0.996x10^{-21} \alpha_1 / \sigma_{12}^3) - (2.922x10^{21}/T) (\epsilon_1/k)^{1/2} d/dI_v (\sum c_i (\epsilon_i/k)^{1/2} \sigma_{1i}^3) \dots\dots\dots (A5)$$

where A, B, C, and  $A_v$  are temperature-dependent coefficients tabulated in the original paper,  $I_v$  is the ionic strength, and the terms  $\sigma_{1i}$  are calculated from the usual mixing rules

$$\sigma_{1i} = (\sigma_1 + \sigma_i)/2 \dots\dots\dots (A6)$$

and the subscripts have the same meaning as before, except that i refers to the individual ions.



## APPENDIX B

### Program SEAWATER.

The program SEAWATER calculates the effective pressure exerted by seasalt as defined in the Tamman-Tait-Gibson model. This program, written in BASIC, calculates  $P_e$  as a function of both temperature and salinity. It also transforms the seasalt concentration from the salinity scale to molality and ionic strength.

```
10 PRINT "THE PRESSURE IS"
20 INPUT P
30 FOR T=0 TO 40 STEP 5
40 A=54.6746-0.6035*T+0.0110999*T**2-6.167E-5*T**3
50 B=0.07944+0.01648*T-5.3009E-4*T**2
60 C=2.2838E-3-1.098*T-1.6078E-6*T**2
70 D=1.91075E-4
80 E=2.0816E-8*T+9.1697E-10*T**2-9.9348E-7
90 F=2671.8+19.454*T-0.27028*T**2+9.798E-4*T**3
100 A1=0.9998414+6.79395E-5*T-9.0953E-6*T**2
110 A2=1.00169E-7*T**3-1.1201E-9*T**4+6.5363E-12*T**5
120 A3=8.2592E-4-4.449E-6*T+1.0485E-7*T**2
130 A4=-1.258E-9*T**3+3.315E-12*T**4
140 A5=-6.3376E-6+2.8441E-7*T-1.687E-8*T**2
150 A6=2.83258E-10*T**3
160 A7=5.4705E-7-1.97975E-8*T+1.6641E-9*T**2
170 A8=-3.1203E-11*T**3
```

```
180 B1=A1+A2
190 B2=A3+A4
200 B3=A5+A6
210 B4=A7+A8
220 L1=19652.21+148.4206*T-2.32711*T**2+0.0136048*T**3
230 L2=5.15529E-5*T**4
240 L=L1+L2
250 M=3.23991+1.4371E-3*T+1.16092E-4*T**2-5.77905E-7*T**3
260 N=8.50935E-5-6.12293E-6*T+5.2787E-8*T**2
270 PRINT "T=";T
280 FOR S=0 TO 40 STEP 5
290 W=B1+B2*S+B3*(S**3/2)+B4*S**2
300 V0=1.000028/W
310 O=M+C*S+D*S**3/2
320 U=N+E*S
330 R=L+A*S+B*S**3/2
340 Q=R+O*(P-1)+U*(P-1)**2
350 Z1=V0*(R-U*(P-1)**2)
360 Z2=V0*(1-(P-1)/Q)
370 B5=1.000028/B1
380 Q2=Z1/Z2/Q**2
390 C1=1-(S/1000)
400 P2=((0.1368*B5*C1)/(Q2*Z2))-F-P
410 I=(0.01994*S)/(1-0.001*S)
420 M1=S/68.0811*(1-0.001*S)
430 I2=S*0.019927*V0
440 PRINT "SALINITY=";S,"IONIC STRENGTH=";I,"MOLALITY=";M1
```

```
450 PRINT "VOLUME IONIC STRENGTH=";I2
460 PRINT "EFFECTIVE PRESSURE=";P2
470 NEXT S
480 NEXT T
490 END
```