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Solubility of organic compounds in non-aqueous systems

Mishra, Dinesh Shyamdeo, Ph.D.

The University of Arizona, 1989

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SOLUBILITY OF
ORGANIC COMPOUNDS IN
NON-AQUEOUS SYSTEMS

by

Dinesh Shyamdeo Mishra

A Dissertation Submitted to the Faculty of the

DEPARTMENT OF PHARMACEUTICAL SCIENCES

In Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY

In the Graduate College

THE UNIVERSITY OF ARIZONA

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THE UNIVERSITY OF ARIZONA
GRADUATE COLLEGE

As members of the Final Examination Committee, we certify that we have read
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entitled SOLUBILITY OF ORGANIC COMPOUNDS IN NON-AQUEOUS SYSTEMS

and recommend that it be accepted as fulfilling the dissertation requirement
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ABSTRACT

Solubility of drugs in non-aqueous systems is very important in understanding the partitioning and transport. The solubility of a solid solute involves two parts: the ideal solubility (crystal contribution) and the activity coefficient (mixing of the supercooled solute and the solvent).

The present study was undertaken to evaluate the entropic and enthalpic contribution to the activity coefficient in non aqueous solvent systems. The activity coefficient can be written as:

$$\ln \gamma_1 = \ln \gamma_1^c + \ln \gamma_1^r \quad (1)$$

where superscript "c" and "r" denote entropic and enthalpic contribution respectively. In this study three solvent systems i.e. benzene, triolein and octanol were selected. The solutes were mainly polycyclic aromatic hydrocarbons fatty acids and alcohols.

There are several models available to evaluate the entropic and enthalpic activity coefficient. In this study we considered the following models: Flory-Huggins and UNIQUAC for entropic and Scatchard-Hildebrand and UNIQUAC residual for enthalpic contribution.

CHAPTER 1
INTRODUCTION

It has long been recognized that solubility and diffusion govern the transport of organic molecules in the synthetic and biological membranes (Yalkowsky et al., 1973, Flynn et al., 1974). The flux (J) across a membrane is given by Fick's first law of diffusion (Crank, 1975).

$$J = D \frac{dc}{dx} \quad (1.1)$$

where D is the diffusion coefficient in the membrane, dC/dX is the concentration gradient.

If it is assumed that the concentration on the receiver side of the diffusion cell is approximately zero, and X is the length of diffusion, then equation 1.1 can be written as:

$$J = D \frac{C_{sat}}{X} \quad (1.2)$$

where C_{sat} is the saturation solubility in the membrane. It is clear that the flux across a membrane is primarily

controlled by the solubility in the membrane and the diffusion coefficient.

Recently there has been a lot of interest in controlled delivery of drugs (Robinson et al, 1987). One way to control the delivery of drugs is to encapsulate the drug solution in a polymer membrane type device. The rate of delivery is controlled by the diffusion of the drug in the polymeric membrane.

The importance of solubility in non-aqueous systems is clearly evident. Various simple solvent models have been suggested for use in these studies (Stein, 1986).

The present study deals with the solubility of organic compounds in non-aqueous systems. The solvents selected for the study were: benzene, triolein, and n-octanol. Triolein and n-octanol have been used as model solvent systems for partitioning behavior in biological membranes (Leo et al., 1971; Hansch et al., 1979; Patton et al., 1984). Benzene was chosen as one of the solvents as it is a simple solvent, and solutes like polycyclic aromatic hydrocarbons would be expected to behave very close to ideality.

The solubility of a solid solute involves two parts: the ideal solubility (crystal contribution) and the activity

coefficient (mixing of the supercooled solute and solvent). The calculation of the ideal solubility is based upon the melting properties of the solute. Once the ideal solubility is known, there are several theories which describe liquid solutions and their deviations from ideality.

There are several theories which describe the deviations of liquid solutions from ideality (Prausnitz et al., 1986; Scott, 1987). The present study evaluates the ideal solubility and the different theories available for the activity coefficient in three non-aqueous solvent systems.

CHAPTER 2

IDEAL SOLUTIONS

The quantitative description of any phenomenon can often be achieved by first idealizing the phenomenon, i.e., setting up a simplified model which describes the essential features of the phenomenon, while neglecting the details. The real behavior is then described in terms of deviations from the ideal behavior.

A solution is said to be ideal when the chemical potential, $\mu_i(T,P)$ of species i is proportional to its concentration which is usually expressed as mole fraction X (Prausnitz et. al., 1986). This is mathematically written as follows:

$$\mu_i = \mu^\circ + RT \ln X_i \quad (2.1)$$

where R is the gas constant and T is the temperature.

The ideal solution can alternatively be described as one in which the mixing of two components does not involve heat or volume changes. In such a system the enthalpy of each component remains unchanged. The decrease in Gibbs free energy is entirely due to the increase in entropy on mixing.

Thus the conditions for ideal solution are as follows:

$$\Delta H_{\text{mix}} = 0 \quad (2.2a)$$

$$\Delta V_{\text{mix}} = 0 \quad (2.2b)$$

$$\Delta S_{\text{mix}} = -R \sum_{i=1}^n X_i \cdot \ln X_i \quad (2.2c)$$

The entropy of mixing favors complete mixing of all components. Incomplete mixing or partial solubility result from the heat of mixing and/or the volume of mixing being greater than or less than zero.

SOLUBILITY OF A SOLID SOLUTE

Solubility of a solid solute can be viewed as the sum of two processes: (1) breakdown of the crystal structure and (2) mixing of the supercooled liquid produced in (1) above with the liquid solvent. The first step involves only the crystal of the solute and is used to calculate the ideal solubility of the solid solute. The second step involves both the solute and the solvent and accounts for the deviations from ideality. This will be dealt with in the next chapter.

This chapter will discuss the calculation of the ideal solubility of a solid solute.

IDEAL SOLUBILITY OF A SOLID SOLUTE

Consider the equilibrium of a solid solute (1) with the solvent (2). The equilibrium equation is:

$$f_1^s = f_1^l \quad (2.3)$$

where f_1^s is the fugacity of a pure solid and f_1^l is the fugacity of the solid in liquid solution. The above equation can also be written as:

$$f_1^s = X_2 \gamma_2 f_2^\circ \quad (2.4)$$

where X_2 is the mole fractional solubility of the solid solute, γ_2 is the activity coefficient and f_2° is the standard state fugacity. Equation 2.4 is rearranged to:

$$X_2 = \frac{\gamma_2 f_2^\circ}{f_2^s} \quad (2.5)$$

The standard state is chosen as the pure, supercooled liquid at temperature T. The thermodynamic cycle for the

calculation of solubility is given in figure 2.1. The molar Gibbs free energy for the solute in going from 1 to 4 is related to the solubility by the following equation:

$$\frac{\Delta G}{1 \rightarrow 4} = RT \ln X \quad (2.6)$$

The Gibbs free energy change is also related to the enthalpy and entropy changes as follows:

$$\frac{\Delta G}{1 \rightarrow 4} = \frac{\Delta H}{1 \rightarrow 4} + \frac{\Delta S}{1 \rightarrow 4} \quad (2.7)$$

The thermodynamic cycle shown in figure 2.1 provides a means of calculating the enthalpic and entropic changes for the process. Since both the enthalpy and entropy are state functions they can be calculated from the individual steps given in figure 2.1.

$$\frac{\Delta H}{1 \rightarrow 4} = \frac{\Delta H}{1 \rightarrow 2} + \frac{\Delta H}{2 \rightarrow 3} + \frac{\Delta H}{3 \rightarrow 4} \quad (2.8)$$

and

$$\frac{\Delta S}{1 \rightarrow 4} = \frac{\Delta S}{1 \rightarrow 2} + \frac{\Delta S}{2 \rightarrow 3} + \frac{\Delta S}{3 \rightarrow 4} \quad (2.9)$$

The enthalpy and entropy changes in equations 2.8 and 2.9 are written as follows:

$$\Delta H_{1 \rightarrow 4} = \Delta H_f \text{ at } T_m + \int_{T_m}^T \Delta C_p dT \quad (2.10)$$

where ΔC_p is the heat capacity of liquid minus the heat capacity of the solid:

$$\Delta C_p \equiv C_p (\text{liquid}) - C_p (\text{solid})$$

$$\Delta S_{1 \rightarrow 4} = \Delta S_f \text{ at } T_m + \int_{T_m}^T \frac{\Delta C_p}{T} dT \quad (2.11)$$

Thus substituting equations 2.10 and 2.11 into equation 2.7 gives the following expression for Gibbs free energy:

$$\Delta G_{1 \rightarrow 4} = \Delta H_f - T \Delta S_f + \int_T^{T_m} \Delta C_p dT - \int_T^{T_m} \frac{\Delta C_p}{T} dT \quad (2.12)$$

The ideal solubility of a solid solute is obtained by substituting equation 2.12 in 2.6:

$$RT \ln X^i = \Delta H_f - T\Delta S_f + \int_T^{T_m} \Delta C_p dT - \int_T^{T_m} \frac{\Delta C_p}{T} dT \quad (2.13)$$

Assuming that ΔC_p is constant and also realizing that $\Delta S_f = \Delta H_f/T_m$, equation 2.13 becomes:

$$\ln X^i = -\frac{\Delta H_f}{R} \left[\frac{T_m - T}{T_m \cdot T} \right] - \frac{\Delta C_p}{R} \left[\frac{T_m - T}{T_m \cdot T} - \ln \frac{T_m}{T} \right] \quad (2.14)$$

Equation 2.14 shows that only the solute properties like entropy of fusion, melting point, and heat capacity change, are required for the calculation of ideal solubility. Two further assumptions have been suggested which simplify equation 2.14:

Assumption 1: $\Delta C_p = 0$

$$\ln X^i = -\frac{\Delta S_f}{R} \left[\frac{T_m - T}{T} \right] \quad (2.15)$$

Assumption 2: $\Delta C_p = \Delta S_f$

$$\ln x^i = - \frac{\Delta S_f}{R} \left[\ln \frac{T_m}{T} \right] \quad (2.16)$$

Each of the two simplified equations requires only entropy of fusion and melting point for the calculation of ideal solubility. Data on heat capacity change is very scarce and the little data that is available suggests that the approximation 1 i.e. $\Delta C_p \approx 0$, is a more realistic assumption for most of organic compounds (Andrews et. al., 1926; Casellato et. al., 1973; Finke et. al., 1977).

The two equations 2.15 and 2.16 differ in that the entropy term is multiplied in one case by $(T_m - T)/T$ and the other by $\ln (T_m/T)$. Figure 2.2 shows the plot of the two quantities for a different T_m at 25 °C. It is clear from the plot that the difference is not very significant until the melting temperature is very large.

EFFECT OF PHASE TRANSITION ON THE IDEAL SOLUBILITY

The equations derived earlier apply only to molecules which do not undergo any phase transition between solution temperature and melting point. If there is a phase transition then it has to be taken into account in the ideal solubility (Weimer et. al., 1965; Preston et. al., 1971; Hildebrand et. al., 1970).

Phase transition like melting, vaporization are simple and are characterized by considerable changes of volume, entropy and enthalpy, at the point of transition. However there are other types of phase transition which show quite different behavior. In these there seems to be no difference of volume between the two forms, and little or no difference in entropy and enthalpy. The transition however is characterized by sharp change in the heat capacity and compressibility. These types of transition are referred to as lambda transition or second order transition (Denbigh, 1984).

FIRST ORDER TRANSITION

The enthalpy-temperature diagram is given in 2.3 from which the ideal solubility can be calculated as shown earlier. The enthalpy and entropy of the process of creating

a supercooled liquid can be written as follows:

$$\Delta H_{1 \rightarrow 4} = \Delta H_{1 \rightarrow 5} + \Delta H_{5 \rightarrow 6} + \Delta H_{6 \rightarrow 2} + \Delta H_{2 \rightarrow 3} + \Delta H_{3 \rightarrow 4} \quad (2.17)$$

and

$$\Delta S_{1 \rightarrow 4} = \Delta S_{1 \rightarrow 5} + \Delta S_{5 \rightarrow 6} + \Delta S_{6 \rightarrow 2} + \Delta S_{2 \rightarrow 3} + \Delta S_{3 \rightarrow 4} \quad (2.18)$$

$$\Delta H_{1 \rightarrow 4} = \Delta H_{tr} \text{ at } T_{tr} + \Delta H_f \text{ at } T_m + \int_{T_{tr}}^T \Delta C_p^\alpha dT + \int_{T_m}^{T_{tr}} \Delta C_p^\beta dT \quad (2.19)$$

$$\Delta S_{1 \rightarrow 4} = \Delta S_{tr} \text{ at } T_{tr} + \Delta S_f \text{ at } T_m + \int_{T_{tr}}^T \frac{\Delta C_p^\alpha}{T} dT + \int_{T_m}^{T_{tr}} \frac{\Delta C_p^\beta}{T} dT \quad (2.20)$$

Substituting equations 2.19 and 2.20 into 2.7 and in 2.6 and assuming ΔC_p to be constant we get the following equation for ideal solubility:

$$\begin{aligned} \ln X^i = & - \frac{\Delta H_f}{R} \left[\frac{T_m - T_{tr}}{T_m \cdot T_{tr}} \right] - \frac{\Delta C_p^\alpha}{R} \left[\frac{T_m - T_{tr}}{T_m \cdot T_{tr}} - \ln \frac{T_m}{T_{tr}} \right] \\ & - \frac{\Delta H_{tr}}{R} \left[\frac{T_{tr} - T}{T_{tr} \cdot T} \right] - \frac{\Delta C_p^\beta}{R} \left[\frac{T_{tr} - T}{T_{tr} \cdot T} - \ln \frac{T_{tr}}{T} \right] \quad (2.21) \end{aligned}$$

Thus, if there is a first order transition between the solution temperature and the melting point, further data on the heat of transition and heat capacity change in the process is required. Equation 2.21 can be simplified to 2.22 if it is assumed that the terms involving ΔC_p is small compared to ΔH terms.

$$\ln x^i = - \frac{\Delta H_f}{R} \left[\frac{T_m - T_{tr}}{T_m \cdot T_{tr}} \right] - \frac{\Delta H_{tr}}{R} \left[\frac{T_{tr} - T}{T_{tr} \cdot T} \right] \quad (2.22)$$

LAMBDA TRANSITION

The enthalpy-temperature diagram for a compound undergoing lambda transition is given in figure 2.4 (Choi et. al., 1983). The enthalpy and entropy changes involved can be calculated as shown in equation 2.17 and 2.18 as follows.

$$\Delta H_{1 \rightarrow 4} = \Delta H_f \text{ at } T_m + \int_{T_a}^T \Delta C_p^\alpha dT + \int_{T_b}^{T_a} \Delta C_p^\beta dT + \int_{T_m}^{T_b} \Delta C_p dT \quad (2.23)$$

and

$$\Delta S_{1 \rightarrow 4} = \Delta S_f + \int_{T_a}^T \frac{\Delta C_p^\alpha}{T} dT + \int_{T_b}^{T_a} \frac{\Delta C_p^\beta}{T} dT + \int_{T_m}^{T_b} \frac{\Delta C_p}{T} dT \quad (2.24)$$

Substituting equations 2.23 and 2.24 in 2.7 and subsequently in 2.6 we get the following equation for ideal solubility of a solid which undergoes lambda transition.

$$\ln x^i = - \frac{\Delta S_f}{R} \left[\frac{T_m - T_b}{T_b} \right] + \frac{\Delta C_p}{R} \left[\frac{T_m - T_b}{T_b} - \ln \frac{T_m}{T_b} \right] +$$

$$\frac{\Delta C_p^{\beta-\alpha}}{R} \left[\frac{T_a - T}{T} - \ln \frac{T_a}{T} \right] +$$

$$\frac{1}{RT} \int_{T_a}^{T_b} C_p dT - \frac{1}{R} \int_{T_a}^{T_b} \frac{C_p}{T} dT \quad (2.25)$$

The equations for solids showing first order or lambda

transition become extremely complicated and requires large amount of thermal data like heat capacity as a function of temperature, heats of transition and temperatures of transition.

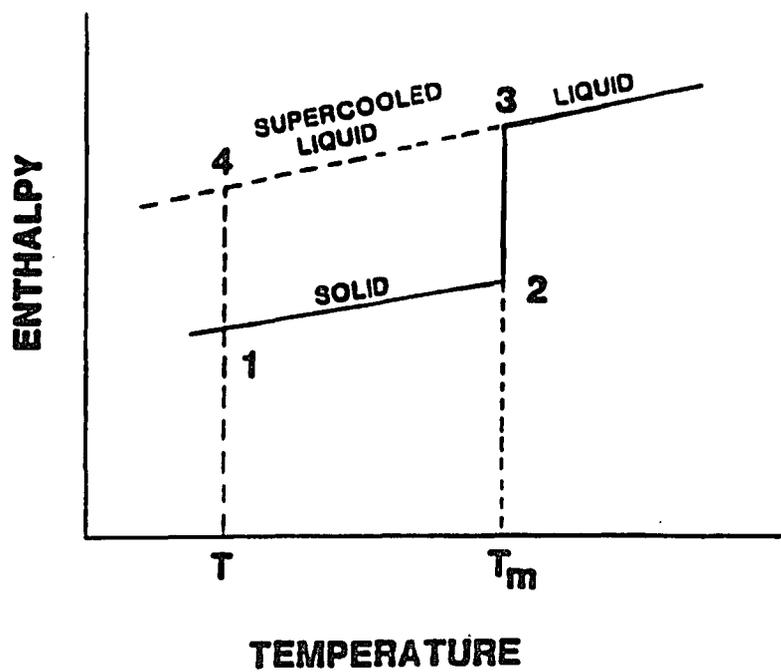


Figure 2.1: Enthalpy-temperature diagram for melting transition.

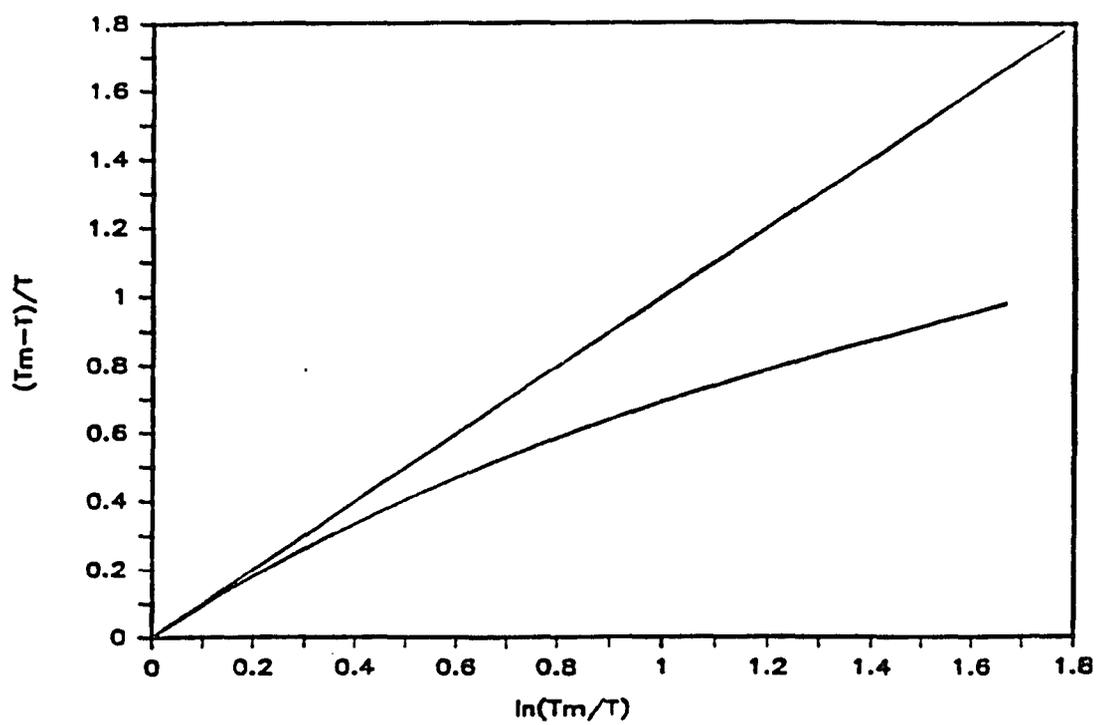


Figure 2.2: Effect of the different assumptions of ΔC_p on ideal solubility.

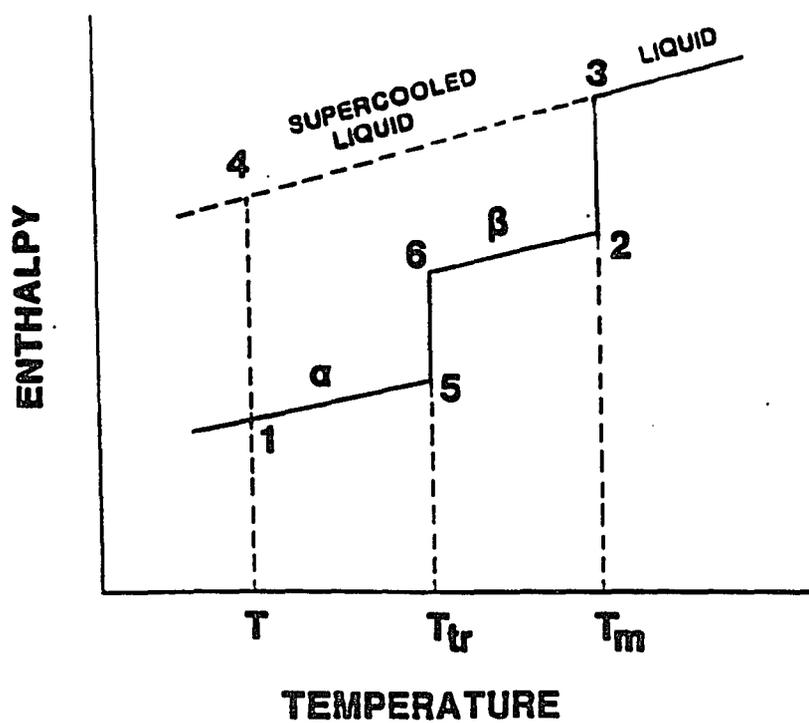


Figure 2.3: Enthalpy-temperature diagram for a solute with a first order transition below melting point.

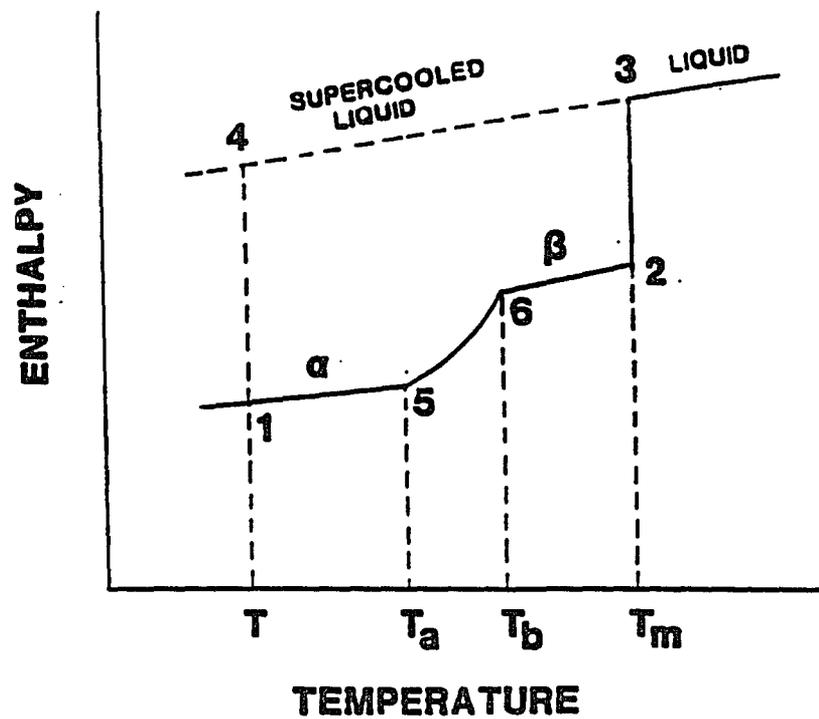


Figure 2.4: Enthalpy-temperature diagram for a solute with a lambda transition below melting point.

CHAPTER 3

REAL SOLUTIONS

Ideal solutions as discussed in chapter 2 form the first approximation to the study of solutions. However, in real practice, one seldom finds an ideal solution. Equations 2.2a-2.2c describe the conditions that must be satisfied for an ideal solution.

Lewis and Randall in 1923 (Lewis et. al., 1961) introduced the concept of thermodynamic activity to characterize real solutions. The idea behind this concept was to maintain the form of ideal equations while representing the behavior of real solutions. The activity of a solute gives an indication of how "active" a solute is relative to its standard state.

The activity a_1 of a component in solution is directly proportional to mole fraction X_1 by:

$$a_1 = \gamma_1 \cdot X_1 \quad (3.1)$$

where the constant γ_1 is referred to as the activity coefficient. The activity coefficient indicates the degree of deviation from the ideal solution. The activity is used

in equation 2.1 instead of mole fraction to describe a real solution.

$$\mu_i = \mu_i^{\circ} + RT \ln a_i \quad (3.2)$$

Using equations described in chapter 2 for ideal solutions, the expression for real solutions is the following:

$$\ln X_1 = \ln X_1^i - \ln \gamma_1 \quad (3.3)$$

where X_1 refers to the real solubility of the solute (1) and X_1^i is the ideal solubility. Using the equation for a solid solute which does not undergo any phase transition, the expression of solubility can be written as:

$$\ln X_1 = - \frac{\Delta H_m}{R} \left[\frac{T_m - T}{T_m \cdot T} \right] - \frac{\Delta C_p}{R} \left[\frac{T_m - T}{T_m \cdot T} - \ln \frac{T_m}{T} \right] - \ln \gamma_1 \quad (3.4)$$

The problem remaining in predicting solubilities lies in the prediction of activity coefficients.

EXCESS FUNCTIONS AND ACTIVITY COEFFICIENTS

The partial molar free energy of mixing is related to activity by the following equation (Denbigh, 1984):

$$\Delta \bar{G}_1 = RT \ln X_1^i - RT \ln \gamma_1 \quad (3.5)$$

The first term in equation 3.5 is the ideal free energy of mixing, thus the second term corresponds to the excess Gibbs free energy. Therefore, the equation for the activity coefficient is:

$$RT \ln \gamma_1 = \Delta \bar{G}_1^E \quad (3.6)$$

where $\Delta \bar{G}_1^E$ is the excess Gibbs free energy.

Equation 3.6 greatly facilitates the study of solutions as excess Gibbs free energy is separated into entropic and enthalpic contributions.

Thus the activity coefficient is written as a sum of two parts, the entropic contribution (combinatorial part, $\ln \gamma_1^C$) and the enthalpic contribution (residual part,

$\ln \gamma_1^F$).

$$\ln \gamma_1 = \ln \gamma_1^C + \ln \gamma_1^R \quad (3.8)$$

The entropic and the enthalpic contribution to the activity coefficient will be discussed separately.

MODELS FOR ENTROPY OF SOLUTION

There are several models which have been proposed for the entropy of mixing of molecules of different size and shape (Staverman, 1950; Tompa, 1952; Flory, 1941; Huggins, 1941). In this chapter we will consider some of the models which are practically useful in describing the entropic contribution to the activity coefficient.

FLORY-HUGGINS THEORY

Flory (1941) and Huggins (1941) independently proposed a theory for the entropy of mixing of polymer molecules with monomeric solvents. The theory is based on a lattice as the model for the polymer and assumes interchangability of polymer segments and solvent. The entropy of mixing is given by the following equation:

$$\Delta S_{\text{mix}}^C = -R \sum N_i \cdot \ln \phi_i \quad (3.9)$$

where the superscript "c" denotes the combinatorial entropy and ϕ_i is the volume fraction defined in equation 3.10.

$$\phi_i = \frac{N_i \cdot V_i}{\sum_{i=1}^n N_i \cdot V_i} \quad (3.10)$$

where V_i is the volume of the molecule.

The Flory-Huggins expression for the combinatorial entropy of mixing is analogous to the ideal entropy of mixing. The only difference is that the mole fraction in ideal expression is replaced by volume fraction. Equation 3.9 satisfies the boundary condition, in that it reduces down to the ideal entropy expression when the volumes of the solute and the solvent are the same. Thus it is clear that the Flory-Huggins theory accounts for any non ideality that may arise due to the size differences between the solvent and the solute. The Flory-Huggins and the ideal model is schematically shown in figure 3.1 and 3.2. The major assumptions of the Flory-Huggins theory are as follows:

$$\Delta H_{\text{mix}} = 0 \quad (3.11)$$

$$\Delta V_{\text{mix}} = 0 \quad (3.12)$$

Flory-Huggins theory leads to the following expression for the Gibbs free energy of mixing:

$$-\frac{\Delta G_{\text{mix}}^c}{RT} = \frac{\Delta S_{\text{mix}}^c}{R} = -\sum_{i=1}^n N_i \cdot \ln \phi_i \quad (3.13)$$

The excess Gibbs free energy is obtained by subtracting 2.2c from 3.13. This is then differentiated with respect to number of moles to give the following expression for the activity coefficient.

$$\ln \gamma_1^c = \left[\ln \left[\frac{\phi_1}{X_1} \right] + 1 - \frac{\phi_1}{X_1} \right] \quad (3.14)$$

Equation 3.14 has been used to describe activity coefficients in polymer solutions. However, it has been shown by other authors (Abe et. al., 1965; Hildebrand, 1947; Silberberg, 1970) that the expression is not only applicable to polymer molecules, but may be more general.

FREE VOLUME APPROACH TO FLORY-HUGGINS ENTROPY OF MIXING

The Flory-Huggins combinatorial entropy of mixing can also be derived by a free volume approach which renders the

the inherent assumptions of the theory more obvious (Napper, 1983).

The free volume considered in this derivation is assumed to be a certain fraction of the total volume. This is similar to the void volume as described by Bondi (Bondi, 1968). The total free volume is given by the following expression:

$$V_{1f} = N_1 \cdot V_1 \cdot f \quad (3.15)$$

where V_{1f} is the total free volume, V_1 , and f are molar volume and fraction free volume, respectively, N_1 is the number of molecules.

If the assumption is made that the fraction free volumes of both solute and solvent are the same, then:

$$V_{2f} = N_2 \cdot V_2 \cdot f \quad (3.16)$$

The total free volume upon mixing is then:

$$V_{f_{mix}} = (N_1 \cdot V_1 + N_2 \cdot V_2) f \quad (3.17)$$

The entropy change on mixing for the solvent can now be expressed as follows:

$$\Delta S_{\text{mix}}^{\text{C}}(\text{solvent}) = - N_1 \cdot k \ln \frac{N_1 \cdot V_1}{N_1 \cdot V_1 + N_2 \cdot lV_2} \quad (3.18)$$

Adding the terms for entropy of mixing change for both the solvent and the solute we get the following equation for the entropy of mixing which is the same as the Flory-Huggins equation.

$$\Delta S_{\text{mix}}^{\text{C}} = -R \sum N_i \cdot \ln \phi_i \quad (3.20)$$

Thus, it is clear from the above derivation that the Flory-Huggins combinatorial entropy of mixing has a further assumption that the free volumes of the solute and the solvent are similar.

LICHTENTHALER'S MODIFICATION OF FLORY-HUGGINS THEORY

Lichtenthaler et. al., (1973) presented a modification to the Flory-Huggins theory. This modification presents a method for calculating entropy for mixing of molecules differing in size as well as shape. The equation, however, is very complicated and cumbersome. Donahue and Prausnitz (1975) presented a generalized equation using Lichtenthaler's equation which is as follows:

$$\Delta S_{\text{mix}}^c = -R \left[N_1 \ln \frac{N_1 (v_1)^{p_1}}{N_1 (v_1)^{p_1} + N_2 (v_2)^{p_2}} + N_2 \ln \frac{N_2 (v_2)^{p_2}}{N_1 (v_1)^{p_1} + N_2 (v_2)^{p_2}} \right] \quad (3.21)$$

The exponent, p_1 and p_2 , depends on the size and shape of the molecule. Equation 3.21 gives the expression for ideal entropy of mixing when $p_1=p_2=0$, and Flory-Huggins entropy of mixing when $p_1=p_2=1$. The authors suggest that the real entropy of mixing is really somewhere between the ideal and the Flory-Huggins expression. Thus the exponent takes a value between 0 and 1. The exponent does not have any theoretical validity and is mostly empirical. The authors have presented a method to calculate the exponent.

LOCAL COMPOSITION MODEL

The models of solution considered earlier in this chapter have one very important assumption: the solution is random. It can be easily seen that most of the solution will not form a random solution. Wilson (1964) proposed a very simple and intuitive idea of local composition. He imagined that at microscopic level the mole fraction is not the same

because of the difference in the intermolecular interaction. Thus, the effect is mainly entropic but enthalpic in origin.

Consider a mixture of two components, 1 and 2, having the bulk mole fractions, X_1 and X_2 , respectively. If the attention is focused on the central molecule 1, probability of finding a molecule of type 2, relative to finding molecule 1, around the central molecule is expressed in terms of the bulk mole fraction and energy of interaction as follows:

$$\frac{X_{21}}{X_{11}} = \frac{X_2 \exp(-g_{12}/RT)}{X_1 \exp(-g_{11}/RT)} \quad (3.22)$$

where g_{12} and g_{11} are interaction energies between 1-1 and 1-2 molecules. Wilson then defines a local volume fraction (ϕ) as:

$$\phi_1 = \frac{V_1 X_{11}}{V_1 X_{11} + V_2 X_{21}} \quad (3.23)$$

where V_1 and V_2 are the molar volumes of component 1 and 2 respectively. Wilson used the local volume fraction instead

of the overall volume fraction in the expressions for the activity coefficient.

UNIQUAC COMBINATORIAL ENTROPY OF MIXING

Abrams and Prausnitz (1975) derived an expression based on the quasichemical theory of Guggenheim to describe the free energy of mixing of molecules differing in size. The extension was therefore called universal quasichemical theory or in short UNIQUAC. The UNIQUAC equation for the excess Gibbs free energy consists of two parts, a combinatorial and a residual. The UNIQUAC combinatorial entropy of mixing is:

$$\frac{G^E(\text{comb})}{RT} = \sum_{i=1}^n X_i \ln \frac{\phi_i}{X_i} + \frac{z}{2} \left[\sum_{i=1}^n q_i X_i \ln \frac{\theta_i}{\phi_i} \right] \quad (3.24)$$

where X_i , ϕ_i , θ_i are mole fraction, volume fraction and area fraction respectively, q_i is the surface area, and z is the coordination number. The authors suggest that for most liquid solutions, z is 10.

Equation 3.24 is then differentiated to give the following expression for the activity coefficient:

$$\ln \gamma_1^c = \left[\ln \left[\frac{\phi_1}{X_1} \right] + 1 - \frac{\phi_1}{X_1} \right] + \frac{z}{2} \left[\ln \left[\frac{\phi_1}{\theta_1} \right] + 1 - \frac{\phi_1}{\theta_1} \right] \quad (3.25)$$

The first term in equation 3.25 is identical to the Flory-Huggins activity coefficient (equation 3.13) and involves only volume fraction and mole fraction. The second term involves volume fraction and area fraction. Equation 3.25 will give a significantly different activity coefficient when the area fraction and the volume fraction of the solute are very different. For most solutes, volumes and areas are highly correlated, and the ratio of the volumes and the areas are usually similar in magnitude. Therefore, the effects of the second term will in most cases be negligible.

MODELS FOR ENTHALPY OF MIXING

VAN LAAR THEORY

The first systematic study of real solutions was attempted by van Laar (1910). The essential contribution of van Laar was that he chose very good simplifying assumptions which made the study of real solutions possible. van Laar considered the mixing of two liquids at a constant temperature and pressure. The major assumptions of van Laar's theory are as follows:

(1) the liquids mix with no volume change, i.e.,

$$\Delta V_{\text{mix}} = 0 \quad (3.26)$$

(2) the entropy of mixing is ideal, i.e.,

$$\Delta S_{\text{mix}} = 0 \quad (3.27)$$

The expression for the excess Gibbs free energy at constant pressure is:

$$\Delta G_{\text{mix}} = \Delta U_{\text{mix}} + P\Delta V_{\text{mix}} - T\Delta S_{\text{mix}} \quad (3.28)$$

From van Laar's assumptions, equation 3.28 can be written as:

$$\Delta G_{\text{mix}} = \Delta U_{\text{mix}} \quad (3.29)$$

van Laar constructed a three step thermodynamic cycle as shown in figure 3.3 to calculate the energy change on mixing. Since energy is a state function the energy change on mixing ΔU , is written as:

$$\Delta U = \Delta U_{\text{mix}} = \Delta U_1 + \Delta U_2 + \Delta U_3 \quad (3.30)$$

Step 1: The two liquids are isothermally vaporized. The vapor is assumed to behave ideally. The energy change involved is:

$$\left[\frac{\delta U}{\delta V} \right]_T = T \left[\frac{\delta P}{\delta T} \right]_V - P \quad (3.31)$$

van Laar then assumed that the volumetric properties of the fluids are represented by the van der Waals equation.

$$\left[\frac{\delta U}{\delta V} \right]_T = \frac{a}{V^2} \quad (3.32)$$

where a is the constant in the van der Waals equation. For

X_1 , moles of liquid 1, and X_2 , moles of liquid 2, the energy change is as follows:

$$\Delta U_1 = \frac{a_1 X_1}{b_1} + \frac{a_2 X_2}{b_2} \quad (3.33)$$

where molar volume is replaced by the constant b .

Step 2: The isothermal mixing of gases proceeds with no change in energy:

$$\Delta U_2 = 0 \quad (3.34)$$

Step 3: In this step the ideal gas mixture produced in step 2 is isothermally compressed and condensed. van Laar assumed that the volumetric properties of the mixture are also described by the van der Waals equation.

$$\Delta U_3 = - \frac{a_{\text{mix}}}{b_{\text{mix}}} \quad (3.35)$$

van Laar expressed the mixture properties as follows:

$$a_{\text{mix}} = a_1 X_1^2 + a_2 X_2^2 + 2a_{12} X_1 X_2 \quad (3.36)$$

where a_1 and a_2 are characteristic of interaction between similar molecules. The constant characteristic of

interaction between dissimilar molecules, a_{12} , is given by the following expression:

$$a_{12} = (a_1 a_2)^{\frac{1}{2}} \quad (3.37)$$

Equation 3.37 assumes that the dissimilar interactions are limited only to dispersion forces where the geometric mean rule is valid. Thus equation 3.34 can be written as:

$$a_{\text{mix}} = a_1 X_1^2 + a_2 X_2^2 + 2(a_1 a_2)^{\frac{1}{2}} X_1 X_2 \quad (3.38)$$

Equations 3.33-3.38 can be substituted into equation 3.30 to get the following expression for the excess Gibbs free energy:

$$G_{\text{mix}} = \frac{X_1 X_2 b_1 b_2}{X_1 b_1 + X_2 b_2} \left[\frac{\frac{1}{2} a_1}{b_1} - \frac{\frac{1}{2} a_2}{b_2} \right]^2 \quad (3.39)$$

The activity coefficient is obtained by differentiating the above expression with respect to number of moles:

$$\ln \gamma_1^r = \frac{A}{\left[1 + \frac{A X_1}{B X_2} \right]^2} \quad (3.40)$$

where

$$A = \frac{b_1}{RT} \left[\frac{\frac{1}{2} a_1}{b_1} - \frac{\frac{1}{2} a_2}{b_2} \right]^2 \quad (3.41)$$

and

$$B = \frac{b_2}{RT} \left[\frac{\frac{1}{2} a_1}{b_1} - \frac{\frac{1}{2} a_2}{b_2} \right]^2 \quad (3.42)$$

The activity coefficient predicted by van Laar is always greater than unity, thus the theory always predicts positive deviations from ideal solution.

SCATCHARD-HILDEBRAND THEORY

Scatchard and Hildebrand realized that the problems in the van Laar theory were mainly due to the adherence to the

van der Waals equation of state (Scatchard, 1931; Hildebrand, 1919). They defined a parameter CED which is the cohesive energy density:

$$\text{CED} = c = \frac{\Delta U^v}{V_m} \quad (3.43)$$

where ΔU^v is the energy of complete vaporization of the liquid and V_m is the molar volume of the liquid. Using similar arguments as van Laar, Scatchard and Hildebrand generalized equation 3.40 to binary mixtures as follows:

$$\Delta U_{\text{mix}} = \frac{c_{11}^2 V_1^2 X_1^2 + 2c_{12} V_1 V_2 X_1 X_2 + c_{22}^2 V_2^2 X_2^2}{X_1 V_1 + X_2 V_2} \quad (3.44)$$

where c_{11} and c_{22} refer to interactions between similar molecules, and c_{12} to interactions between dissimilar molecules. Equation 3.44 can be simplified by introducing the volume fraction.

$$\Delta U_{\text{mix}} = (X_1 V_1 + X_2 V_2) (c_{11}^2 \phi_1^2 + 2c_{12} \phi_1 \phi_2 + c_{22}^2 \phi_2^2) \quad (3.45)$$

The excess Gibbs free energy is obtained by subtracting equation 3.43 from the ideal energy of mixing:

$$\Delta U_{\text{mix}}^E = \Delta U_{\text{mix}} - X_1 U_1 - X_2 U_2 \quad (3.46)$$

Thus the expression for excess Gibbs free energy is:

$$\Delta U_{\text{mix}}^E = (c_{11} + c_{22} - c_{12}) \phi_1 \phi_2 (X_1 V_1 + X_2 V_2) \quad (3.47)$$

Scatchard and Hildebrand made use of the most important assumption originally made by van Laar, that the interaction between dissimilar molecules is given by the geometric mean rule, i.e.

$$c_{12} = (c_{11} c_{22})^{\frac{1}{2}} \quad (3.48)$$

Substituting equation 3.48 into equation 3.47, the excess Gibbs free energy is given by:

$$\Delta G_{\text{mix}} = (X_1 V_1 + X_2 V_2) \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \quad (3.49)$$

where δ is the solubility parameter defined as:

$$\delta_1 = (c_{11})^{1/2} = \left[\frac{\Delta U}{V} \right]^{1/2} \quad (3.50)$$

It should be remembered that the Scatchard-Hildebrand theory has the same assumptions as van Laar's theory, i.e.,

$$\Delta v_{\text{mix}} = 0 \quad (3.51)$$

and

$$\Delta s_{\text{mix}} = 0 \quad (3.52)$$

The activity coefficient now can be written as:

$$\ln \gamma_1 = \frac{1}{RT} V_1 (1 - \phi_1)^2 (\delta_1 - \delta_2)^2 \quad (3.53)$$

Hildebrand described the above solution as a regular solution and the theory is called regular solution theory. This theory also predicts activity coefficient greater than unity i.e. positive deviation from the ideal solution. According to the regular solution theory a solution will behave as an ideal solution when the solubility parameters are similar. The solubility parameters can be easily calculated from the group contribution approach proposed by Fedors (1974).

The most serious assumption made by Scatchard and Hildebrand is the geometric mean rule. The consequence of this is that the theory predicts only positive deviations from ideality. Preston et. al., (1971) modified the equation by using the general equation for c_{12} as follows:

$$c_{12} = (1 - l_{12}) (c_{11}c_{22})^{\frac{1}{2}} \quad (3.54)$$

where the constant l_{12} is a binary parameter characteristic of the 1-2 interaction. The equation for the activity coefficient can now be written as:

$$\ln \gamma_1 = \frac{1}{RT} V_1 (1 - \phi_1)^2 \left[(\delta_1 - \delta_2)^2 + 2l_{12}\delta_1\delta_2 \right] \quad (3.55)$$

Several authors have attempted to correlate the parameter l_{12} to pure component properties, with little or no success (Bazúa et. al., 1971, Preston et. al., 1970). In mixtures of chemically similar components (e.g., cyclohexane/n-hexane) the deviations from the geometric mean rule are primarily due to geometric effects like shape and packing. Thus it is clear that even though the Gibbs free energy was split into entropic and enthalpic effects, in

reality they cannot be separated as they influence each other.

The other consequence of the geometric mean rule is that it is applicable only for molecules which interact only by London dispersion forces. Thus it is not applicable to molecules having specific chemical forces (e.g., H-bonding and polar). Some authors have attempted to remedy the situation by defining the three dimensional solubility parameter as follows:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3.56)$$

where the subscripts d, p and h stand for dispersion, polar and H-bonding respectively. These solubility parameters are called extended solubility parameters (Hansen et al., 1971 and Barton, 1983). The extension, however, is in serious conflict with regular solution theory. Therefore it is not surprising that it is not very successful in predicting behavior in solutions having components which interact with polar or H-bonding.

UNIQUAC RESIDUAL ACTIVITY COEFFICIENT

Abrams and Prausnitz using the idea of local composition developed a theory for activity coefficients. The combinatorial activity coefficient was discussed earlier. The residual excess Gibbs free energy is given by the following expression:

$$\frac{G_{\text{mix}}^E}{RT} = -q_1 X_1 \ln [\theta_1 + \theta_2 g_{21}] - q_2 X_2 \ln [\theta_2 + \theta_1 g_{12}] \quad (3.57)$$

where q_1 is a parameter related to surface area, θ is surface area fraction and g_{11} and g_{12} are defined by the following equation:

$$g_{ij} = \exp - \left[\frac{u_{ij} - u_{jj}}{RT} \right] \quad (3.58)$$

where u_{ij} and u_{jj} are the interaction energies between i - j and j - j , molecules respectively.

The activity coefficient is then obtained by differentiating equation 3.57 with respect to the number of moles.

$$\ln \gamma_1^r = -q_1 \ln [\theta_1 + \theta_2 g_{21}] + \theta_2 q_1 \left[\frac{g_{21}}{\theta_1 + \theta_2 g_{21}} - \frac{g_{12}}{\theta_2 + \theta_1 g_{12}} \right] \quad (3.59)$$

The expression for the UNIQUAC residual activity coefficient is very complex. The parameters g_{21} and g_{12} are binary parameters that must be obtained by reducing data. This poses a problem since a priori prediction may not be possible. In contrast, the Scatchard-Hildebrand theory does not require any binary parameters and prediction is possible from pure component data. The model, however, can be superior to Scatchard-Hildebrand since it does not have assumptions like the geometric mean rule and thus it can be applied to any system.

UNIFAC

UNIFAC (Fredenslund et. al., 1975) is derived from UNIQUAC using the idea of ASOG (Analytical Solution Of Groups) (Pierotti et. a.l., 1959). The basic idea of ASOG is that although there are millions of organic compounds, the basic building blocks of the molecules are relatively few in number. Thus it is worthwhile to relate the activity

coefficient in mixtures to interactions between structural groups. Also the binary parameters have to be determined for fewer groups.

The activity coefficient is once again separated into two parts, entropic and enthalpic.

$$\ln \gamma_1 = \ln \gamma_1^c + \ln \gamma_1^r \quad (3.60)$$

where $\ln \gamma_1^c$ is identical to the UNIQUAC combinatorial activity coefficient (equation 3.25) and the residual activity coefficient is as follows:

$$\ln \gamma_1^r = \sum (\ln \Gamma_k - \ln \Gamma_k^i) \quad (3.61)$$

where Γ_k is the group residual activity coefficient and Γ_k^i is the residual activity coefficient of group k in a reference solution containing only molecules of type i . The group activity coefficient, Γ_k , is given by the following expression:

$$\ln \Gamma_k = Q_k \left[1 - \ln \left[\sum_m \theta_m g_{mk} \right] - \sum_m \frac{\theta_m g_{km}}{\sum_n \theta_n g_{nm}} \right] \quad (3.62)$$

where g is the interaction parameter now defined in terms of interaction between groups, and θ is defined as:

$$\theta = \frac{Q_m X_m}{\sum Q_n X_n} \quad (3.63)$$

where X_m is the mole fraction of group m in the mixture.

UNIFAC is a relatively complex method for the calculation of activity coefficients. Compared to the other methods like Flory-Huggins and Scatchard-Hildebrand which can be calculated easily, UNIFAC requires a computer program to calculate the activity coefficient.

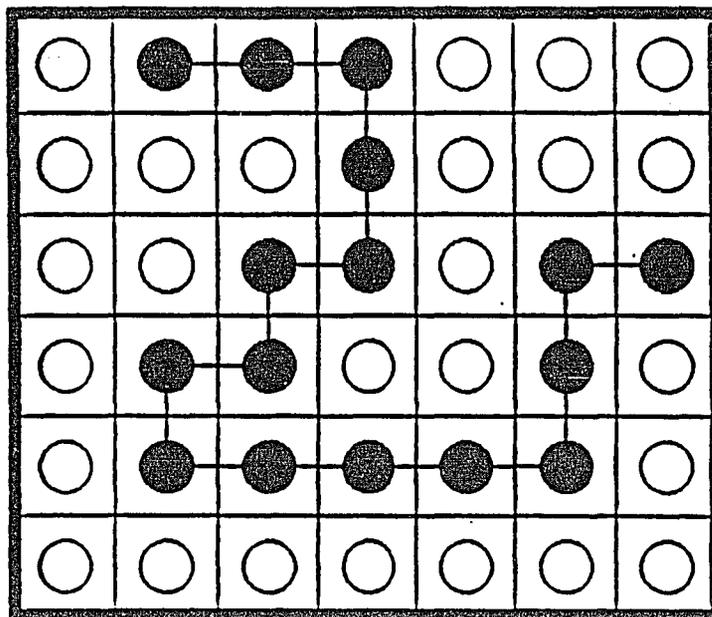


Figure 3.1: Schematic lattice model (two dimension) for a polymer molecule in solution.

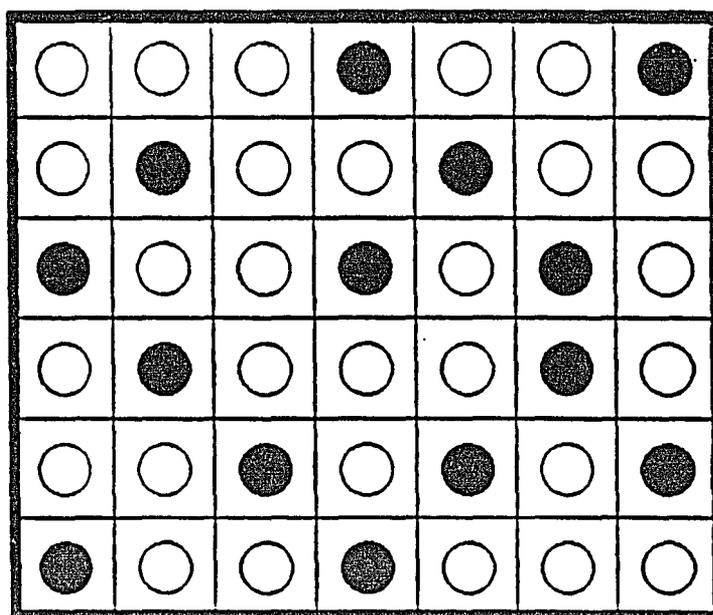


Figure 3.2: Schematic lattice model (two dimension) for molecules of similar size (ideal system).

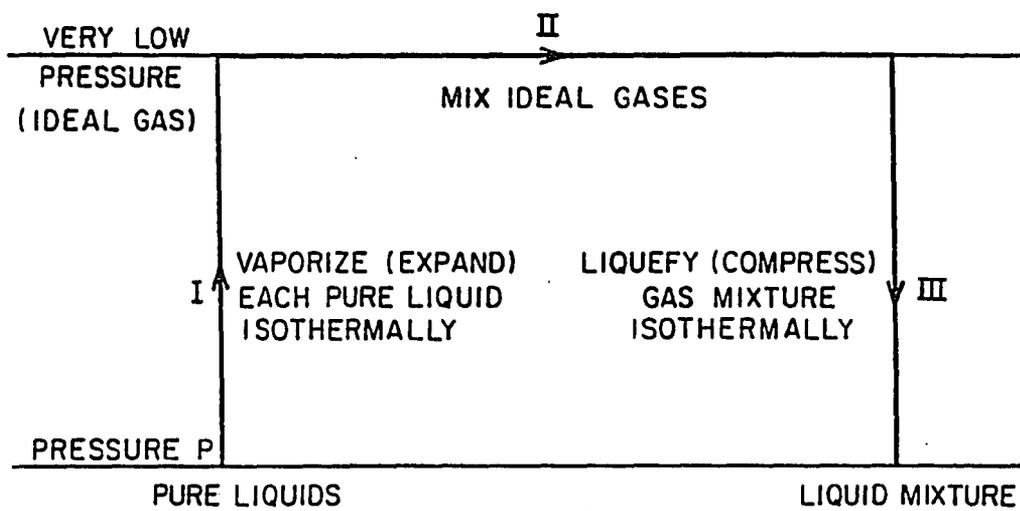


Figure 3.3: Thermodynamic cycle to evaluate the energy of mixing.

CHAPTER 4

EXPERIMENTAL

SYSTEMS CONSIDERED FOR THE STUDY:

The equations for the solubility of a solid solute are given in Chapters 2 and 3. The present study evaluates the different models for ideal solubility and the activity coefficients for their suitability in the prediction of the solubility. The systems used in the study are as follows:

Solvent	Solutes
Benzene	Polycyclic Aromatic Hydrocarbons
N-Octanol	Polycyclic Aromatic Hydrocarbons Polychlorinated Biphenyls
Triolein	Polycyclic Aromatic Hydrocarbons Aliphatic Hydrocarbons Aliphatic Alcohols, Acids etc.

Polycyclic Aromatic Hydrocarbons (PAH) were selected as solutes in all the solvent systems considered, as they are

simple solid solutes which do not undergo any specific chemical interactions like H-bonding, etc. Also they are stable, easy to assay, and covers a wide range of solubilities. Benzene was chosen as one of the solvents as it is a simple solvent and one would expect PAH's to behave very close to ideality. The other two solvent systems were chosen as they are widely used as model solvent systems for the study of partitioning behavior in biological membranes (Hansch et. al., 1979; Leo et. al., 1971; Patton et. al., 1984). The non-hydrocarbon solutes in both N-octanol and triolein are rather complex and deviate considerably from ideal behavior.

PARAMETERS REQUIRED FOR SOLUBILITY ESTIMATION

Calculation of solubility requires various pure component properties as well as binary parameters in some of the models considered. In this chapter the calculation and measurement of all the parameters are given.

The parameters needed for the calculation are as follows:

IDEAL SOLUBILITY:

- (1) Melting point
- (2) Entropy of fusion

(3) Heat capacity change on melting

COMBINATORIAL ACTIVITY COEFFICIENT:

(4) Molar and molecular volume for Flory-Huggins
and UNIFAC

(5) Molecular surface area for UNIFAC

RESIDUAL ACTIVITY COEFFICIENT:

(6) Solubility parameter for Scatchard-Hildebrand

(a) Energy of vaporization

(b) Molar volume

(7) UNIFAC binary interaction parameters.

We will now consider the calculation and/or measurement of all the parameters listed above.

SOLUBILITY

Solubility of selected polycyclic aromatic hydrocarbons was determined in all the solvents studied. All the other solubility data were obtained from the literature.

The solvents and the solutes were of reagent grade and were used as received. The solvent and the solute were equilibrated at 25° C in 5 ml teflon lined screw capped test tube for at least 3 days on a test tube rotator. A

second measurement was made after 7 days. The samples were centrifuged for 30 minutes and then assayed by UV using a Beckman DU-8 spectrophotometer. In all the cases the 3 and 7 day solubility values did not differ by more than 5% between the two measurements.

MELTING POINT

The melting point and heats of fusion of the polycyclic aromatic hydrocarbons were determined by differential scanning calorimetry (DSC) using a Du Pont 1090 thermal analyzer with a 910 DSC module. Accurately weighed samples (1-10mg) were placed in copper crucibles and sealed. An empty copper crucible served as a reference. Samples were heated at 5 deg/min and the thermograms were recorded. For some of the compounds we used the literature values for the melting point.

ENTROPY OF FUSION:

The entropies of fusion were determined using the above data from the following equation:

$$\Delta S_f = \frac{\Delta H_f}{T_m} \quad (4.1)$$

The entropy of fusion is related to the probability of

melting by the following expression:

$$\Delta S_f = -R \ln (P) \quad (4.2)$$

The probability of melting is the ratio of the number of different arrangements, orientations, and conformations in the liquid state to that of the crystal. Thus the total entropy of fusion is:

$$\Delta S_f = \Delta S_{\text{pos}} + \Delta S_{\text{exp}} + \Delta S_{\text{rot}} + \Delta S_{\text{conf}} \quad (4.3)$$

The different contributions to the entropy of fusion are given in Table 4.1. Figure 4.1 gives the schematic diagram of the melting process. Yalkowsky (1979) has proposed the following general expression for the entropy of fusion:

$$\Delta S_f = 13.5 + 2.5 (n-5) \quad (4.4)$$

where n is the number of carbon atoms in the longest chain of the molecule. The second term is taken as zero for rigid molecules or when $n \leq 5$. The entropy of fusion for a rigid molecule is constant at around 13.5 cal/deg•mole (Yalkowsky, 1979; Martin et. al., 1979).

The entropy of fusion for all of the polycyclic

aromatic hydrocarbons was measured by DSC. The values were estimated for the other molecules using the above expression. If there is a phase transition below melting point then the ideal equation has to be modified to include the phase transition. In our study two compound should first order transition below melting point. The differential scanning thermogram for these compounds are shown in figure 4.2 and 4.3.

VOLUME AND AREA:

There are several definitions of volume and area of a molecule. The van der Waals volume and area is defined as the volume or surface area occupied by the collection of van der Waals spheres which make up the molecule. This definition assumes that each individual atom in the molecule can be considered as a sphere with well defined boundary surface (Bondi, 1968; Meyer, 1986).

Several other definitions of volume and area have been suggested by other authors such as: accessible volume and area (Herman, 1972; Richards, 1977; Amidon et. al., 1975), contact volume and area (Richards, 1977; Bultsma, 1980).

The volume and the surface area is approximated by adding up the group contributions (Bondi 1964, 1968).

Herman (1972) developed an algorithm for computing the van der Waals surface area. Pearlman (1980) developed an algorithm for computing volumes and areas, as well as the accessible volumes and areas.

The computational method is also available in the chemical modeling package CHEMLAB (Pearlstein 1985). The molecule is assembled using fragments in the CHEMLAB library, which in turn are assembled using standard van der Waals spheres. This creates 3 dimensional coordinate for the molecule. The volume is then calculated by numerical integration (Connolly, 1985).

Several authors have made use of non-computational methods to calculate the molecular volume and surface area (Harris et. al., 1973; Reynolds et. al., 1974). The method involves construction of the Corey-Pauling-Koltun (CPK) space filling model (solute) and gluing styrofoam balls (representing solvent spheres), then the surface area can be calculated by counting the number of solvent spheres which can be packed around the CPK model. However, this method is very cumbersome.

The volumes considered above involve a single molecule and can be considered as volume in the gas phase of the molecule. Molar volume on the other hand is defined as the

ratio of mass over volume. There are several group contribution schemes available to estimate molar volumes (Edward, 1970; Fedors, 1974).

SOLUBILITY PARAMETERS:

The solubility parameter is defined as the square root of the cohesive energy density. Fedors (1974) suggested a group contribution method to calculate the solubility parameters. The solubility parameter as such is not an additive or constitutive property. However, it is the square root of the ratio of the energy of vaporization and the molar volume. These two parameters are additive and constitutive properties. In Fedor's method this fact is taken advantage of and the energy of vaporization and volume are calculated separately. Fedors (1974) gives the group contribution for both parameters required to calculate the solubility parameters. All the solubility parameters used in the present study were calculated by Fedors method. The group contributions from Fedor's for energy of vaporization and molar volume are given in Table 4.2.

UNIFAC PARAMETERS:

The calculation of UNIFAC activity coefficients requires the volume and surface area parameters, "q" and

"r". The values were taken from Magnussen et. al., (1981).

The binary interaction parameters are required in the UNIFAC method to calculate the residual activity coefficients. Magnussen et. al., (1981) has published a compilation of binary parameters for liquid-liquid equilibria. It is assumed that the binary parameters obtained from a totally different data set are valid in the system under study (Abrams et. al., 1975).

In the UNIFAC method, the calculation of the combinatorial activity coefficients requires the parameters, "q" and "r", which are reduced volume and surface area respectively. The group contributions for "q" and "r" from Magnussen et. al., (1981) are given in Table 4.3.

This chapter considered the measurement and/or estimation of all the parameters needed for the estimation of ideal solubility and activity coefficients. The pure component physicochemical properties are listed in Table 4.4-4.5.

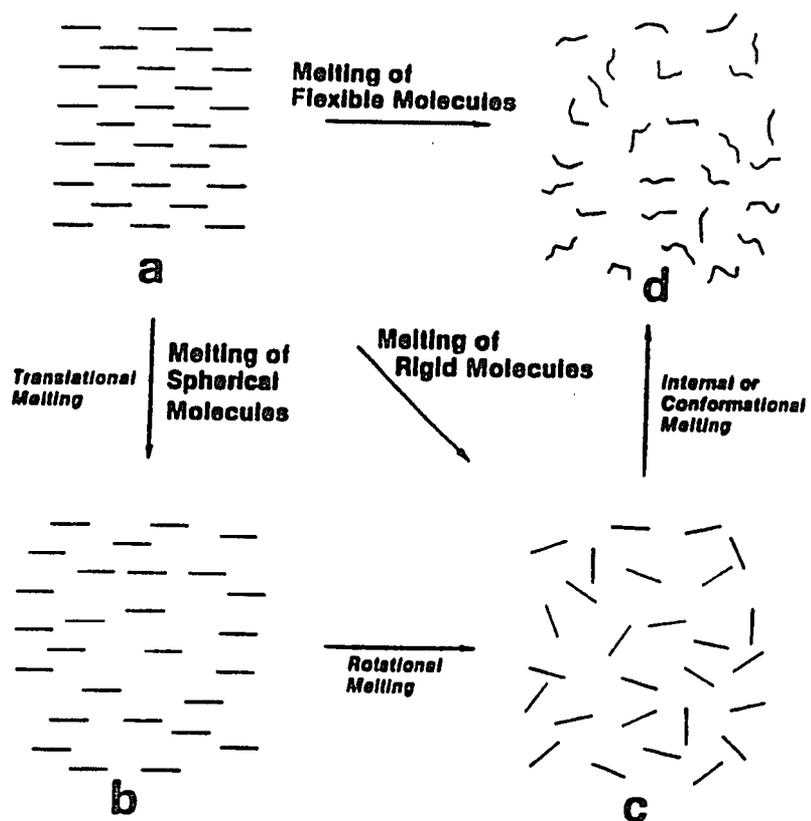


Figure 4.1: Schematic diagram of the melting process.

Table 4.1
 Components of the Entropies of Fusion. †

Type of entropy	most likely value	normal range of values	
		low	high
expansional	2	1	3
positional	2.5	2	3
rotational	9	7	11
total (rigid molecule)	13.5	10	17
conformational	$2.5(n-5)$	$(2.3-2.7) \cdot (n-5)$	$[(n-3)-(n-6)]$
total (flexible molecule)	$13.5 + 2.5(n-5)$		

† Taken from Yalkowsky (1979).
 All the values are eu or cal/deg•mole.

Table 4.2

Group contributions to the energy of vaporization and the molar volume.

Group	ΔE_v	Δv
CH ₃	1125	33.5
CH ₂	1180	16.1
CH	820	-1.0
C	350	-19.2
H ₂ C=	1030	28.5
-CH=	1030	13.5
C=	1030	-5.5
HC≡	920	27.4
Ring closure 5 or more atoms	250	16.0
Ring closure 3 or 4 atoms	750	18.0
Conjugation in ring for each double bond	400	-2.2
Phenyl	7630	71.4
Phenylene (o,m,p)	7630	52.4
Phenyl (trisubstituted)	7630	33.4
Phenyl (tetrasubstituted)	7630	14.4
Phenyl (pentasubstituted)	7630	-4.6
Phenyl (hexasubstituted)	7630	-23.6
Halogen attached to carbon atom with double bond	-20% of ΔE_v of halogen	4.0
COOH	6600	28.5
CO ₂	4300	18.0
CO	4150	10.8
O	800	3.8
OH	7120	10.0
Cl	2760	24.0
Cl (disubstituted)	2300	26.0
Br	3700	30.0
Br (disubstituted)	2950	31.0

¥ Fedors, 1974.

Table 4.3

Group contributions to the UNIFAC parameters "q" and "r". †

Main Group	Subgroup	No.	R _k	Q _k
1 "CH ₂ "	CH ₃	1	0.9011	0.848
	CH ₂	2	0.6744	0.540
	CH	3	0.4469	0.228
	C	4	0.2195	0.000
2 "C=C"	CH ₂ =CH	5	1.3454	1.176
	CH=CH	6	1.1167	0.867
	CH=C	7	0.8886	0.676
	CH ₂ =C	8	1.1183	0.988
3 "ACH"	ACH	9	0.5313	0.400
	AC	10	0.3652	0.120
4 "ACCH ₂ "	ACCH ₃	11	1.2663	0.968
	ACCH ₂	12	1.0396	0.660
	ACCH	13	0.8121	0.348
5 "OH"	OH	14	1.0000	1.200
6	P1(1-propanol)	15	3.2499	3.128
7	P2(2-propanol)	16	3.2491	3.124
8	H ₂ O	17	0.9200	1.400
9	ACOH	18	0.8952	0.680
10 "CH ₂ CO"	CH ₃ CO	19	1.6724	1.488
	CH ₂ CO	20	1.4457	1.180
13 "COOH"	COOH	23	1.3013	1.224
14 "COOC"	CH ₃ COO	25	1.9031	1.728
	CH ₂ COO	26	1.6764	1.420
	CH ₂ Cl	31	1.4654	1.264
16 "CCl"	CHCl	32	1.2380	0.952
	CCl	33	1.0060	0.724
	20	ACCl	40	1.1562

† Magnussen, 1981.

TABLE 4.4

Physicochemical properties of the solutes used in the study.

NAME	MP ^a	ΔH_f^b	ΔS_f^c
NAPHTHALENE	80.2	4490.0	12.70
ANTHRACENE	216.0	6890.0	14.10
PHENANTHRENE	99.0	4450.0	12.00
BIPHENYL	69.0	4460.0	13.00
ACENAPHTHALENE	94.0	4950.0	13.50
FLUORENE	112.0	4480.0	11.60
FLUORANTHENE	108.0	4510.0	11.84
PYRENE	156.0	4090.0	9.64
CHRYSENE	258.0	6250.0	11.76
TRIPHENYLENE	200.0	6000.0	12.65
O-TERPHENYL	56.0	—	13.50
M-TERPHENYL	87.0	—	13.50
P-TERPHENYL	213.0	—	13.50
1:3:5-TRIPHENYLBENZENE	175.0	—	13.50
PERYLENE	277.0	7975.0	14.50
NAPHTHACENE	351.0	9235.2	14.80
BENZO[A]PYRENE ^d	118.0	2541.5	6.50
	178.0	4149.2	9.20
9,10-DIPHENYL ANTHRACENE ^d	210.0	478.5	0.99
	245.0	7200.2	12.19
DECANOIC ACID	32.0	—	22.00
DODECANOIC ACID	43.1	—	27.60
TETRADECANOIC ACID	54.0	—	32.90
HEXADECANOIC ACID	61.8	—	38.70
OCTADECANOIC ACID	68.8	—	39.50
EICOSANOIC ACID	75.3	—	48.80
DOCOSANOIC ACID	80.0	—	53.20
DODECANOL	24.0	—	31.00
TETRADECANOL	38.0	—	36.00
HEXADECANOL	49.9	—	37.00
OCTADECANOL	58.4	—	46.00
EICOSANOL	65.4	—	51.00
DOCOSANOL	70.9	—	56.00

^a degrees centigrade

^b cal/mole

^c cal/deg·mole

^d Compound has a first order transition below melting point

TABLE 4.4 (continued)

Physicochemical properties of the solutes used in the study.

NAME	MP	ΔH_f	ΔS_f
HEXADECANOL	49.9	—	37.00
OCTADECANOL	58.4	—	46.00
EICOSANOL	65.4	—	51.00
DOCOSANOL	70.9	—	56.00
OCTADECANE	28.2	—	46.00
EICOSANE	36.8	—	53.90
DOCOSANE	44.4	—	36.90
TRIPALMITOYL GLYCEROL	65.8	—	94.90
TRISTEAROYL GLYCEROL	71.2	—	105.90
P-DICHLOROBENZENE	53.1	—	13.50
2,6-DIMETHYL NAPHTHALENE	108.0	—	13.50
2,3-DIMETHYL NAPHTHALENE	105.0	—	13.50
4,4-DICHLOROBIPHENYL	149.0	—	13.50
P,P'-DDT	109.0	—	13.50
HEXACHLOROBENZENE	230.0	—	13.50

TABLE 4.5 (continued)

Physicochemical properties of all the solutes used in the study.

NAME	V_CHEM ^e	A_CHEM ^f	Ev ^g	δ^h
NAPHTHALENE	114.74	161.59	12458.0	10.42
ANTHRACENE	153.10	203.92	18897.4	11.11
PHENANTHRENE	152.04	201.40	18766.2	11.11
BIPHENYL	137.92	189.32	14745.8	10.34
ACENAPHTHALENE	138.40	188.10	15316.8	10.52
FLUORENE	157.06	200.43	13701.9	9.95
FLUORANTHENE	176.09	231.78	17538.6	9.98
PYRENE	165.74	216.21	23077.6	11.80
CHRYSENE	189.64	249.72	25342.3	11.56
TRIPHENYLENE	189.02	246.34	25215.7	11.55
O-TERPHENYL	188.83	246.34	20188.8	10.34
M-TERPHENYL	199.78	264.36	20188.8	10.34
P-TERPHENYL	199.80	265.93	20188.8	10.34
1:3:5-TRIPHENYLBENZENE	250.75	322.95	26809.1	10.34
PERLYENE	229.48	320.12	24916.1	10.42
NAPHTHACENE	192.10	245.03	25336.2	11.48
BENZO[A]PYRENE	204.12	258.54	29516.0	12.02
9,10-DIPHENYL- ANTHRACENE	277.10	362.32	34157.3	11.10
DECANOIC ACID	188.70	252.20	16958.5	9.48
DODECANOIC ACID	223.00	223.41	19536.9	9.36
TETRADECANOIC ACID	255.20	344.41	21865.6	9.26
HEXADECANOIC ACID	287.40	293.12	24219.8	9.18
OCTADECANOIC ACID	319.60	438.79	26582.5	9.12
EICOSANOIC ACID	351.80	485.99	28940.7	9.07
DOCOSANOIC ACID	384.00	533.18	31311.7	9.03
DODECANOL	220.60	288.97	21229.6	9.81
TETRADECANOL	252.80	336.27	23590.2	9.66

e Angstroms 3

f Angstroms 2

g calories

h (cal/cm³)^{1/2}

TABLE 4.5 (continued)

Physicochemical properties of all the solutes used in the study.

NAME	V_CHEM	A_CHEM	E ^V	δ
HEXADECANOL	285.00	383.57	25938.3	9.54
OCTADECANOL	317.20	430.87	28344.6	9.45
EICOSANOL	349.40	478.18	30676.2	9.37
DOCOSANOL	381.60	525.47	33004.5	9.30
OCTADECANE	324.60	283.91	21139.5	8.07
EICOSANE	356.80	331.22	23467.5	8.11
DOCOSANE	389.00	378.52	25838.3	8.15
TRIPALMITOYL GLYCEROL	861.90	1273.17	69040.3	8.95
TRISTEAROYL GLYCEROL	958.50	1415.08	76093.5	8.91
P-DICHLOROBENZENE	106.20	148.23	13898.7	11.44
2,6-DIMETHYL NAPHTHALENE	150.29	208.15	15391.8	10.12
2,3-DIMETHYL NAPHTHALENE	149.61	204.38	15322.2	10.12
BENZO(A)PYRENE	203.44	268.07	29884.2	12.12
4,4-DICHLOROBIPHENYL	152.80	225.31	20774.0	11.66
P,P'-DDT	183.85	275.24	23434.3	11.29
HEXACHLOROBENZENE	120.40	201.45	24174.9	14.17

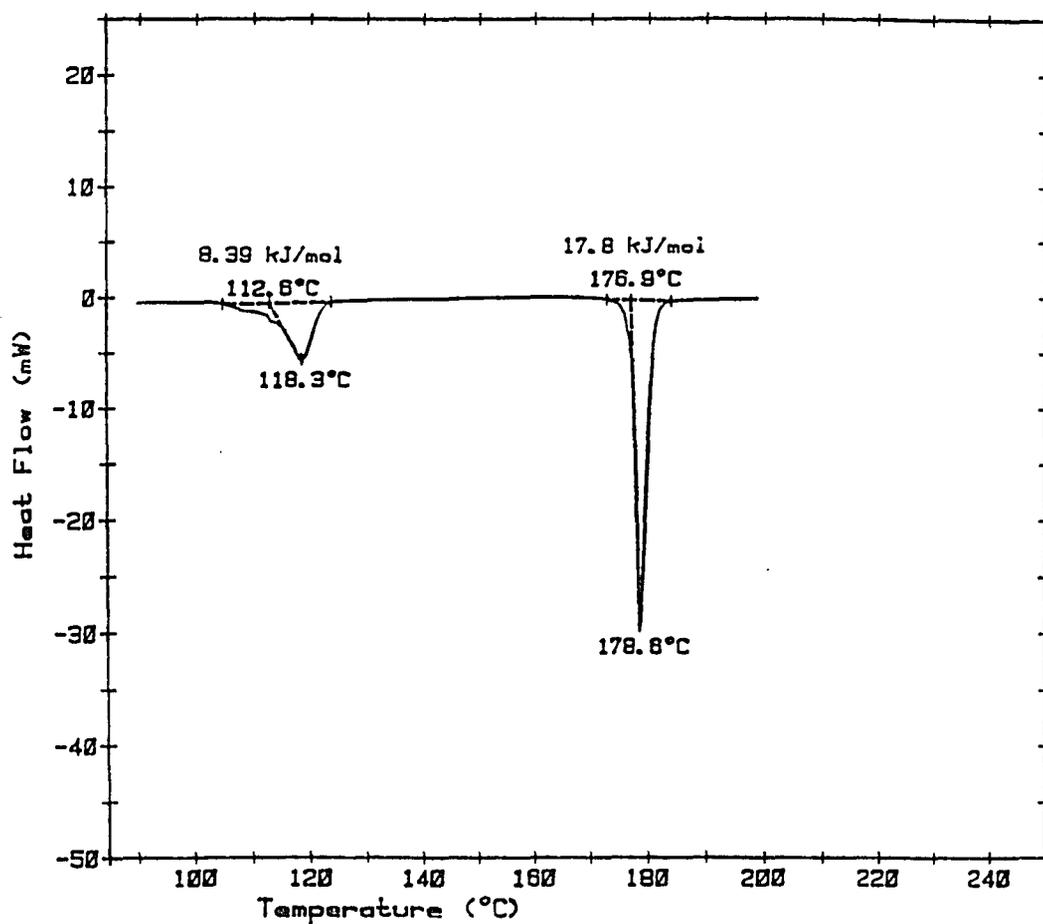


Figure 4.2: DSC thermogram of benz[a]pyrene heated at the rate of 5 degrees per minute.

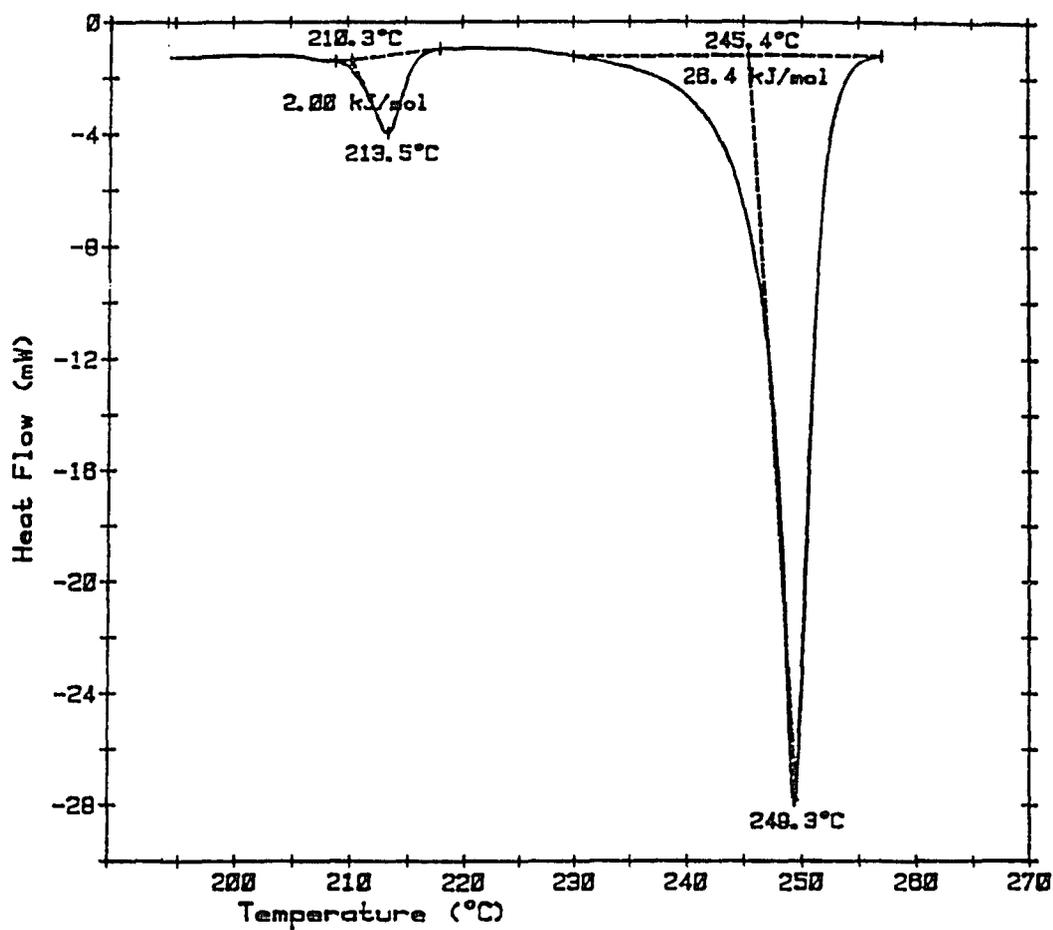


Figure 4.3: DSC thermogram of 9,10-Diphenylanthracene heated at the rate of 5 degrees per minute.

CHAPTER 5

RESULTS AND DISCUSSION

ACTIVITY COEFFICIENTS

In Chapter 4 we considered several models for activity coefficients. These models look at activity coefficients from different points of view. Some of them look entirely at the entropic effects (Flory-Huggins), while others look at the enthalpic effects (Scatchard-Hildebrand). There are also other models like UNIQUAC which include both the enthalpic and entropic contributions activity coefficients.

We selected two models for the entropic activity coefficient and two models for enthalpic activity coefficient. In this section we will consider the calculation of the different activity coefficients and their comparisons. Specifically, we will compare the Flory-Huggins combinatorial to the UNIFAC combinatorial activity coefficient and Scatchard-Hildebrand residual to UNIFAC residual activity coefficient.

COMBINATORIAL ACTIVITY COEFFICIENT

The activity coefficients from Flory-Huggins and UNIFAC are given in the following equations:

Flory-Huggins

$$\ln \gamma_1^c = \left[\ln \left[\frac{\phi_1}{X_1} \right] + 1 - \frac{\phi_1}{X_1} \right] \quad (5.1)$$

where ϕ and X are volume fraction and mole fraction, respectively.

UNIFAC combinatorial

$$\ln \gamma_1^c = \left[\ln \left[\frac{\phi_1}{X_1} \right] + 1 - \frac{\phi_1}{X_1} \right] + \frac{z}{2} \left[\ln \left[\frac{\phi_1}{\theta_1} \right] + 1 - \frac{\phi_1}{\theta_1} \right] \quad (5.2)$$

where θ is the surface area fraction and z is the coordination number.

The two equations for the entropic contribution to the activity coefficient differ in the second term. The Flory-Huggins activity coefficient involves only volume fractions and mole fractions. The UNIFAC model has in addition to the Flory-Huggins activity coefficient a term which involves surface area fraction (θ) and coordination number (z). If the second term in equation 5.2 is close to zero, then the UNIFAC activity coefficient is equivalent to the one obtained from the Flory-Huggins model.

The second term in equation 5.2 has the ratio of volume fraction to surface area fraction (ϕ/θ). This ratio can also be written as:

$$\frac{\phi_1}{\theta_1} = \frac{\frac{X_1}{X_1 + X_2 (V_2/V_1)}}{\frac{X_1}{X_1 + X_2 (A_2/A_1)}} \quad (5.3)$$

The numerator and the denominator differ only by the ratio of volumes and areas. If the ratios, i.e., V_2/V_1 and A_2/A_1 are similar, the ratio of the volume fraction and the surface area fraction will be close to unity and the second term in equation 5.2 will become negligible.

Several authors have reported that there is a linear relationship between volume and area (Pearlman, 1986). In the present study, we found that the volumes and areas of all the solutes used have a linear relationship. This can be seen in figure 5.1 which gives the plot of volumes and the areas calculated from CHEMLAB.

As mentioned earlier, if the ratio of volumes and areas are equivalent, then the second term in UNIFAC combinatorial activity coefficient vanishes and the model is equivalent to that of Flory and Huggins. Figure 5.2 gives a plot of the ratio of volumes vs areas. The plot shows that there is not only a linear trend but the two are equivalent.

The UNIFAC model requires volume and area to calculate the combinatorial activity coefficient. However, the volume and area are defined in terms of parameters "q" and "r", which are reduced volume and areas. These parameters were calculated and compared to the molecular volume and surface area calculated from CHEMLAB. Figures 5.3 and 5.4 gives the plot of volume vs "q" and surface area vs "r". The plots clearly show a linear relationship between the CHEMLAB volume and areas and the parameters from UNIFAC.

Computer programs were written to calculate the Flory-

Huggins and the UNIFAC combinatorial activity coefficients. The combinatorial activity coefficients are presented in Tables 5.1-5.3, for the three solvent systems i.e. benzene, triolein and n-octanol. Figures 5.5 -5.6 gives a plot of the Flory-Huggins vs. UNIFAC combinatorial activity coefficient for benzene and triolein. The plot for n-octanol is not presented as the combinatorial activity coefficient is very close to zero. The plots show that the combinatorial activity coefficients obtained from the two models are not only similar but equivalent in magnitude.

This result is very important due to the fact that the UNIFAC calculation is more involved and does not do a better job than the simpler model of Flory-Huggins in the prediction of activity coefficients.

RESIDUAL ACTIVITY COEFFICIENTS

The residual activity coefficients from Scatchard-Hildebrand and UNIFAC theories are given by the following equations:

Scatchard-Hildebrand:

$$\ln \gamma_1^r = \frac{1}{RT} V_1 (1 - \phi_1)^2 (\delta_1 - \delta_2)^2 \quad (5.4)$$

where V_1 is the molar volume, δ is the solubility parameter and ϕ is the volume fraction.

UNIFAC residual:

$$\ln \gamma_1 = \sum (\ln \Gamma_k - \ln \Gamma_k^i) \quad (5.5)$$

where Γ_k is the group residual activity coefficient and Γ_k^i is the residual activity coefficient of group k in a reference solution containing only molecules of type i . The group activity coefficient, Γ_k , is given by the following equation.

$$\ln \Gamma_k = Q_k \left[1 - \ln \left[\frac{\sum_m \theta_m g_{mk}}{m} \right] - \sum_m \frac{\theta_m g_{km}}{\sum_n \theta_n g_{nm}} \right] \quad (5.6)$$

where g is the interaction parameter defined in terms of interaction between groups, θ is the surface area fraction.

The residual activity coefficient in both models are directly proportional to a parameter describing size. In the case of Scatchard-Hildebrand's theory, the activity coefficient is proportional to volume and in UNIFAC, to

surface area. Thus increasing the volume or the area of the solute increases the activity coefficient and decreases solubility. This is to be expected as increasing the size of the solute molecule would require the creation of bigger cavities for the incorporation of the molecule in the solvent. This will involve greater energy and thus decrease the solubility (Hermann, 1972). However, size works in a different manner as in the case of combinatorial activity coefficient. As the size difference between the solute and the solvent increases the entropy of mixing will increase, thus promoting solubility.

The interaction parameters in the case of UNIFAC are derived from nonlinear regression analyses from liquid-liquid equilibrium data (Magnussen, 1981). The model uses group contribution and lists the interaction parameters of the groups. The model assumes that there is no interaction between similar groups and in such a case the activity coefficient is unity.

Tables 5.4-5.6 list the residual activity coefficients calculated from the two models. Figures 5.7-5.8 give the plots of the residual activity coefficients obtained from the two models. The values of the activity coefficient calculated from the two models do not compare at all. In

fact in the case of the polycyclic aromatic hydrocarbons in benzene, the UNIFAC model predicts a logarithm of the residual activity coefficient values of zero in all cases. The Scatchard-Hildebrand model however predicts a positive deviation from ideality.

TOTAL ACTIVITY COEFFICIENT:

The Flory-Huggins model combined with the Scatchard-Hildebrand model predicts total activity coefficient close to unity as one gives a negative deviation, while other a positive deviation. The total UNIFAC model, however shows a negative deviation for all the solutes in benzene. The real situation, however, is that the solutes behave very close to ideality and is well represented by the Flory-Huggins and the Scatchard-Hildebrand combination.

In the case of triolein some trends can be seen. The alcohols and acids are extremely sensitive to the UNIFAC model but not to the Scatchard-Hildebrand. The predictions in the case of aliphatic hydrocarbons are very close for both the models. On the other hand in the case of polycyclic aromatic hydrocarbons the Scatchard-Hildebrand model is more sensitive compared to the UNIFAC.

It should be remembered that the activity coefficient

calculated for the alcohols and acids in triolein, seriously violates the assumption of the Scatchard-Hildebrand theory. Triolein has an H-bond acceptor and alcohol has a H-bond donor, thus allowing the formation of H-bond in the solution. The Scatchard-Hildebrand theory's assumption does not allow for any specific interactions. Actually it is only valid for the molecules where the geometric mean rule is valid. This is only true in the case of molecules which interact by London dispersion forces. This is one of the major limitations of the Scatchard-Hildebrand theory. It however gives very good results when the assumptions are satisfied.

In the case of n-octanol the two activity coefficient once again are not related in any way.

TABLE 5.1

Combinatorial activity coefficients from the Flory-Huggins and UNIFAC model in benzene.

NAME	TEMP	$\ln X_1^i$	$\ln \gamma_1$ (FH)	$\ln \gamma_1$ (UNIFAC)
1:3:5-TRIPHENYLBENZENE	25.2	-3.425	-0.946	-0.968
1:3:5-TRIPHENYLBENZENE	28.6	-3.309	-0.929	-0.949
1:3:5-TRIPHENYLBENZENE	40.4	-2.928	-0.859	-0.878
1:3:5-TRIPHENYLBENZENE	46.2	-2.751	-0.819	-0.836
1:3:5-TRIPHENYLBENZENE	59.4	-2.371	-0.716	-0.730
1:3:5-TRIPHENYLBENZENE	66.6	-2.176	-0.653	-0.668
9-10-DIPHENYLANTHRACENE	23.0	-2.950	-1.351	-1.238
ACENAPHTHALENE	30.6	-1.423	-0.101	-0.054
ACENAPHTHALENE	41.4	-1.140	-0.075	-0.041
ACENAPHTHALENE	63.2	-0.624	-0.029	-0.017
ACENAPHTHALENE	69.4	-0.489	-0.019	-0.011
ANTHRACENE	35.8	-4.155	-0.297	-0.167
ANTHRACENE	42.4	-3.919	-0.293	-0.165
ANTHRACENE	50.6	-3.639	-0.287	-0.162
ANTHRACENE	59.6	-3.348	-0.279	-0.215
ANTHRACENE	70.2	-3.025	-0.267	-0.153
BENZO[A]PYRENE	23.0	-1.626	-0.697	-0.540
BIPHENYL	37.0	-0.677	-0.033	-0.032
BIPHENYL	47.6	-0.438	-0.015	-0.015
BIPHENYL	59.2	-0.193	-0.003	-0.031
BIPHENYL	63.2	-0.113	-0.001	-0.011
BIPHENYL	34.8	-0.729	-0.038	-0.036
BIPHENYL	40.7	-0.592	-0.027	-0.025
BIPHENYL	43.7	-0.524	-0.021	-0.020
BIPHENYL	50.5	-0.375	-0.012	-0.011
BIPHENYL	55.8	-0.263	-0.006	-0.005
BIPHENYL	60.0	-0.177	-0.002	-0.028
CHRYSENE	35.6	-4.280	-0.549	-0.332
CHRYSENE	45.8	-3.953	-0.538	-0.326
CHRYSENE	60.6	-3.514	-0.517	-0.316
CHRYSENE	72.2	-3.196	-0.495	-0.305
FLUORANTHENE	44.8	-1.189	-0.150	-0.051
FLUORANTHENE	56.0	-0.945	-0.105	-0.039

TABLE 5.1 (continued)

NAME	TEMP	$\ln X_1^i$	$\ln \gamma_1$ (FH)	$\ln \gamma_1$ (UNIFAC)
FLUORANTHENE	64.4	-0.772	-0.075	-0.029
FLUORANTHENE	77.2	-0.525	-0.038	-0.016
FLUORENE	33.6	-1.498	-0.156	-0.066
FLUORENE	54.4	-1.030	-0.093	-0.042
FLUORENE	58.4	-0.947	-0.082	-0.037
FLUORENE	69.4	-0.728	-0.053	-0.025
FLUORENE	72.8	-0.664	-0.045	-0.022
FLUORENE	34.6	-1.474	-0.153	-0.064
FLUORENE	40.3	-1.340	-0.135	-0.058
FLUORENE	45.0	-1.234	-0.121	-0.053
FLUORENE	49.9	-1.126	-0.106	-0.047
FLUORENE	57.3	-0.970	-0.085	-0.039
FLUORENE	63.1	-0.852	-0.069	-0.003
FLUORENE	67.5	-0.765	-0.058	-0.028
FLUORENE	75.2	-0.619	-0.040	-0.019
FLUORENE	81.7	-0.500	-0.027	-0.013
M-TERPHENYL	36.8	-1.104	-0.172	-0.035
M-TERPHENYL	47.0	-0.852	-0.112	-0.029
M-TERPHENYL	60.8	-0.535	-0.048	-0.016
M-TERPHENYL	67.4	-0.392	-0.027	-0.010
M-TERPHENYL	74.2	-0.251	-0.011	-0.004
M-TERPHENYL	77.6	-0.182	-0.006	-0.002
NAPHTHALENE	35.0	-0.941	-0.028	-0.005
NAPHTHALENE	45.0	-0.710	-0.018	-0.032
NAPHTHALENE	47.4	-0.656	-0.016	-0.029
NAPHTHALENE	63.2	-0.324	-0.005	-0.008
NAPHTHALENE	75.8	-0.080	-0.000	-0.000
NAPHTHALENE	37.2	-0.889	-0.026	-0.046
NAPHTHALENE	42.4	-0.768	-0.021	-0.037
NAPHTHALENE	50.3	-0.593	-0.014	-0.024
NAPHTHALENE	61.2	-0.364	-0.006	-0.010
NAPHTHALENE	71.0	-0.171	-0.001	-0.002
NAPHTHACENE	23.0	-3.866	-0.599	-0.623
O-TERPHENYL	28.0	-0.634	-0.060	-0.062
O-TERPHENYL	32.4	-0.526	-0.043	-0.045
O-TERPHENYL	44.8	-0.240	-0.009	-0.010

TABLE 5.1 (continued)

NAME	TEMP	$\ln X_1^i$	$\ln \gamma_1$ (FH)	$\ln \gamma_1$ (UNIFAC)
O-TERPHENYL	50.4	-0.118	-0.002	-0.002
P-TERPHENYL	38.0	-3.836	-0.606	-0.567
P-TERPHENYL	60.2	-3.126	-0.555	-0.520
P-TERPHENYL	64.2	-3.008	-0.543	-0.509
P-TERPHENYL	68.0	-2.899	-0.530	-0.498
P-TERPHENYL	77.6	-2.633	-0.496	-0.466
PERYLENE	23.0	-3.328	-0.910	-0.882
PHENANTHRENE	32.0	-1.331	-0.123	-0.078
PHENANTHRENE	40.0	-1.142	-0.099	-0.065
PHENANTHRENE	41.8	-1.101	-0.094	-0.061
PHENANTHRENE	50.2	-0.915	-0.071	-0.048
PHENANTHRENE	58.0	-0.750	-0.052	-0.035
PHENANTHRENE	39.6	-1.151	-0.101	-0.065
PHENANTHRENE	43.6	-1.060	-0.089	-0.058
PHENANTHRENE	52.1	-0.874	-0.066	-0.044
PHENANTHRENE	61.6	-0.677	-0.043	-0.030
PHENANTHRENE	68.7	-0.537	-0.029	-0.020
PHENANTHRENE	69.0	-0.531	-0.028	-0.019
PYRENE	32.4	-1.970	-0.244	-0.077
PYRENE	58.6	-1.430	-0.169	-0.061
PYRENE	66.8	-1.278	-0.145	-0.055
PYRENE	76.2	-1.112	-0.119	-0.047
PYRENE	84.6	-0.972	-0.096	-0.040
TRIPHENYLENE	39.4	-3.284	-0.498	-0.308
TRIPHENYLENE	47.6	-3.037	-0.478	-0.298
TRIPHENYLENE	63.8	-2.583	-0.430	-0.273
TRIPHENYLENE	69.4	-2.436	-0.411	-0.263
TRIPHENYLENE	82.8	-2.104	-0.360	-0.234

TABLE 5.2

Combinatorial activity coefficients from the Flory-Huggins and UNIFAC models for solutes in triolein.

NAME	TEMP	$\ln X_1^i$	$\ln \gamma_1$ (FH)	$\ln \gamma_1$ (UNIFAC)
2,3-DIMETHYLNAPHTHALENE	23.0	-1.888	-1.049	-0.745
2,6-DIMETHYLNAPHTHALENE	23.0	-1.957	-1.046	-0.745
4,4-DICHLOROBIPHENYL	23.0	-2.902	-1.031	-0.867
9-10-DIPHENYLANTHRACENE	23.0	-2.950	-0.533	-0.589
ACENAPHTHALENE	23.0	-1.635	-1.116	-0.568
BENZO(A)PYRENE	23.0	-1.626	-0.796	-0.696
BIPHENYL	23.0	-1.020	-1.119	-0.781
DECANOIC ACID	14.0	-0.696	-0.856	-0.821
DECANOIC ACID	27.0	-0.185	-0.856	-0.821
DECANOIC ACID	37.0	-0.179	-0.856	-0.821
DOCOSANE	14.0	-1.974	-0.333	-0.334
DOCOSANE	27.0	-1.080	-0.333	-0.334
DOCOSANE	37.0	-0.444	-0.333	-0.334
DOCOSANOIC ACID	27.0	-4.746	-0.341	-0.317
DOCOSANOIC ACID	37.0	-3.726	-0.341	-0.317
DOCOSANOL	14.0	-5.607	-0.345	-0.286
DOCOSANOL	27.0	-4.138	-0.345	-0.286
DOCOSANOL	37.0	-3.092	-0.345	-0.286
DODECANOIC ACID	14.0	-1.413	-0.723	-0.697
DODECANOIC ACID	27.0	-0.748	-0.723	-0.697
DODECANOIC ACID	37.0	-0.274	-0.723	-0.697
DODECANOL	14.0	-0.545	-0.732	-0.677
EICOSANE	14.0	-2.162	-0.387	-0.436
EICOSANE	27.0	-0.889	-0.387	-0.436
EICOSANOIC ACID	27.0	-3.968	-0.396	-0.371
EICOSANOIC ACID	37.0	-3.045	-0.396	-0.371
EICOSANOL	14.0	-4.613	-0.400	-0.336
EICOSANOL	27.0	-3.297	-0.400	-0.336
EICOSANOL	37.0	-2.359	-0.400	-0.336
FLUORENE	23.0	-1.761	-1.008	-0.488

TABLE 5.2 (continued)

NAME	TEMP	$\ln X_1^i$	$\ln \gamma_1$ (FH)	$\ln \gamma_1$ (UNIFAC)
HEXADECANOIC ACID	14.0	-3.255	-0.534	-0.508
HEXADECANOIC ACID	27.0	-2.267	-0.534	-0.508
HEXADECANOIC ACID	37.0	-1.563	-0.534	-0.508
HEXADECANOL	14.0	-2.337	-0.540	-0.459
HEXADECANOL	27.0	-1.426	-0.540	-0.459
NAPHTHELENE	23.0	-1.239	-1.280	-0.948
NAPHTHACENE	23.0	-3.866	-0.814	-0.678
OCTADECANE	14.0	-1.149	-0.449	-0.458
OCTADECANE	27.0	-0.092	-0.449	-0.458
OCTADECANOIC ACID	14.0	-3.809	-0.460	-0.412
OCTADECANOIC ACID	27.0	-2.779	-0.460	-0.412
OCTADECANOIC ACID	37.0	-2.046	-0.460	-0.412
OCTADECANOL	14.0	-3.594	-0.465	-0.393
OCTADECANOL	27.0	-2.431	-0.465	-0.393
OCTADECANOL	37.0	-1.603	-0.465	-0.393
PERYLENE	23.0	-3.320	-0.701	-0.499
PHENANTHRENE	23.0	-1.556	-1.035	-0.413
TETRADECANOIC ACID	14.0	-2.315	-0.620	-0.594
TETRADECANOIC ACID	27.0	-1.495	-0.620	-0.594
TETRADECANOIC ACID	37.0	-0.911	-0.620	-0.594
TETRADECANOL	14.0	-1.520	-0.628	-0.535
TETRADECANOL	27.0	-0.666	-0.628	-0.535
TETRADECANOL	37.0	-0.058	-0.628	-0.535

TABLE 5.3

Combinatorial activity coefficients from the Flory Huggins and UNIFAC models in n-octanol.

NAME	$\ln X_1^i$	$\ln \gamma_1$ (FH)	$\ln \gamma_1$ (UNIFAC)
1,2,3,5-TETRACHLORO- BENZENE	-0.260	-0.001	-0.001
1,2,3-TRICHLORO- BENZENE	-0.280	0.000	-0.001
1,2,4,5-TETRACHLORO- BENZENE	-1.140	-0.005	-0.008
1,4-DICHLOROBENZENE	-0.280	-0.001	-0.001
2,2',5,5'-TETRACHLORO- BIPHENYL	-0.620	-0.024	-0.034
2,3,4,5-TETRACHLORO- BIPHENYL	-0.660	-0.027	-0.030
2,4,5-TRICHLOROBIPHENYL	-0.530	-0.014	-0.019
4,4'-DICHLOROBIPHENYL	-1.240	-0.033	-0.032
4-MONOCHLOROBIPHENYL	-0.530	-0.005	-0.009
9,10-DIPHENYLANTHRACENE	-2.950	-0.208	-0.136
ACENAPHTHENE	-0.710	-0.001	-0.004
ANTHRACENE	-1.910	-0.000	-0.000
BENZO[A]PYRENE	-1.626	-0.003	-0.020
BIPHENYL	-0.450	0.000	0.000
CHRYSENE	-2.300	-0.016	-0.019
FLUORENE	-0.910	0.000	-0.000
HEXABROMOBENZENE	-2.810	-0.112	-0.132
HEXACHLOROBENZENE	-2.040	-0.049	-0.046
NAPHTHALENE	-0.550	-0.010	-0.008
NAPHTHACENE	-3.866	-0.003	-0.000
PENTACHLOROBENZENE	-0.600	-0.006	-0.008
PERYLENE	-3.320	-0.008	-0.007
PHENANTHRENE	-0.760	-0.000	-0.000
PYRENE	-1.310	-0.026	-0.030

TABLE 5.4

Residual activity coefficients from the Scatchard-Hildebrand and UNIFAC models in benzene.

NAME	TEMP	$\ln X_1^i$	$\ln \gamma_1$ (SH)	$\ln \gamma_1$ (UNIFAC)
1:3:5-TRIPHENYLBENZENE	25.2	-3.425	1.255	0.000
1:3:5-TRIPHENYLBENZENE	28.6	-3.309	1.210	0.000
1:3:5-TRIPHENYLBENZENE	40.4	-2.928	1.047	0.000
1:3:5-TRIPHENYLBENZENE	46.2	-2.751	0.964	0.000
1:3:5-TRIPHENYLBENZENE	59.4	-2.371	0.774	0.000
1:3:5-TRIPHENYLBENZENE	66.6	-2.176	0.672	0.000
9,10,DIPHENYLANTHRACENE	23.0	-2.950	1.564	0.000
ACENAPHTHALENE	30.6	-1.423	0.163	0.001
ACENAPHTHALENE	41.4	-1.140	0.114	0.008
ACENAPHTHALENE	63.2	-0.624	0.038	0.003
ACENAPHTHALENE	69.4	-0.489	0.024	0.002
ANTHRACENE	35.8	-4.155	0.866	0.000
ANTHRACENE	42.4	-3.919	0.834	0.000
ANTHRACENE	50.6	-3.639	0.792	0.000
ANTHRACENE	59.6	-3.348	0.744	0.000
ANTHRACENE	70.2	-3.025	0.683	0.000
BENZO[A]PYRENE	23.0	-1.626	2.720	0.000
BIPHENYL	37.0	-0.677	0.036	0.000
BIPHENYL	47.6	-0.438	0.015	0.000
BIPHENYL	59.2	-0.193	0.003	0.000
BIPHENYL	63.2	-0.113	0.001	0.000
BIPHENYL	34.8	-0.729	0.041	0.000
BIPHENYL	40.7	-0.592	0.027	0.000
BIPHENYL	43.7	-0.524	0.022	0.000
BIPHENYL	50.5	-0.375	0.011	0.000
BIPHENYL	55.8	-0.263	0.005	0.000
BIPHENYL	60.0	-0.177	0.002	0.000
CHRYSENE	35.6	-4.280	1.627	0.000
CHRYSENE	45.8	-3.953	1.534	0.000
CHRYSENE	60.6	-3.514	1.391	0.000
CHRYSENE	72.2	-3.196	1.273	0.000
FLUORANTHENE	44.8	-1.189	0.043	0.000
FLUORANTHENE	56.0	-0.945	0.027	0.000

TABLE 5.4 (continued)

NAME	TEMP	$\ln X_1^i$	$\ln \gamma_1$ (SH)	$\ln \gamma_1$ (UNIFAC)
FLUORANTHENE	64.4	-0.772	0.018	0.000
FLUORANTHENE	77.2	-0.525	0.008	0.000
FLUORENE	33.6	-1.498	0.058	0.003
FLUORENE	54.4	-1.030	0.030	0.002
FLUORENE	58.4	-0.947	0.026	0.001
FLUORENE	69.4	-0.728	0.015	0.001
FLUORENE	72.8	-0.664	0.013	0.001
FLUORENE	34.6	-1.474	0.057	0.003
FLUORENE	40.3	-1.340	0.048	0.002
FLUORENE	45.0	-1.234	0.042	0.002
FLUORENE	49.9	-1.126	0.035	0.002
FLUORENE	57.3	-0.970	0.027	0.001
FLUORENE	63.1	-0.852	0.021	0.001
FLUORENE	67.5	-0.765	0.017	0.001
FLUORENE	75.2	-0.619	0.011	0.001
FLUORENE	81.7	-0.500	0.007	0.001
M-TERPHENYL	36.8	-1.104	0.081	0.000
M-TERPHENYL	47.0	-0.852	0.047	0.000
M-TERPHENYL	60.8	-0.535	0.018	0.000
M-TERPHENYL	67.4	-0.392	0.009	0.000
M-TERPHENYL	74.2	-0.251	0.003	0.000
M-TERPHENYL	77.6	-0.182	0.001	0.000
NAPHTHALENE	35.0	-0.941	0.073	0.000
NAPHTHALENE	45.0	-0.710	0.045	0.000
NAPHTHALENE	47.4	-0.656	0.039	0.000
NAPHTHALENE	63.2	-0.324	0.010	0.000
NAPHTHALENE	75.8	-0.080	0.000	0.000
NAPHTHALENE	37.2	-0.889	0.067	0.000
NAPHTHALENE	42.4	-0.768	0.052	0.000
NAPHTHALENE	50.3	-0.593	0.033	0.000
NAPHTHALENE	61.2	-0.364	0.013	0.000
NAPHTHALENE	71.0	-0.171	0.003	0.000
NAPHTHACENE	23.0	-3.866	1.671	0.000
O-TERPHENYL	28.0	-0.634	0.029	0.000
O-TERPHENYL	32.4	-0.526	0.019	0.000
O-TERPHENYL	44.8	-0.240	0.003	0.000

TABLE 5.4 (continued)

NAME	TEMP	$\ln X_1^i$	$\ln \gamma_1$ (SH)	$\ln \gamma_1$ (UNIFAC)
O-TERPHENYL	50.4	-0.118	0.0009	0.000
P-TERPHENYL	38.0	-3.836	0.7515	0.000
P-TERPHENYL	60.2	-3.126	0.6252	0.000
P-TERPHENYL	64.2	-3.008	0.6007	0.000
P-TERPHENYL	68.0	-2.899	0.5769	0.000
P-TERPHENYL	77.6	-2.633	0.5152	0.000
PERYLENE	23.0	-3.323	0.5714	0.000
PHENANTHRENE	32.0	-1.331	0.3146	0.000
PHENANTHRENE	40.0	-1.142	0.2411	0.000
PHENANTHRENE	41.8	-1.101	0.2258	0.000
PHENANTHRENE	50.2	-0.915	0.1606	0.000
PHENANTHRENE	58.0	-0.750	0.1101	0.000
PHENANTHRENE	39.6	-1.151	0.2446	0.000
PHENANTHRENE	43.6	-1.060	0.2109	0.000
PHENANTHRENE	52.1	-0.874	0.1474	0.000
PHENANTHRENE	61.6	-0.677	0.0902	0.000
PHENANTHRENE	68.7	-0.537	0.0571	0.000
PHENANTHRENE	69.0	-0.531	0.0559	0.000
PYRENE	32.4	-1.970	1.0200	0.000
PYRENE	58.6	-1.430	0.6053	0.000
PYRENE	66.8	-1.278	0.4949	0.000
PYRENE	76.2	-1.112	0.3822	0.000
PYRENE	84.6	-0.972	0.2948	0.000
TRIPHENYLENE	39.4	-3.284	1.4150	0.000
TRIPHENYLENE	47.6	-3.037	1.3098	0.000
TRIPHENYLENE	63.8	-2.583	1.0909	0.000
TRIPHENYLENE	69.4	-2.436	1.0130	0.000
TRIPHENYLENE	82.8	-2.104	0.8260	0.000

TABLE 5.5

Residual activity coefficients from the Scatchard-Hildebrand and UNIFAC models for solutes in triolein.

NAME	TEMP	$\ln X_1^i$	$\ln \gamma_1$ (SH)	$\ln \gamma_1$ (UNIFAC)
2,3-DIMETHYL NAPHTHALENE	23.0	-1.888	0.010	0.187
2,6-DIMETHYL NAPHTHALENE	23.0	-1.957	0.010	0.187
4,4-DICHLOROBIPHENYL	23.0	-2.902	0.023	0.000
9,10-DIPHENYLANTHRACENE	23.0	-2.950	2.340	0.212
ACENAPHTHALENE	23.0	-1.635	0.531	0.155
BENZO(A) PYRENE	23.0	-1.626	2.622	0.112
BIPHENYL	23.0	-1.020	0.000	0.173
DECANOIC ACID	14.0	-0.696	0.053	0.396
DECANOIC ACID	27.0	-0.185	0.050	0.397
DECANOIC ACID	37.0	-0.179	0.049	0.396
DOCOSANE	14.0	-1.974	0.554	0.786
DOCOSANE	27.0	-1.080	0.530	0.834
DOCOSANE	37.0	-0.444	0.513	0.864
DOCOSANOIC ACID	27.0	-4.746	0.000	0.700
DOCOSANOIC ACID	37.0	-3.726	0.000	0.717
DOCOSANOL	14.0	-5.607	0.060	0.997
DOCOSANOL	27.0	-4.138	0.057	1.016
DOCOSANOL	37.0	-3.092	0.056	1.025
DODECANOIC ACID	14.0	-1.413	0.035	0.426
DODECANOIC ACID	27.0	-0.748	0.033	0.432
DODECANOIC ACID	37.0	-0.274	0.032	0.434
DODECANOL	14.0	-0.545	0.248	1.020
EICOSANE	14.0	-2.162	0.508	0.665
EICOSANE	27.0	-0.889	0.486	0.705
EICOSANOIC ACID	27.0	-3.968	0.000	0.640
EICOSANOIC ACID	37.0	-3.045	0.000	0.654
EICOSANOL	14.0	-4.613	0.055	0.979
EICOSANOL	27.0	-3.297	0.052	0.990
EICOSANOL	37.0	-2.359	0.051	0.995
FLUORENE	23.0	-1.761	0.217	0.162

TABLE 5.5 (continued)

NAME	TEMP	$\ln X_1^i$	$\ln \gamma_1$ (SH)	$\ln \gamma_1$ (UNIFAC)
HEXADECANOIC ACID	14.0	-3.255	0.005	0.511
HEXADECANOIC ACID	27.0	-2.267	0.004	0.527
HEXADECANOIC ACID	37.0	-1.563	0.004	0.535
HEXADECANOL	14.0	-2.337	0.125	0.965
HEXADECANOL	27.0	-1.426	0.119	0.962
NAPHTHELENE	23.0	-1.239	0.383	0.140
NAPHTHACENE	23.0	-3.866	1.673	0.213
OCTADECANE	14.0	-1.149	0.571	0.650
OCTADECANE	27.0	-0.092	0.546	0.690
OCTADECANOIC ACID	14.0	-3.809	0.005	0.576
OCTADECANOIC ACID	27.0	-2.779	0.005	0.598
OCTADECANOIC ACID	37.0	-2.046	0.005	0.610
OCTADECANOL	14.0	-3.594	0.089	0.967
OCTADECANOL	27.0	-2.431	0.085	0.972
OCTADECANOL	37.0	-1.603	0.082	0.972
PERYLENE	23.0	-3.320	1.211	0.228
PHENANTHRENE	23.0	-1.556	1.143	0.182
TETRADECANOIC ACID	14.0	-2.315	0.018	0.465
TETRADECANOIC ACID	27.0	-1.495	0.017	0.476
TETRADECANOIC ACID	37.0	-0.911	0.016	0.482
TETRADECANOL	14.0	-1.520	0.160	0.974
TETRADECANOL	27.0	-0.666	0.153	0.963
TETRADECANOL	37.0	-0.058	0.148	0.953

Table 5.6

Residual activity coefficients from the Scatchard-Hildebrand and UNIFAC models in n-octanol.

NAME	$\ln X_1^i$	$\ln \gamma_1$ (SH)	$\ln \gamma_1$ (UNIFAC)
1,2,3,5-TETRACHLORO- BENZENE	-0.260	1.473	2.070
1,2,3-TRICHLORO- BENZENE	-0.280	0.597	2.303
1,2,4,5-TETRACHLORO- BIPHENYL	-1.140	1.473	2.070
1,4-DICHLOROBENZENE	-0.280	0.095	1.963
2,2',5,5'-TETRACHLORO- BIPHENYL	-0.620	1.658	3.706
2,3,4,5-TETRACHLORO- BIPHENYL	-0.660	1.658	3.706
2,4,5-TRICHLOROBIPHENYL	-0.530	0.833	3.139
4,4'-DICHLOROBIPHENYL	-1.240	0.283	1.373
4-MONOCHLOROBIPHENYL	-0.530	0.020	1.409
9,10-DIPHENYLANTHRACENE	-2.950	1.481	0.366
ACENAPHTHENE	-0.710	0.021	0.180
ANTHRACENE	-1.910	0.023	0.306
BENZO[A]PYRENE	-1.626	1.890	0.393
BIPHENYL	-0.450	0.064	0.289
CHRYSENE	-2.300	0.080	0.377
FLUORENE	-0.910	0.170	0.251
HEXABROMOBENZENE	-2.810	3.851	0.000
HEXACHLOROBENZENE	-2.040	4.337	-2.885
NAPHTHALENE	-0.550	0.031	0.235
NAPHTHACENE	-3.866	1.657	0.265
PENTACHLOROBENZENE	-0.600	2.721	0.844
PERYLENE	-3.320	0.620	0.393
PHENANTHRENE	-0.760	0.023	0.306
PYRENE	-1.310	0.362	0.322

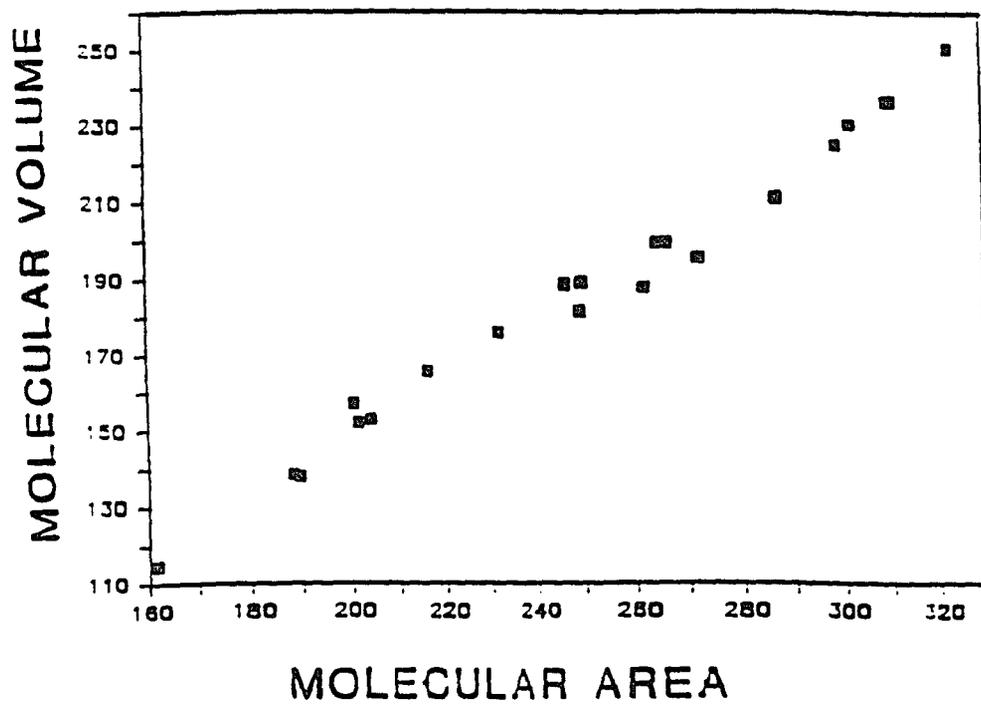


Figure 5.1: Plot of molecular volume and surface area for all the solutes obtained from CHEMLAB.

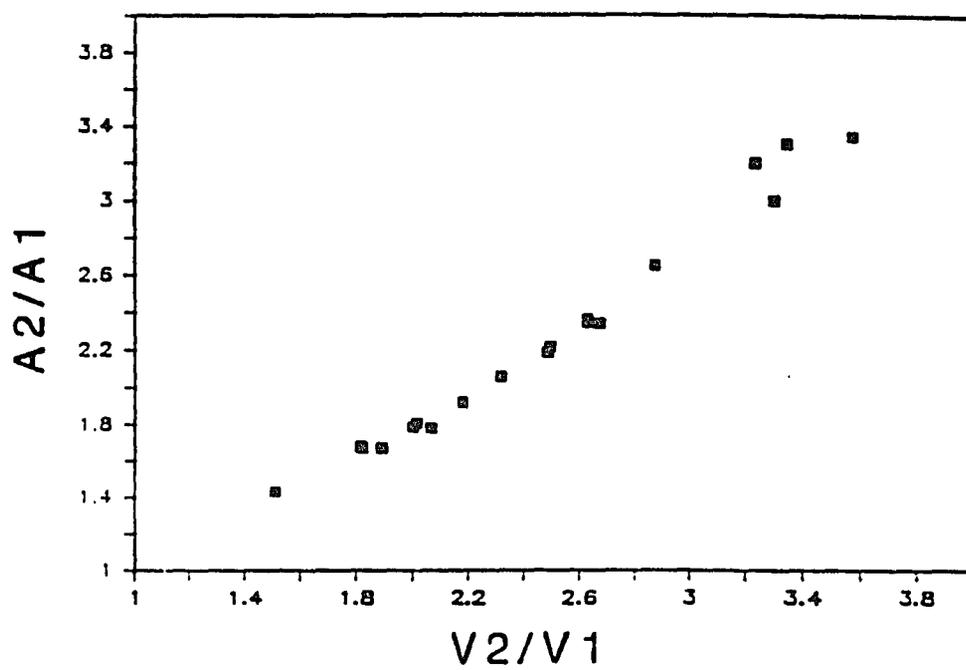


Figure 5.2: Plot of the ratio of molecular volume (V_2/V_1) vs ratio of molecular surface area (A_2/A_1).

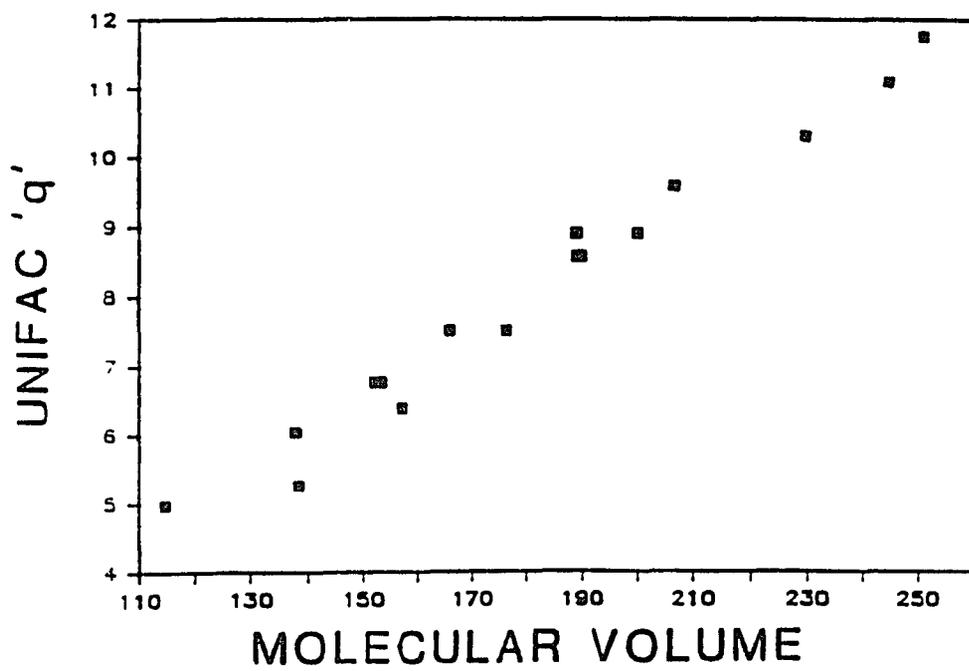


Figure 5.3: Molecular volume (CHEMLAB) vs UNIFAC volume parameter "q".

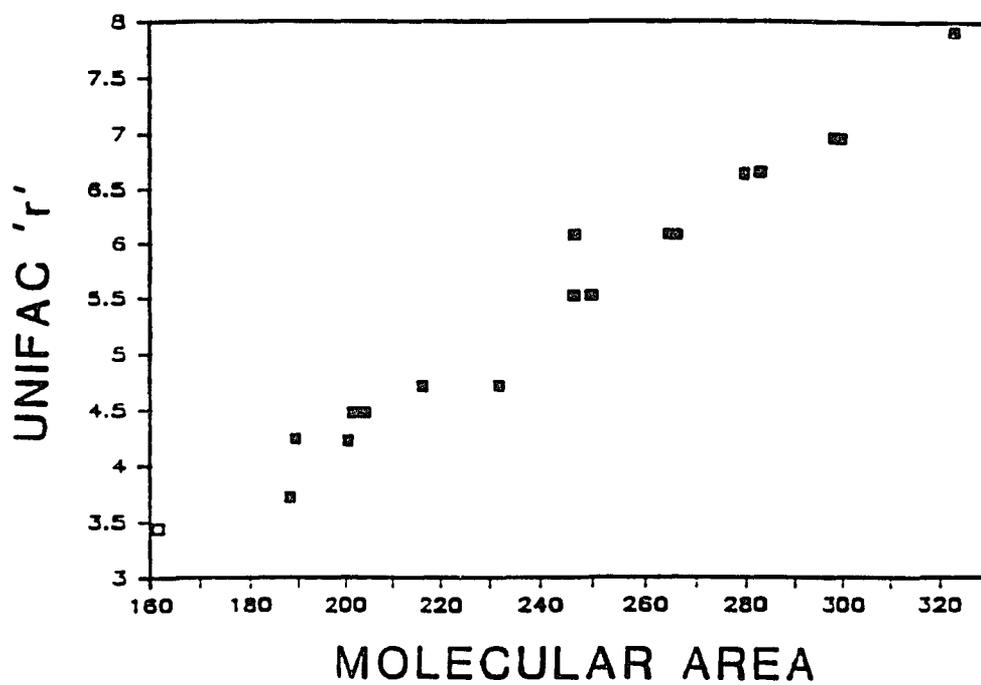


Figure 5.4: Molecular surface area (CHEMLAB) vs UNIFAC area parameter "r".

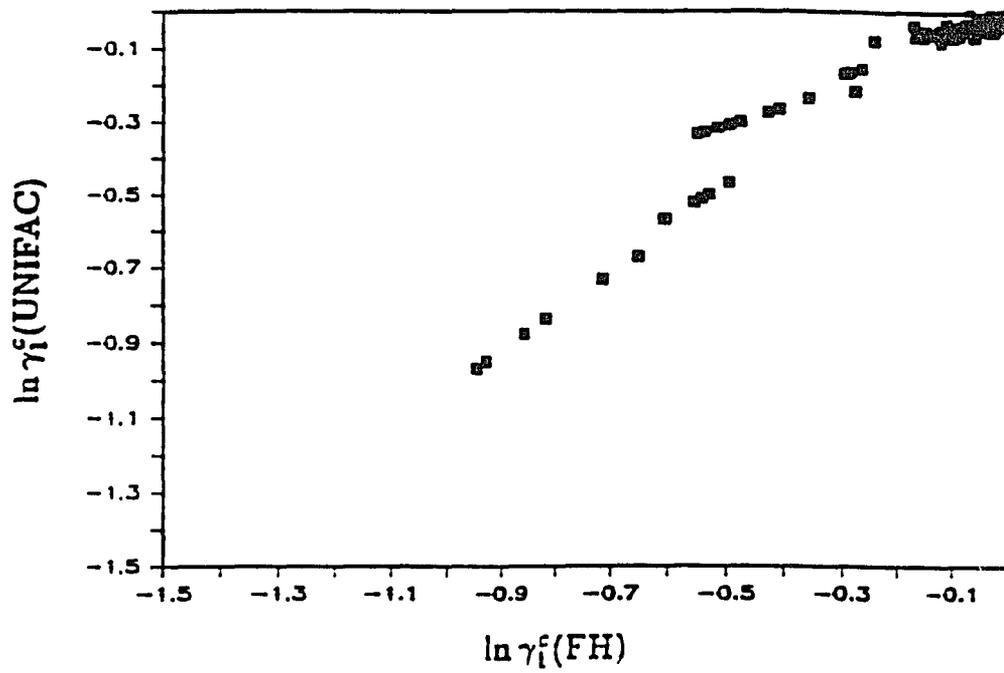


Figure 5.5: Plot of combinatorial activity coefficient of the solutes in benzene from the Flory-Huggins and UNIFAC models.

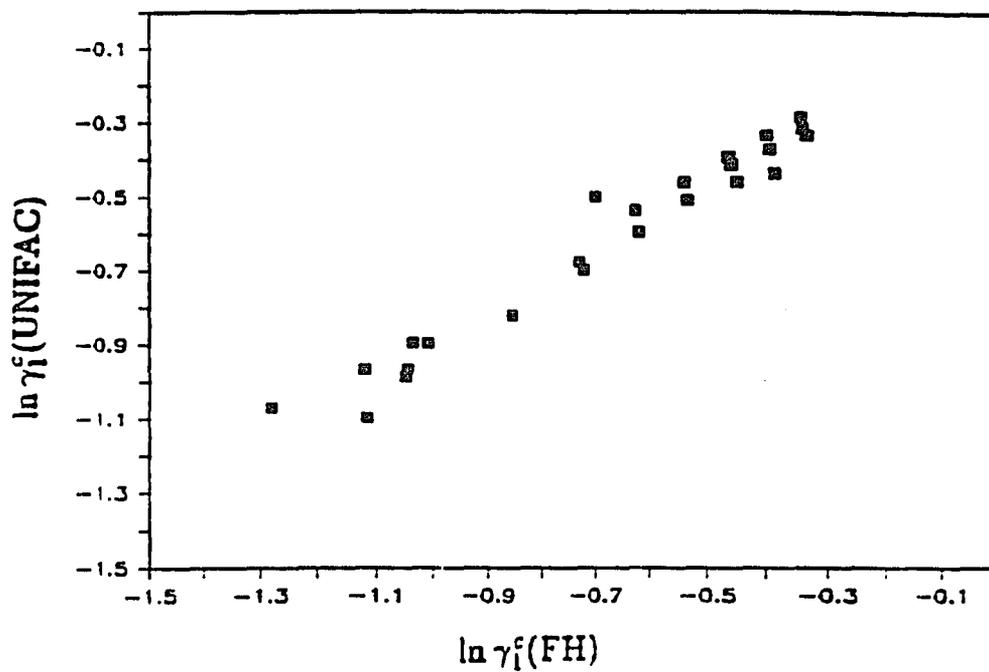


Figure 5.6: Plot of combinatorial activity coefficient of the solutes in triolein from the Flory-Huggins and UNIFAC models.

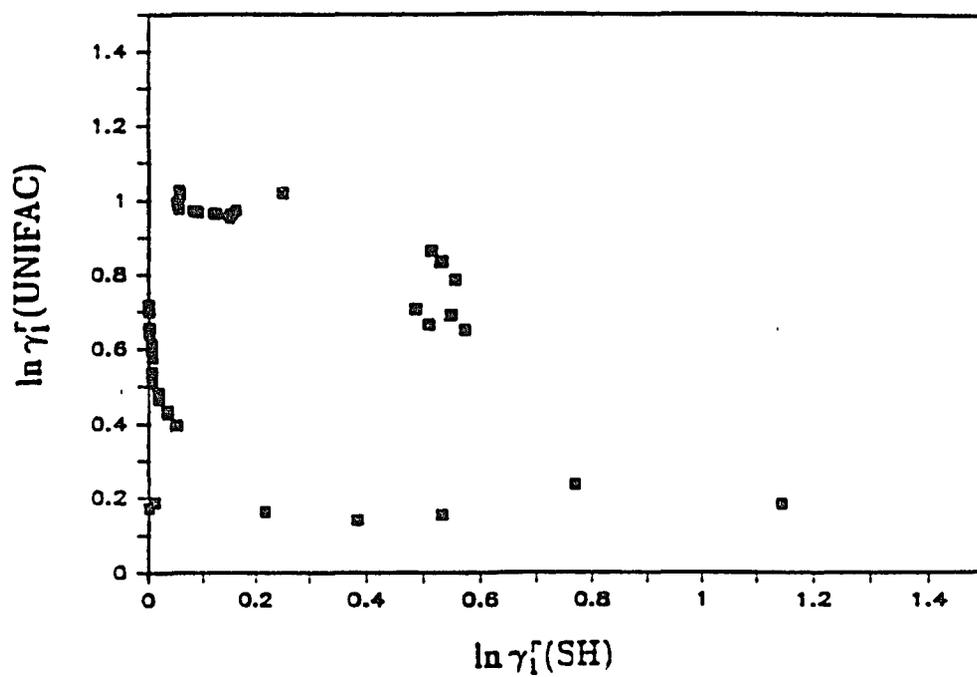


Figure 5.7: Residual activity coefficient of the solutes in triolein from the Scatchard-Hildebrand and UNIFAC models.

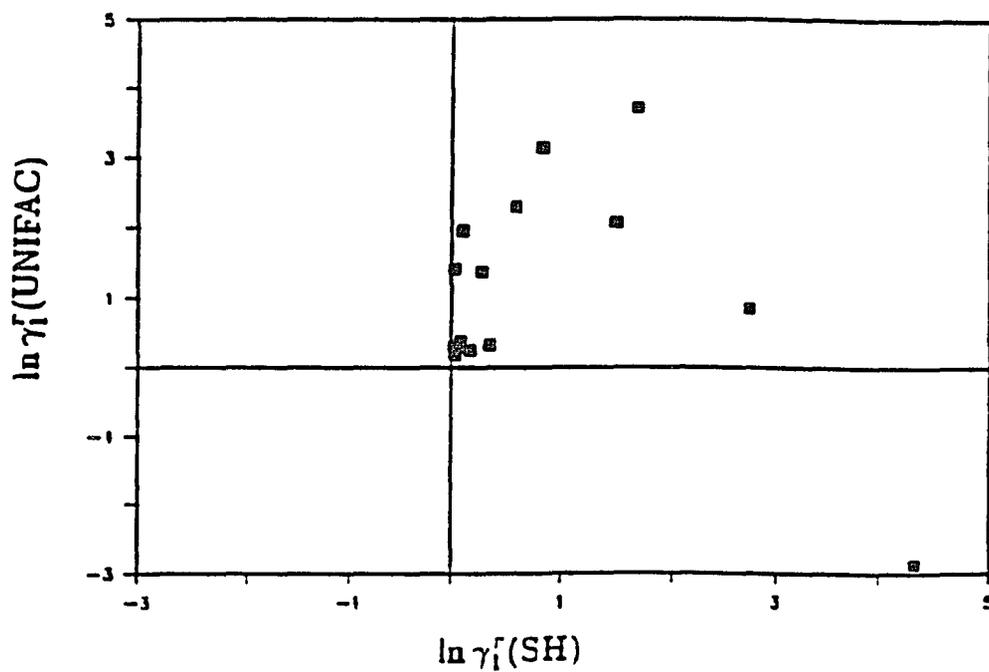


Figure 5.8: Residual activity coefficient of the solutes in n-octanol from the Scatchard-Hildebrand and UNIFAC models.

PREDICTION OF SOLUBILITY

In an earlier part of this chapter we discussed the different models for the activity coefficient and their comparisons. For the prediction of solubility the following information is needed: ideal solubility, combinatorial activity coefficient and residual activity coefficient.

PREDICTION COEFFICIENT

To select the best model in the three systems we studied we use the prediction coefficient (P^2) which is defined by the following equation:

$$P^2 = 1 - \frac{\sum_i (X_{\text{obs}} - X_{\text{pred}})^2}{\sum_i (X_{\text{obs}} - \bar{X})^2} \quad (5.9)$$

where X_{obs} , X_{pred} are the observed and predicted solubilities and \bar{X} is the mean of the observed solubility. The way to interpret the prediction coefficient is as follows:

(1) if $X_{\text{obs}} \approx X_{\text{pred}}$ then the second term is zero and the prediction coefficient is unity. Thus if a model gives

perfect prediction the prediction coefficient will be unity.

(2) if $(X_{\text{obs}} - X_{\text{pred}}) \ll (X_{\text{obs}} - \bar{X})$ then the prediction coefficient will be close to unity. Thus the model which gives prediction coefficient closer to unity is the better model.

(3) if $(X_{\text{obs}} - X_{\text{pred}}) \gg (X_{\text{obs}} - \bar{X})$ then the prediction coefficient will be less than zero. This suggests that the model is in fact very bad and it would be better to use the average value of the property as the estimate.

SOLUBILITY

The following general equation can be written for the solubility:

$$\ln X_1 = \ln X_1^i + \ln \gamma (\text{comb.}) + \ln \gamma (\text{resid.}) \quad (5.8)$$

For each of the components of the solubility i.e. ideal solubility, combinatorial activity coefficient, residual activity coefficient, we have two approximations or models. This gives a total of eight different models for the calculation of solubility.

PREDICTIONS FROM THE MODELS

The different models used in the study are shown in Table 5.7. The solubility values were calculated from the eight models considered and are listed in Tables 5.8-5.10 for all the systems. Figures 5.9-5.24 show the plots of the observed solubility versus the predicted solubility from the different models.

It is important to note that none of the predictions described below use any adjustable parameters. All calculations are based upon the equations described above.

IDEAL SOLUBILITY

The ideal solubility was discussed in chapter 2 in detail. The calculation of ideal solubility involves the melting properties of the solute. Specifically the parameters required are: melting point, entropy of fusion, and the heat capacity change on melting. Melting point is one of first properties measured whenever a compound is synthesized. Thus the melting point of a compound is almost always known. The entropy of fusion is determined by measuring the heat of fusion and the melting point. Alternatively it can be calculated using the theoretical model for the melting process (Yalkowsky, 1979). The

parameter which is most difficult to obtain from the literature as well as to measure is the heat capacity change on melting (Finke, 1977; Casellato, 1973). Some approximations have been introduced which simplify the equation for the ideal solubility in such a way that the heat capacity is not required for the calculation. The two approximations which were used were introduced in chapter 2. The two approximations lead to the following equations for the ideal solubility;

Approximation 1: ΔC_p term is negligible leads to,

$$\ln X_1^i = \frac{\Delta S_f}{R} \left[\frac{T_m - T}{T} \right] \quad (5.6)$$

Approximation 2: $\Delta C_p = \Delta S_f$ leads to,

$$\ln X_1^i = \frac{\Delta S_f}{R} \left[\ln \frac{T_m}{T} \right] \quad (5.7)$$

The above approximations reduce the ideal solubility equation such that only entropy of fusion and melting point are needed for the calculation. Both the equations were used in the study to calculate the ideal solubility. Predictions

based on both calculation were compared and the model which gives the best representation of the data was taken to be the superior model.

In nearly every case the odd numbered model is equivalent to or better than the even numbered model immediately below it (see Table 5.11). This indicates that the models based upon equation 5.6 for ideal solubility (ΔC_p term is negligible), consistently gives better prediction than models based on equation 5.7 ($\Delta C_p = \Delta S_f$), for all the systems studied.

BENZENE

The prediction of solubility of polycyclic aromatic hydrocarbons in benzene is very interesting. The best model is the one using the ideal solubility which ignores the terms involving heat capacity terms, Flory-Huggins for the combinatorial activity coefficient and Scatchard-Hildebrand for the residual activity coefficient (see figure 5.9). The prediction coefficient value for this model is 0.96. The UNIFAC combinatorial activity coefficient is almost identical to the Flory-Huggins combinatorial activity coefficient. Thus model 1 and 7 are equivalent. This is seen in the prediction coefficient value for model 7 which is

0.97. Figure 5.21 gives the predicted solubility versus the experimental solubility for model 7.

In the case of the combined Flory-Huggins and Scatchard-Hildebrand theories for activity coefficient, the total logarithm of activity coefficient is close to zero. The Flory-Huggins combinatorial activity coefficient predicts a negative deviation, and Scatchard-Hildebrand residual activity coefficient predicts a positive deviation. In most cases the activity coefficients cancel, thus accounting for the ideal behavior.

The UNIFAC model for activity coefficient predicts negative deviation from ideal solubility mostly arising from negative combinatorial activity coefficient. The residual activity coefficient is unity in almost all the cases. The real case however is that the polycyclic aromatic hydrocarbons behave very close to ideality in benzene whereas the UNIFAC model predicts a negative deviation from ideality.

The prediction coefficient values for models 3 and 4 which use UNIFAC models for both the combinatorial and residual are 0.86 and 0.71 respectively. These models give relatively poor predictions is seen from figures 5.13 and

5.15.

OCTANOL

In the case of solubility in octanol, model 1 and 7 are the best models as in benzene. This is to be expected as the Flory-Huggins combinatorial and UNIFAC combinatorial activity coefficients are almost identical. Other models like the total UNIFAC do not represent the data very well. This is seen in figures 5.11, 5.13, 5.15, 5.17 and 5.19. The prediction coefficient values for these models are much lower compared to models 1 and 7 which are the best models.

TRIOLEIN

In triolein the solutes were separated into two groups: non H-bonding solutes and H-bonding solutes. This was done as two different trends were observed for these solutes. Also the models we have used in the present study are not applicable for molecules which undergo specific chemical interactions like H-bonding. Thus it is expected that the models considered will give poor results in H-bonding solutes.

In the case of non H-bonding solutes the best models once again are 1 and 7. The reason for this once again is

the similarity in Flory-Huggins and UNIFAC combinatorial activity coefficients. Figures 5.10 and 5.22 show plots of observed solubility versus the predicted solubility from models 1 and 7. Other models give relatively poor results as is seen from figures 5.12, 5.14, 5.16, 5.18, 5.20 and 5.24. The prediction coefficient values for the different models are given in Table 5.11.

The prediction of solubility of H-bonding solutes were very poor from all the models considered in this study. Since H-bonding is a specific chemical interaction theory like Scatchard-Hildebrand is not appropriate for the reasons mentioned earlier in the activity coefficient section. The prediction coefficient values for all the models are negative (see Table 5.11). Figures 5.10, 5.12, 5.14, 5.16, 5.18, 5.20, and 5.22 give the plots of observed solubility versus predicted solubility from the different models. Thus all the models fail to describe the solubility of H-bonding solutes in triolein.

ALL SYSTEMS

Models 1 and 7 are the best models in all the systems considered except in the case of H-bonding solutes in triolein. The difference between the two models is the

combinatorial activity coefficient. The model 1 is based on the Flory-Huggins model which is simpler than the UNIFAC combinatorial (model 7). Thus from this study it is clear that in the systems considered in this study the best and the simplest method of predicting solubility is by using the equations from model 1.

TABLE 5.7

Different models considered in the study.

MODEL	IDEAL SOLUBILITY	COMBINATORIAL ^a	RESIDUAL ^b
1	$\Delta C_p = 0$	FH	SH
2	$\Delta C_p = \Delta S_f$	FH	SH
3	$\Delta C_p = 0$	UNIFAC	UNIFAC
4	$\Delta C_p = \Delta S_f$	UNIFAC	UNIFAC
5	$\Delta C_p = 0$	FH	UNIFAC
6	$\Delta C_p = \Delta S_f$	FH	UNIFAC
7	$\Delta C_p = 0$	UNIFAC	SH
8	$\Delta C_p = \Delta S_f$	UNIFAC	SH

a FH is the Flory-Huggins activity coefficient.

b SH is the Scatchard-Hildebrand activity coefficient.

Table 5.8

Solubility predictions from different models for the solutes in benzene.

NAME	TEMP	LN χ _{OB}	MODEL 1	MODEL 2	MODEL 3	MODEL 4	MODEL 5	MODEL 6	MODEL 7	MODEL 8
1,3,5-TRIPHENYLBENZENE	25.2	-3.51	-3.73	-3.08	-2.46	-1.81	-2.48	-1.83	-3.71	-3.06
1,3,5-TRIPHENYLBENZENE	28.6	-3.35	-3.59	-2.98	-2.36	-1.75	-2.38	-1.77	-3.57	-2.96
1,3,5-TRIPHENYLBENZENE	40.4	-3.03	-3.12	-2.62	-2.05	-1.56	-2.07	-1.58	-3.10	-2.61
1,3,5-TRIPHENYLBENZENE	46.2	-2.88	-2.90	-2.46	-1.91	-1.47	-1.93	-1.49	-2.88	-2.44
1,3,5-TRIPHENYLBENZENE	59.4	-2.53	-2.43	-2.09	-1.64	-1.30	-1.66	-1.32	-2.42	-2.08
1,3,5-TRIPHENYLBENZENE ‡	66.6	-2.34	-2.20	-1.91	-1.51	-1.22	-1.52	-1.23	-2.18	-1.89
9,10-DIPHENYLANTHRACENE ‡	23.0	-3.56	-3.16	-3.80	-1.72	-2.36	-1.60	-2.23	-3.28	-3.92
ACENAPHTHALENE	30.6	-1.71	-1.49	-1.36	-1.37	-1.24	-1.32	-1.19	-1.53	-1.40
ACENAPHTHALENE	41.4	-1.37	-1.18	-1.09	-1.11	-1.02	-1.07	-0.99	-1.21	-1.13
ACENAPHTHALENE	63.2	-0.75	-0.63	-0.61	-0.61	-0.58	-0.60	-0.57	-0.65	-0.62
ACENAPHTHALENE	69.4	-0.59	-0.49	-0.48	-0.48	-0.46	-0.47	-0.46	-0.50	-0.49
ANTHRACENE	35.8	-4.58	-4.72	-3.84	-3.99	-3.11	-3.86	-2.98	-4.85	-3.97
ANTHRACENE	42.4	-4.34	-4.46	-3.66	-3.75	-2.96	-3.63	-2.83	-4.59	-3.79
ANTHRACENE	50.6	-4.06	-4.14	-3.45	-3.48	-2.78	-3.35	-2.65	-4.27	-3.57
ANTHRACENE	59.6	-3.79	-3.81	-3.21	-3.13	-2.53	-3.07	-2.47	-3.88	-3.27
ANTHRACENE ‡	70.2	-3.46	-3.44	-2.94	-2.87	-2.37	-2.76	-2.25	-3.56	-3.05
BENZ[<i>a</i>]PYRENE ‡	23.0	-3.34	-3.65	-3.55	-0.87	-0.77	-0.93	-0.83	-3.59	-3.49
BIPHENYL	37.0	-0.67	-0.68	-0.65	-0.65	-0.61	-0.64	-0.61	-0.68	-0.65
BIPHENYL	47.6	-0.43	-0.44	-0.42	-0.42	-0.41	-0.42	-0.41	-0.44	-0.42
BIPHENYL	59.2	-0.20	-0.19	-0.19	-0.16	-0.16	-0.19	-0.19	-0.16	-0.16
BIPHENYL	63.2	-0.11	-0.11	-0.11	-0.10	-0.10	-0.11	-0.11	-0.10	-0.10
BIPHENYL	34.8	-0.73	-0.73	-0.70	-0.69	-0.66	-0.69	-0.65	-0.73	-0.70
BIPHENYL	40.7	-0.59	-0.59	-0.57	-0.57	-0.54	-0.57	-0.54	-0.59	-0.57
BIPHENYL	43.7	-0.52	-0.52	-0.50	-0.50	-0.48	-0.50	-0.48	-0.53	-0.51

‡ Solubility determined in this work.

Table 5.8 (continued)

NAME	TEMP	LN χ _{OB}	MODEL 1	MODEL 2	MODEL 3	MODEL 4	MODEL 5	MODEL 6	MODEL 7	MODEL 8
BIPHENYL	50.5	-0.37	-0.37	-0.36	-0.36	-0.35	-0.36	-0.35	-0.38	-0.36
BIPHENYL	55.8	-0.26	-0.26	-0.26	-0.26	-0.25	-0.26	-0.25	-0.26	-0.26
BIPHENYL	60.0	-0.17	-0.18	-0.17	-0.15	-0.15	-0.17	-0.17	-0.15	-0.15
CHRYSENE	35.6	-6.17	-5.36	-4.30	-3.95	-2.89	-3.73	-2.67	-5.58	-4.52
CHRYSENE	45.8	-5.74	-4.95	-4.03	-3.63	-2.70	-3.41	-2.49	-5.16	-4.24
CHRYSENE	60.6	-5.26	-4.39	-3.64	-3.20	-2.44	-3.00	-2.24	-4.59	-3.84
CHRYSENE	72.2	-4.84	-3.97	-3.34	-2.89	-2.25	-2.70	-2.06	-4.16	-3.53
FLUORANTHENE	44.8	-1.53	-1.08	-0.98	-1.14	-1.03	-1.04	-0.93	-1.18	-1.08
FLUORANTHENE	56.0	-1.20	-0.87	-0.80	-0.91	-0.84	-0.84	-0.77	-0.93	-0.87
FLUORANTHENE	64.4	-0.96	-0.72	-0.67	-0.74	-0.70	-0.70	-0.65	-0.76	-0.72
FLUORANTHENE	77.2	-0.63	-0.50	-0.47	-0.51	-0.49	-0.49	-0.47	-0.52	-0.50
FLUORENE	33.6	-1.83	-1.40	-1.24	-1.43	-1.27	-1.34	-1.18	-1.49	-1.33
FLUORENE	54.4	-1.28	-0.97	-0.89	-0.99	-0.91	-0.94	-0.86	-1.02	-0.94
FLUORENE	58.4	-1.17	-0.89	-0.82	-0.91	-0.84	-0.87	-0.80	-0.94	-0.87
FLUORENE	69.4	-0.90	-0.69	-0.65	-0.70	-0.66	-0.68	-0.63	-0.72	-0.68
FLUORENE	72.8	-0.82	-0.63	-0.60	-0.64	-0.61	-0.62	-0.58	-0.65	-0.62
FLUORENE	34.6	-1.79	-1.38	-1.22	-1.41	-1.25	-1.32	-1.16	-1.47	-1.31
FLUORENE	40.3	-1.63	-1.25	-1.12	-1.28	-1.15	-1.21	-1.07	-1.33	-1.20
FLUORENE	45.0	-1.51	-1.16	-1.04	-1.18	-1.07	-1.12	-1.00	-1.22	-1.11
FLUORENE	49.9	-1.38	-1.06	-0.96	-1.08	-0.98	-1.02	-0.93	-1.11	-1.02
FLUORENE	57.3	-1.19	-0.91	-0.84	-0.93	-0.86	-0.89	-0.81	-0.96	-0.89
FLUORENE	63.1	-1.04	-0.80	-0.75	-0.85	-0.79	-0.78	-0.73	-0.87	-0.81
FLUORENE	67.5	-0.93	-0.72	-0.68	-0.74	-0.69	-0.71	-0.66	-0.75	-0.71
FLUORENE	75.2	-0.75	-0.59	-0.56	-0.60	-0.57	-0.58	-0.55	-0.61	-0.58
FLUORENE	81.7	-0.60	-0.48	-0.46	-0.49	-0.47	-0.47	-0.45	-0.49	-0.47

‡ Solubility determined in this work.

Table 5.8 (continued)

NAME	TEMP	LN χ _{OB}	MODEL 1	MODEL 2	MODEL 3	MODEL 4	MODEL 5	MODEL 6	MODEL 7	MODEL 8
M-TERPHENYL	36.8	-1.26	-1.01	-0.93	-1.07	-0.99	-0.93	-0.85	-1.15	-1.07
M-TERPHENYL	47.0	-0.96	-0.79	-0.74	-0.82	-0.77	-0.74	-0.69	-0.87	-0.82
M-TERPHENYL	60.8	-0.60	-0.50	-0.48	-0.52	-0.50	-0.49	-0.47	-0.54	-0.52
M-TERPHENYL	67.4	-0.45	-0.37	-0.36	-0.38	-0.37	-0.37	-0.35	-0.39	-0.38
M-TERPHENYL	74.2	-0.28	-0.24	-0.24	-0.25	-0.24	-0.24	-0.24	-0.25	-0.25
M-TERPHENYL	77.6	-0.18	-0.18	-0.18	-0.18	-0.18	-0.18	-0.17	-0.18	-0.18
NAPHTHALENE	35.0	-0.98	-0.99	-0.92	-0.94	-0.87	-0.91	-0.85	-1.01	-0.95
NAPHTHALENE	45.0	-0.73	-0.74	-0.70	-0.68	-0.64	-0.69	-0.65	-0.72	-0.69
NAPHTHALENE	47.4	-0.67	-0.68	-0.65	-0.63	-0.60	-0.64	-0.61	-0.67	-0.64
NAPHTHALENE	63.2	-0.34	-0.33	-0.32	-0.32	-0.31	-0.32	-0.31	-0.33	-0.32
NAPHTHALENE	75.8	-0.09	-0.08	-0.08	-0.08	-0.08	-0.08	-0.08	-0.08	-0.08
NAPHTHALENE	37.2	-0.93	-0.93	-0.87	-0.84	-0.79	-0.86	-0.81	-0.91	-0.85
NAPHTHALENE	42.4	-0.80	-0.80	-0.76	-0.73	-0.69	-0.75	-0.70	-0.78	-0.74
NAPHTHALENE	50.3	-0.62	-0.61	-0.59	-0.57	-0.54	-0.58	-0.55	-0.60	-0.58
NAPHTHALENE	61.2	-0.37	-0.37	-0.36	-0.35	-0.34	-0.36	-0.35	-0.37	-0.36
NAPHTHALENE	71.0	-0.17	-0.17	-0.17	-0.17	-0.17	-0.17	-0.17	-0.17	-0.17
NAPHTHACENE [‡]	23.0	-4.25	-4.94	-6.53	-3.23	-4.83	-3.27	-4.86	-4.91	-6.47
O-TERPHENYL	28.0	-0.54	-0.60	-0.57	-0.57	-0.54	-0.57	-0.55	-0.60	-0.57
O-TERPHENYL	32.4	-0.44	-0.50	-0.48	-0.48	-0.46	-0.48	-0.46	-0.50	-0.48
O-TERPHENYL	44.8	-0.21	-0.23	-0.23	-0.23	-0.23	-0.23	-0.23	-0.23	-0.23
O-TERPHENYL	50.4	-0.10	-0.12	-0.12	-0.12	-0.11	-0.12	-0.11	-0.12	-0.12
P-TERPHENYL	38.0	-4.95	-3.98	-3.19	-3.27	-2.48	-3.23	-2.44	-4.02	-3.23
P-TERPHENYL	60.2	-4.16	-3.20	-2.64	-2.61	-2.05	-2.57	-2.02	-3.23	-2.68
P-TERPHENYL	64.2	-4.03	-3.07	-2.55	-2.50	-1.98	-2.47	-1.95	-3.10	-2.58
P-TERPHENYL	68.0	-3.89	-2.95	-2.46	-2.40	-1.92	-2.37	-1.88	-2.98	-2.49

[‡] Solubility determined in this work.

Table 5.8 (continued)

NAME	TEMP	LN χ _{OB}	MODEL 1	MODEL 2	MODEL 3	MODEL 4	MODEL 5	MODEL 6	MODEL 7	MODEL 8
P-TERPHEYL	77.6	-3.58	-2.65	-2.25	-2.17	-1.76	-2.14	-1.73	-2.68	-2.28
PERYLENE [‡]	23.0	-3.23	-2.98	-4.12	-3.43	-3.56	-2.41	-3.53	-3.01	-4.13
PHENANTHRENE	32.0	-1.50	-1.52	-1.39	-1.25	-1.12	-1.21	-1.08	-1.57	-1.44
PHENANTHRENE	40.0	-1.26	-1.28	-1.19	-1.08	-0.98	-1.04	-0.95	-1.32	-1.22
PHENANTHRENE	41.8	-1.21	-1.23	-1.14	-1.04	-0.95	-1.01	-0.92	-1.27	-1.18
PHENANTHRENE	50.2	-0.98	-1.00	-0.94	-0.87	-0.80	-0.84	-0.78	-1.03	-0.96
PHENANTHRENE	58.0	-0.78	-0.81	-0.77	-0.72	-0.67	-0.70	-0.66	-0.83	-0.78
PHENANTHRENE	39.6	-1.27	-1.30	-1.20	-1.09	-0.99	-1.05	-0.95	-1.33	-1.23
PHENANTHRENE	43.6	-1.16	-1.18	-1.10	-1.00	-0.92	-0.97	-0.89	-1.21	-1.13
PHENANTHRENE	52.1	-0.93	-0.96	-0.90	-0.83	-0.77	-0.81	-0.75	-0.98	-0.92
PHENANTHRENE	61.6	-0.70	-0.72	-0.69	-0.65	-0.61	-0.63	-0.60	-0.74	-0.70
PHENANTHRENE	68.7	-0.55	-0.57	-0.54	-0.52	-0.49	-0.51	-0.49	-0.57	-0.55
PHENANTHRENE	69.0	-0.55	-0.56	-0.54	-0.51	-0.49	-0.50	-0.48	-0.57	-0.55
PYRENE	32.4	-2.61	-2.75	-2.43	-1.89	-1.58	-1.73	-1.41	-2.91	-2.60
PYRENE	58.6	-1.89	-1.87	-1.69	-1.37	-1.19	-1.26	-1.08	-1.97	-1.80
PYRENE	66.8	-1.66	-1.63	-1.48	-1.22	-1.08	-1.13	-0.99	-1.72	-1.57
PYRENE	76.2	-1.41	-1.38	-1.27	-1.06	-0.95	-0.99	-0.88	-1.45	-1.34
PYRENE	84.6	-1.20	-1.17	-1.08	-0.93	-0.85	-0.88	-0.79	-1.23	-1.14
TRIPHENYLENE	39.4	-4.27	-4.20	-3.57	-2.98	-2.34	-2.79	-2.15	-4.39	-3.76
TRIPHENYLENE	47.6	-4.01	-3.87	-3.32	-2.74	-2.19	-2.56	-2.01	-4.05	-3.50
TRIPHENYLENE	63.8	-3.54	-3.24	-2.83	-2.31	-1.90	-2.15	-1.74	-3.40	-2.99
TRIPHENYLENE	69.4	-3.38	-3.04	-2.67	-2.17	-1.80	-2.03	-1.65	-3.19	-2.81
TRIPHENYLENE	82.8	-3.00	-2.57	-2.28	-1.87	-1.58	-1.74	-1.46	-2.70	-2.41

[‡] Solubility determined in this work.

Table 5.9

Solubility predictions from different models for solutes in triolein.

NAME	TEMP	LN _X OB	MODEL 1	MODEL 2	MODEL 3	MODEL 4	MODEL 5	MODEL 6	MODEL 7	MODEL 8
2,3-DIMETHYL NAPHTHALENE	23.0	-0.51	-1.16	-0.94	-1.33	-1.11	-1.03	-0.81	-1.15	-0.93
2,6-DIMETHYL NAPHTHALENE [‡]	23.0	-0.63	-1.23	-1.00	-1.40	-1.16	-1.10	-0.86	-1.22	-0.99
9,10-DIPHENYLANTHRACENE [‡]	23.0	-3.95	-4.75	-5.41	-2.38	-3.01	-2.63	-3.27	-4.51	-5.15
ACENAPHTHALENE [‡]	23.0	-0.43	-1.25	-1.22	-1.22	-1.05	-0.67	-0.51	-1.60	-1.43
BENZ[<i>a</i>]PYRENE [‡]	23.0	-3.12	-3.84	-3.74	-0.95	-0.86	-1.08	-0.99	-3.71	-3.61
BIPHENYL	23.0	-0.27	-0.32	-0.25	-0.41	-0.34	-0.07	-0.00	-0.24	-0.17
DOCOSANE	14.0	-1.77	-2.14	-2.04	-2.43	-2.33	-2.43	-2.33	-2.19	-2.10
DOCOSANE	27.0	-1.24	-1.22	-1.19	-1.58	-1.55	-1.58	-1.55	-1.28	-1.25
DOCOSANE	37.0	-0.58	-0.57	-0.56	-0.98	-0.97	-0.98	-0.97	-0.62	-0.62
EICOSANE	14.0	-0.95	-2.27	-2.19	-2.39	-2.31	-2.44	-2.36	-2.24	-2.15
EICOSANE	27.0	-0.64	-0.98	-0.96	-1.16	-1.14	-1.21	-1.19	-0.94	-0.93
FLUBRENE	23.0	-0.47	-1.00	-0.77	-1.44	-1.21	-0.92	-0.69	-1.49	-1.27
NAPHTHELENE	23.0	-0.25	-0.32	-0.36	-0.43	-0.33	-0.10	0.01	-0.67	-0.57
OCTADECANE	14.0	-0.61	-1.19	-1.17	-1.34	-1.31	-1.35	-1.32	-1.26	-1.23
OCTADECANE	27.0	-0.13	-0.12	-0.12	-0.32	-0.32	-0.33	-0.33	-0.18	-0.18
PERLYENE	23.0	-2.19	-3.50	-4.50	-5.67	-4.02	-5.47	-3.82	-6.20	-4.55
PHENANTHRENE	23.0	-0.47	-1.68	-1.50	-1.33	-1.15	-0.70	-0.53	-2.29	-2.12
DOCOSANOL	27.0	-1.48	-5.32	-4.83	-4.87	-4.59	-4.81	-4.53	-3.91	-3.63
DOCOSANOL	37.0	-1.36	-3.85	-3.58	-3.83	-3.67	-3.77	-3.62	-2.86	-2.70
DODECANOL	14.0	-0.51	-0.07	-0.07	-0.89	-0.88	-0.83	-0.82	-0.12	-0.11
EICOSANOL	14.0	-1.85	-4.30	-3.93	-5.26	-4.89	-5.19	-4.82	-4.33	-3.96
EICOSANOL	27.0	-1.23	-2.98	-2.78	-3.95	-3.76	-3.89	-3.69	-3.01	-2.82
EICOSANOL	37.0	-1.03	-2.04	-1.93	-3.02	-2.92	-2.95	-2.85	-2.07	-1.97
HEXADECANOL	14.0	-1.08	-1.94	-1.81	-2.84	-2.71	-2.76	-2.63	-2.00	-1.87
HEXADECANOL	27.0	-0.82	-1.03	-0.97	-1.93	-1.88	-1.85	-1.80	-1.09	-1.04

[‡] Solubility determined in this work.

Table 5.9 (continued)

NAME	TEMP	LNXOB	MODEL 1	MODEL 2	MODEL 3	MODEL 4	MODEL 5	MODEL 6	MODEL 7	MODEL 8
OCTADECANOL	14.0	-1.60	-3.24	-2.99	-4.17	-3.92	-4.10	-3.84	-3.29	-3.04
OCTADECANOL	27.0	-1.13	-2.07	-1.96	-3.01	-2.89	-2.94	-2.82	-2.12	-2.00
OCTADECANOL	37.0	-0.77	-1.24	-1.19	-2.18	-2.13	-2.11	-2.06	-1.29	-1.24
TETRADECANOL	14.0	-0.89	-1.09	-1.03	-1.96	-1.90	-1.87	-1.81	-1.14	-1.08
TETRADECANOL	27.0	-0.35	-0.22	-0.21	-1.09	-1.08	-1.00	-0.99	-0.28	-0.27
TETRADECANOL	37.0	-0.05	-0.39	-0.39	-0.48	-0.48	-0.38	-0.38	0.33	0.33
DECANOIC ACID	14.0	-0.36	-0.30	-0.32	-0.27	-0.25	-0.24	-0.22	0.07	0.09
DECANOIC ACID	27.0	-0.06	-0.25	-0.27	-0.24	-0.24	-0.27	-0.27	-0.59	0.59
DODECANOIC ACID	27.0	-1.74	-4.41	-4.03	-5.13	-4.75	-5.11	-4.73	-4.43	-4.05
DODECANOIC ACID	37.0	-1.57	-3.39	-3.15	-4.13	-3.89	-4.10	-3.87	-3.41	-3.17
DODECANOIC ACID	14.0	-0.79	-0.74	-0.67	-1.14	-1.07	-1.12	-1.05	-0.75	-0.68
DODECANOIC ACID	27.0	-0.38	-0.07	-0.05	-0.48	-0.46	-0.46	-0.44	-0.08	-0.06
DODECANOIC ACID	37.0	-0.13	-0.40	-0.40	-0.01	-0.01	0.01	0.02	0.39	0.39
EICOSANOIC ACID	27.0	-1.62	-3.57	-3.29	-4.24	-3.95	-4.21	-3.92	-3.60	-3.31
EICOSANOIC ACID	37.0	-1.54	-2.65	-2.48	-3.33	-3.15	-3.30	-3.13	-2.67	-2.50
HEXADECANOIC ACID	14.0	-1.59	-2.74	-2.49	-3.26	-3.01	-3.23	-2.99	-2.75	-2.51
HEXADECANOIC ACID	27.0	-1.25	-1.75	-1.63	-2.29	-2.16	-2.26	-2.14	-1.76	-1.64
HEXADECANOIC ACID	37.0	-0.85	-1.04	-0.99	-1.59	-1.53	-1.57	-1.51	-1.06	-1.00
NAPHTHACENE [‡]	23.0	-4.02	-4.72	-7.51	-3.38	-4.97	-3.20	-4.79	-6.08	-7.65
OCTADECANOIC ACID	14.0	-1.89	-3.36	-3.03	-3.97	-3.65	-3.93	-3.60	-3.40	-3.08
OCTADECANOIC ACID	27.0	-1.49	-2.33	-2.15	-2.97	-2.79	-2.92	-2.74	-2.37	-2.20
OCTADECANOIC ACID	37.0	-1.19	-1.59	-1.50	-2.24	-2.15	-2.20	-2.10	-1.64	-1.54
PERYLENE [‡]	23.0	-3.45	-4.05	-5.17	-3.04	-4.17	-2.87	-3.99	-4.23	-5.35
TETRADECANOIC ACID	14.0	-1.08	-1.73	-1.58	-2.19	-2.04	-2.16	-2.01	-1.74	-1.59
TETRADECANOIC ACID	27.0	-0.80	-0.90	-0.84	-1.38	-1.31	-1.35	-1.29	-0.92	-0.85
TETRADECANOIC ACID	37.0	-0.47	-0.32	-0.29	-0.80	-0.77	-0.77	-0.75	-0.33	-0.31

[‡] Solubility determined in this work.

Table 5.10

Solubility predictions from different models for solutes in n-octanol at 25 °C.

NAME	LNXOBS	MODEL 1	MODEL 2	MODEL 3	MODEL 4	MODEL 5	MODEL 6	MODEL 7	MODEL 8
1,2,3,5-TETRACHLOROBENZENE	-0.65	-1.73	-2.04	-2.68	-2.99	-2.33	-2.63	-1.79	-2.39
1,2,3-TRICHLOROBENZENE	-0.55	-0.88	-1.20	-2.86	-3.19	-2.59	-2.91	-0.83	-1.48
1,2,4,5-TETRACHLOROBENZENE	-1.56	-2.61	-3.66	-3.56	-4.61	-3.21	-4.25	-2.29	-4.01
1,4-DICHLOROBENZENE	-0.55	-0.38	-0.70	-2.43	-2.76	-2.24	-2.57	-0.39	-0.89
2,2',5,5'-TETRACHLOROBIPHENYL	-1.43	-2.25	-2.91	-5.10	-5.75	-4.30	-4.96	-2.29	-3.71
2,3,4,5-TETRACHLOROBIPHENYL	-1.65	-2.29	-2.98	-5.14	-5.83	-4.34	-5.03	-2.29	-3.78
2,4,5-TRICHLOROBIPHENYL	-1.55	-1.35	-1.92	-4.40	-4.98	-3.65	-4.23	-1.45	-2.67
4,4'-DICHLOROBIPHENYL	-1.95	-1.49	-2.60	-3.23	-4.34	-2.58	-3.69	-1.42	-3.25
4-MONOCHLOROBIPHENYL	-1.02	-0.54	-1.12	-2.58	-3.16	-1.93	-2.51	-0.49	-1.77
9,10-DIPHENYLANTHRACENE‡	-4.56	-4.23	-4.81	-3.13	-3.77	-3.11	-3.75	-4.25	-4.89
ACENAPHTENE	-1.39	-0.73	-1.46	-1.29	-2.02	-0.89	-1.62	-0.80	-1.86
ANTHRACENE	-2.73	-1.93	-3.37	-3.22	-4.66	-2.22	-3.65	-1.89	-4.37
BENZ[<i>a</i>]PYRENE‡	-3.82	-4.26	-4.17	-1.91	-1.82	-1.98	-1.09	-3.84	-4.11
BIPHENYL	-0.96	-0.51	-1.01	-1.32	-1.82	-0.74	-1.24	-0.59	-1.60
CHRYSENE	-3.50	-2.36	-3.93	-4.13	-5.69	-2.66	-4.22	-2.67	-5.40
FLUORENE	-1.45	-1.08	-1.97	-2.15	-3.03	-1.16	-2.05	-1.11	-2.95
HEXACHLOROBENZENE	-2.64	-6.33	-7.81	0.37	-1.11	0.89	-0.59	-6.40	-8.33
NAPHTHALENE‡	-0.82	-0.57	-1.16	-1.30	-1.89	-0.78	-1.37	-0.54	-1.69
NAPHTHACENE‡	-4.87	-5.48	-7.08	-4.05	-5.64	-4.04	-5.63	-5.49	-7.09
PENTACHLOROBENZENE	-1.29	-3.32	-3.95	-1.86	-2.50	-1.44	-2.08	-3.39	-4.38
PERYLENE‡	-3.01	-3.86	-4.98	-3.59	-4.73	-3.63	-4.75	-3.82	-4.94
PHENANTHRENE	-1.20	-0.78	-1.56	-2.07	-2.85	-1.07	-1.84	-0.82	-2.56
PYRENE	-1.65	-1.65	-2.80	-3.11	-4.26	-1.61	-2.76	-1.59	-4.30

‡ Solubility determined in this work at 23 °C.

TABLE 5.11

Prediction coefficients for all the models in all the systems.

MODEL	BENZENE	TRIOLEIN (NON H-BONDING)	TRIOLEIN (H-BONDING)	OCTANOL
1	0.96	0.75	-0.54	0.78
2	0.90	0.74	-0.52	0.68
3	0.86	0.67	-0.45	0.23
4	0.71	0.69	-0.44	-0.34
5	0.84	0.65	-0.42	0.64
6	0.68	0.68	-0.43	-0.30
7	0.97	0.74	-0.46	0.77
8	0.92	0.73	-0.46	0.18

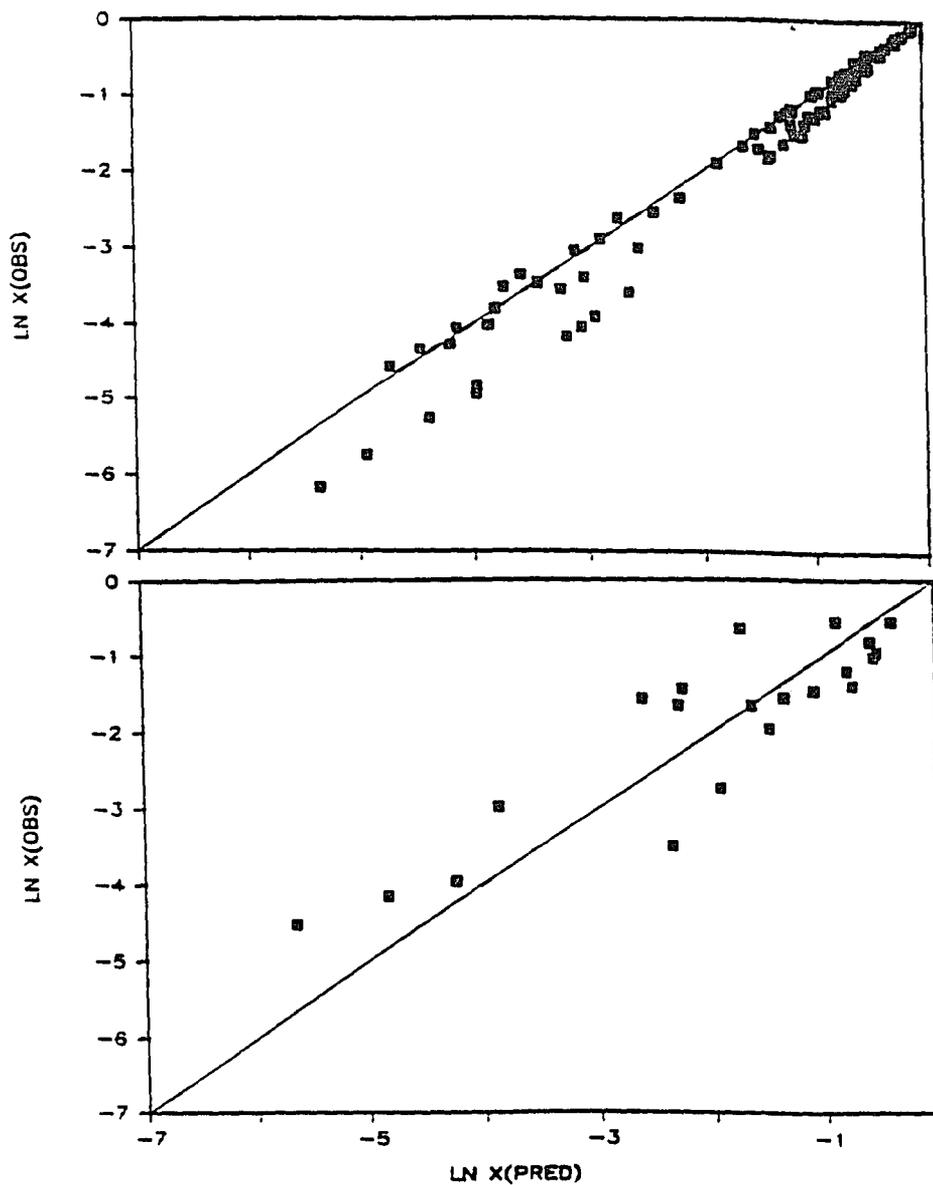


Figure 5.9: Solubility predictions from model 1 in benzene (top) and octanol (bottom).

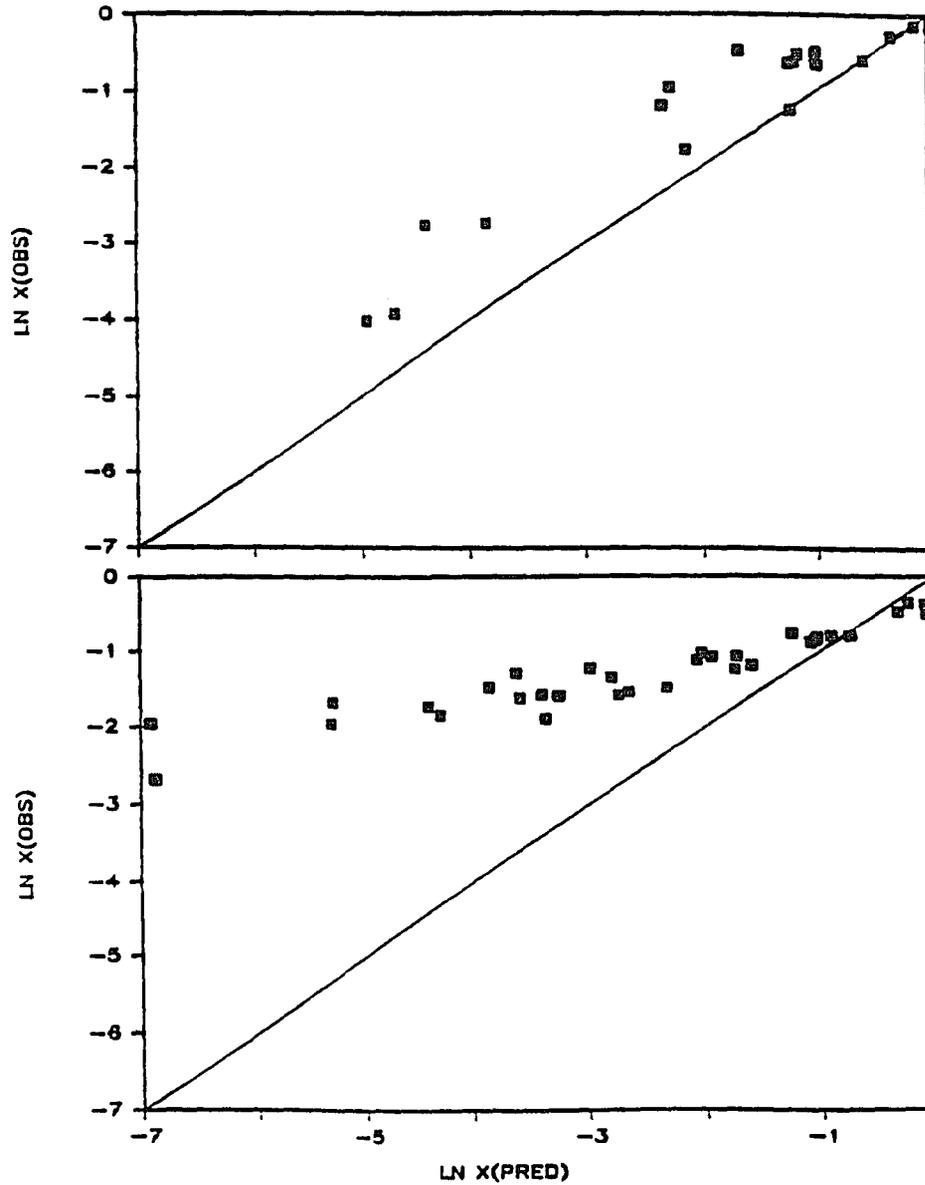


Figure 5.10: Solubility predictions from model 1 in triolein for non H-bonding (top) and H-bonding solutes (bottom).

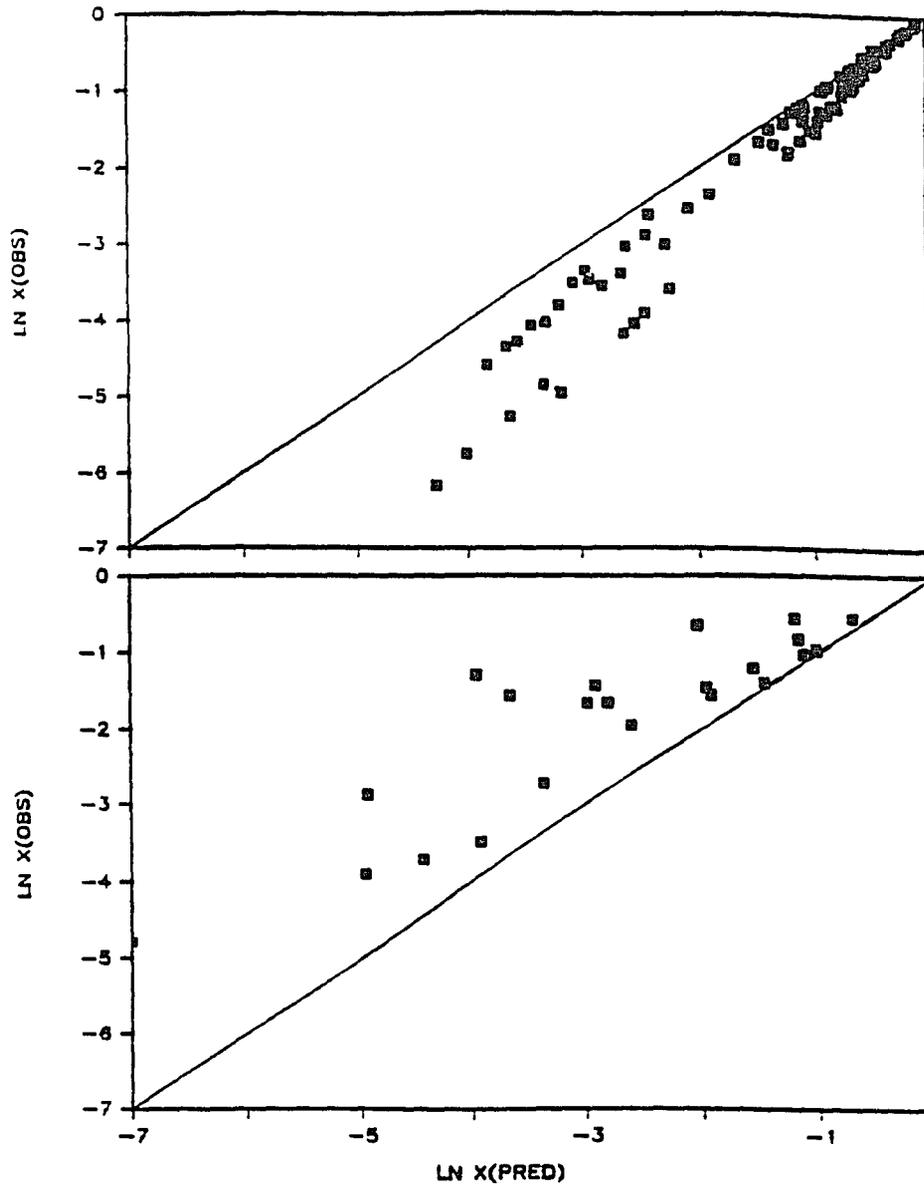


Figure 5.11: Solubility predictions from model 2 for solutes in benzene (top) and n-octanol (bottom).

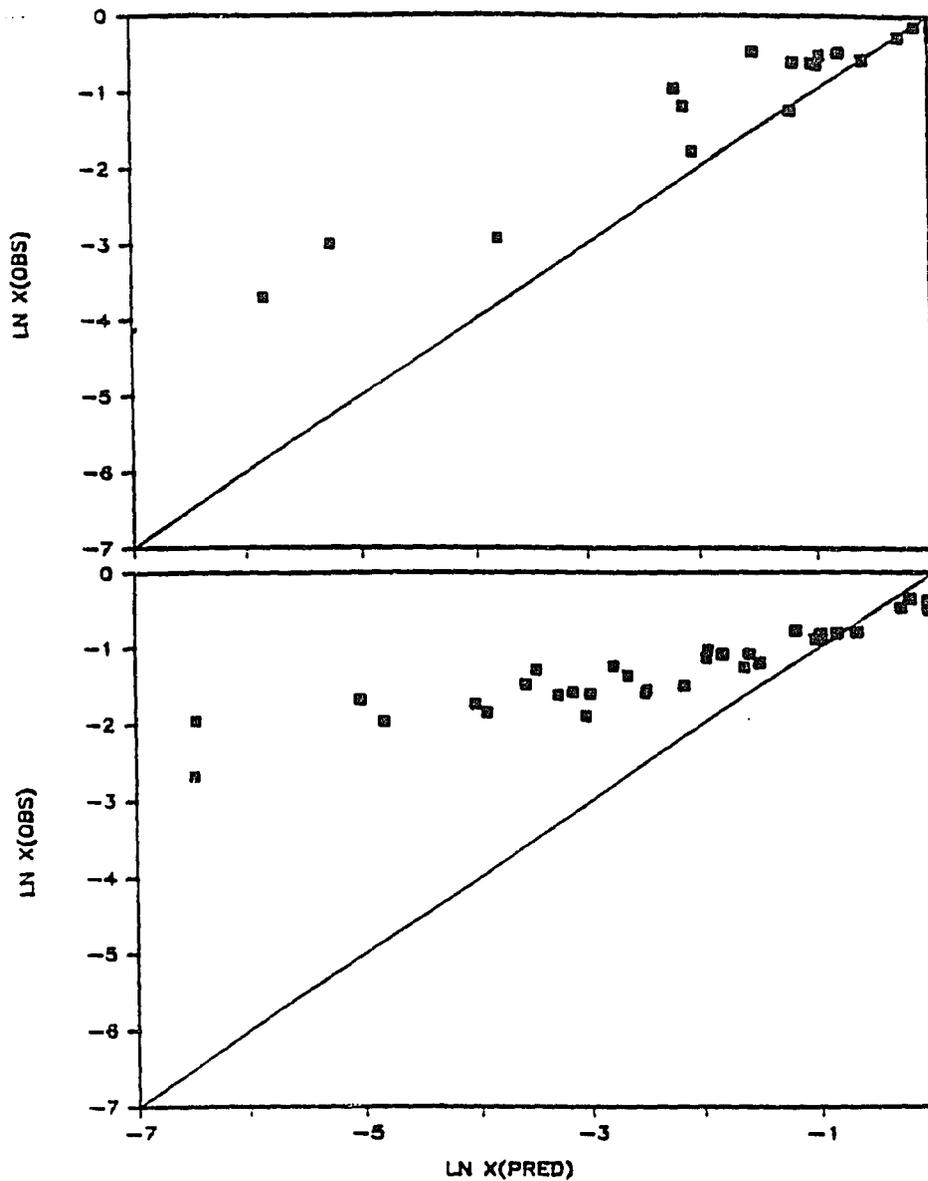


Figure 5.12: Solubility predictions from model 2 in triolein for non H-bonding (top) and H-bonding solutes (bottom).

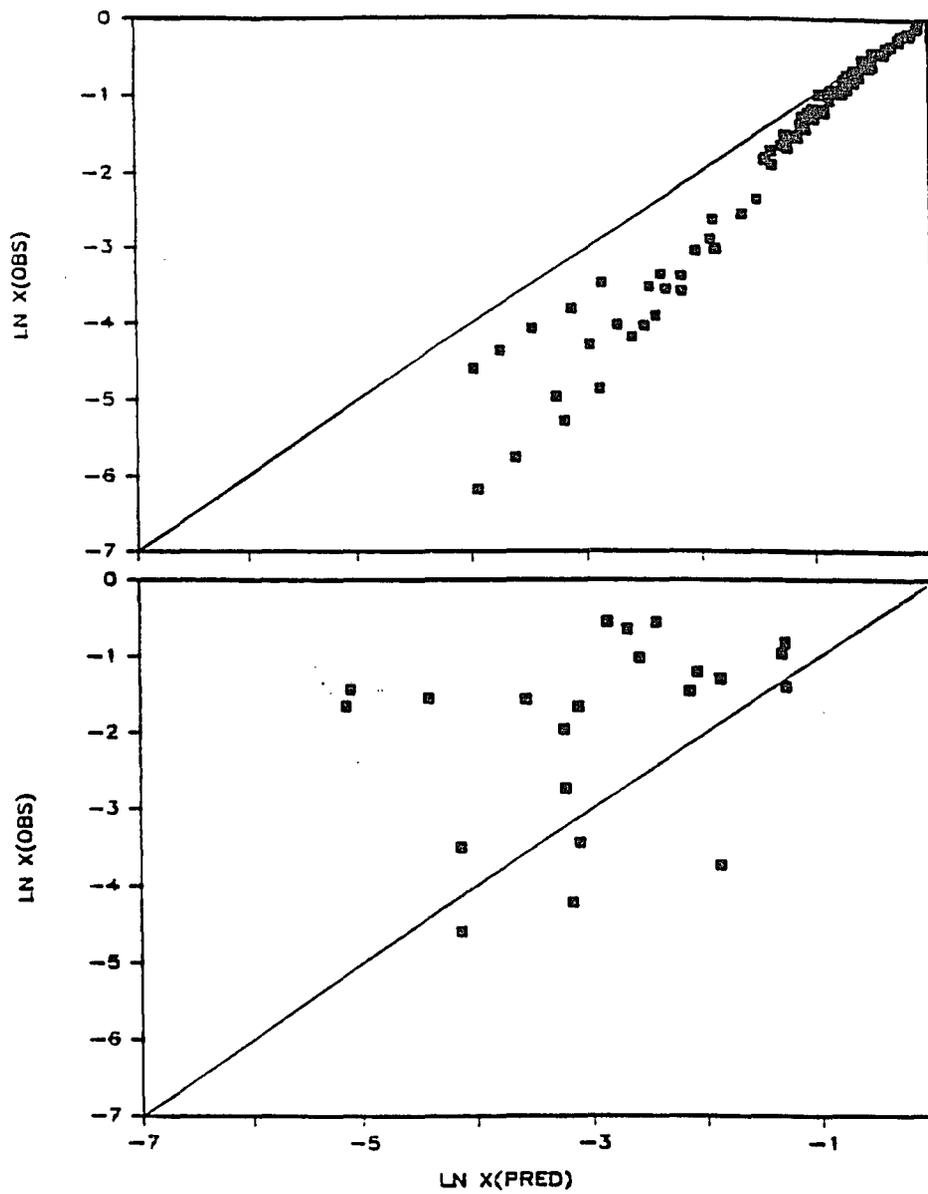


Figure 5.13: Solubility predictions from model 3 for solutes in benzene (top) and n-octanol (bottom).

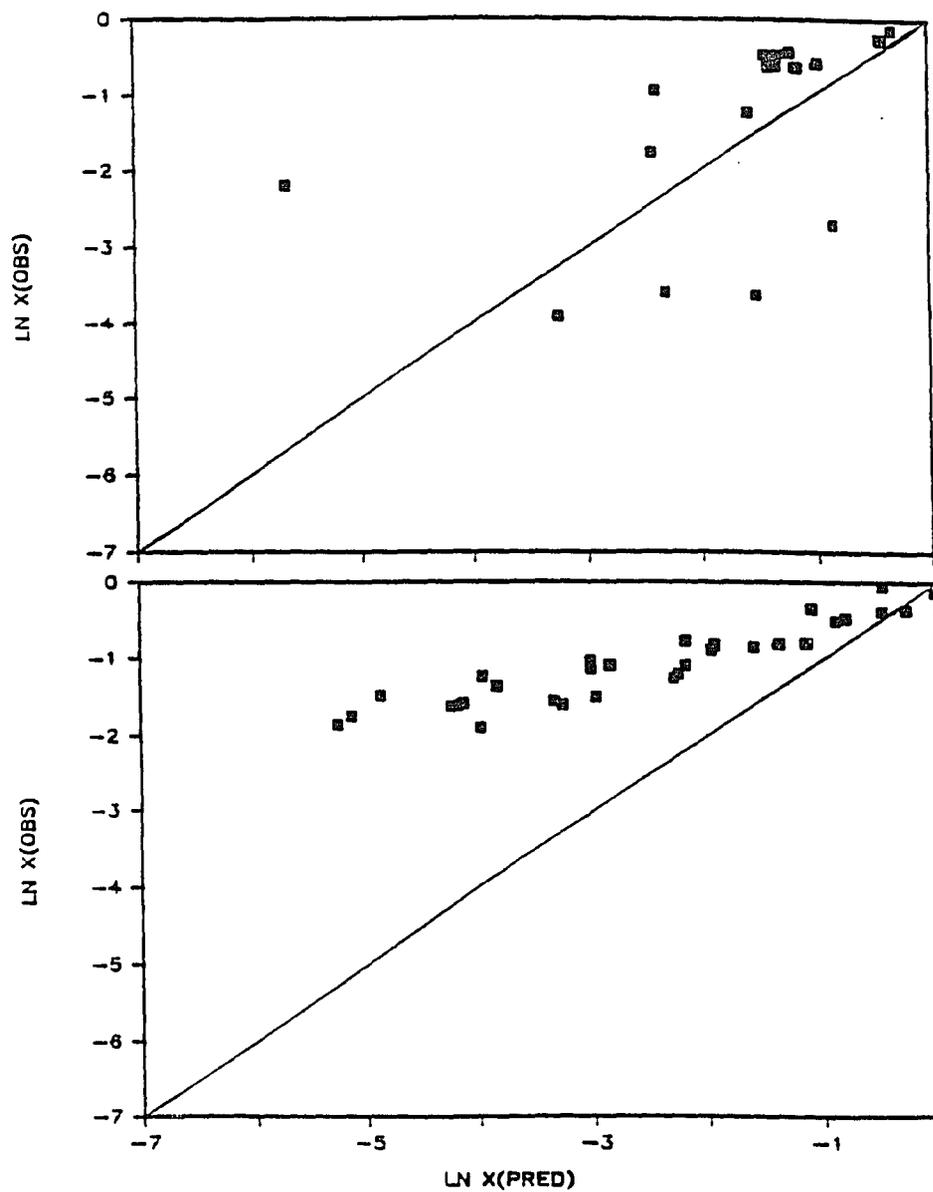


Figure 5.14: Solubility predictions from model 3 in triolein for non H-bonding (top) and H-bonding solutes (bottom).

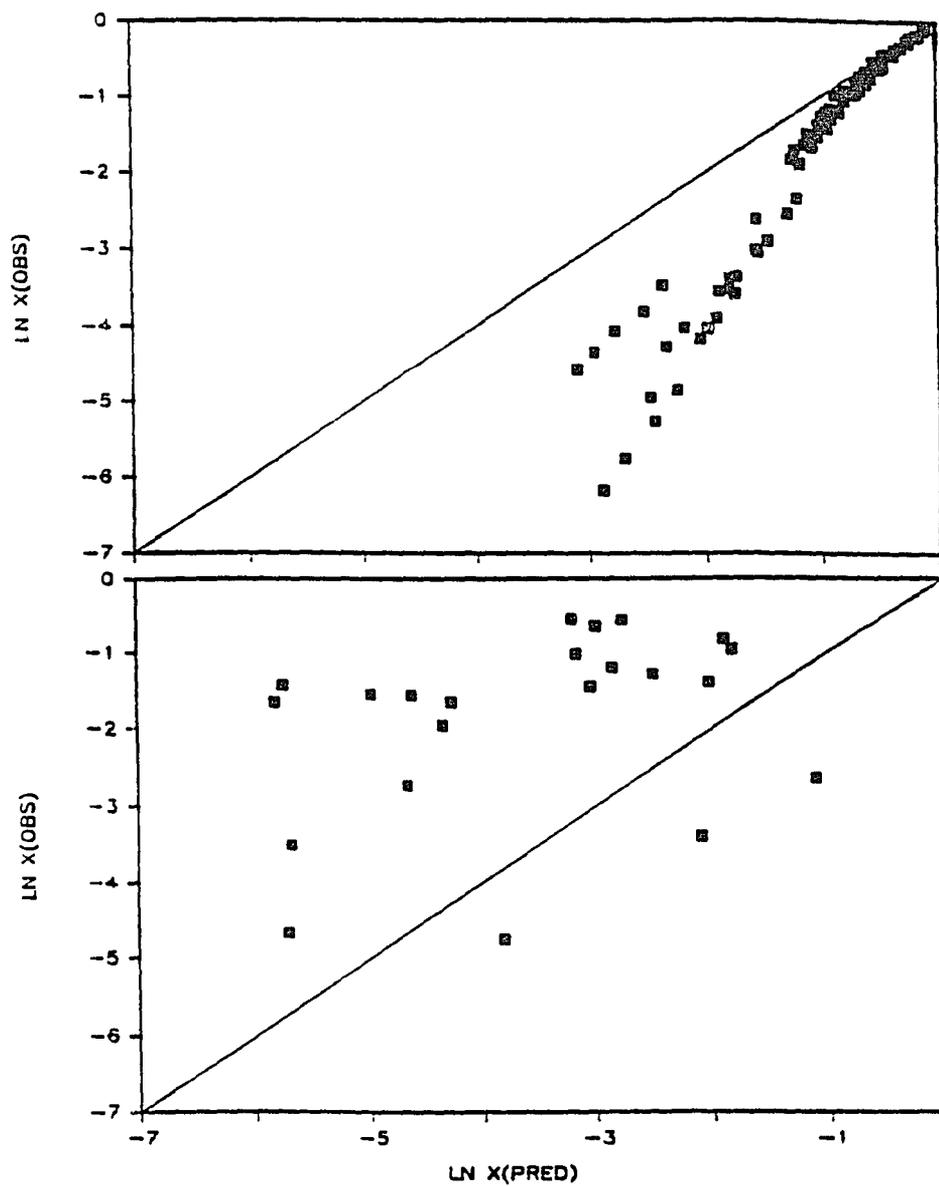


Figure 5.15: Solubility predictions from model 4 for solutes in benzene (top) and n-octanol (bottom).

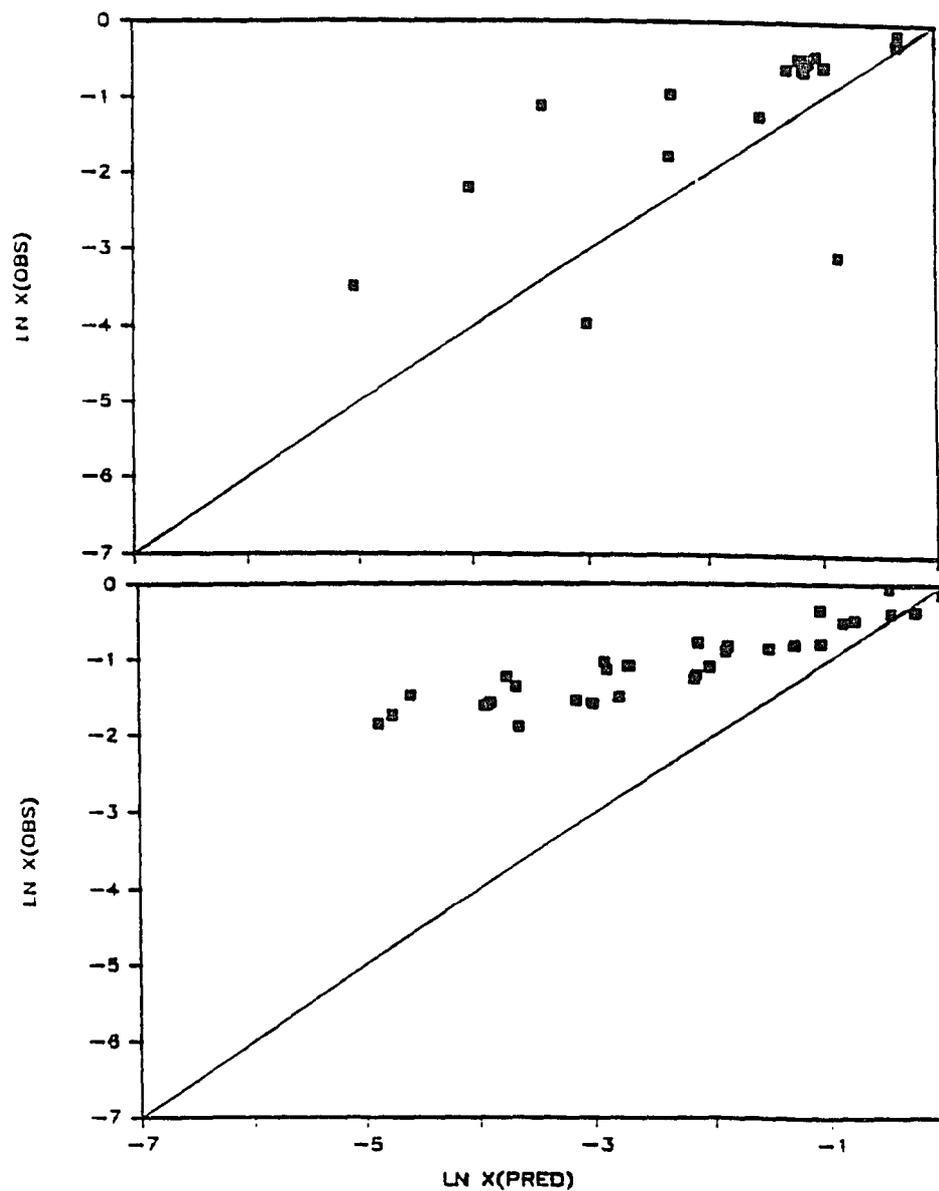


Figure 5.16: Solubility predictions from model 4 in triolein for non H-bonding (top) and H-bonding solutes (bottom).

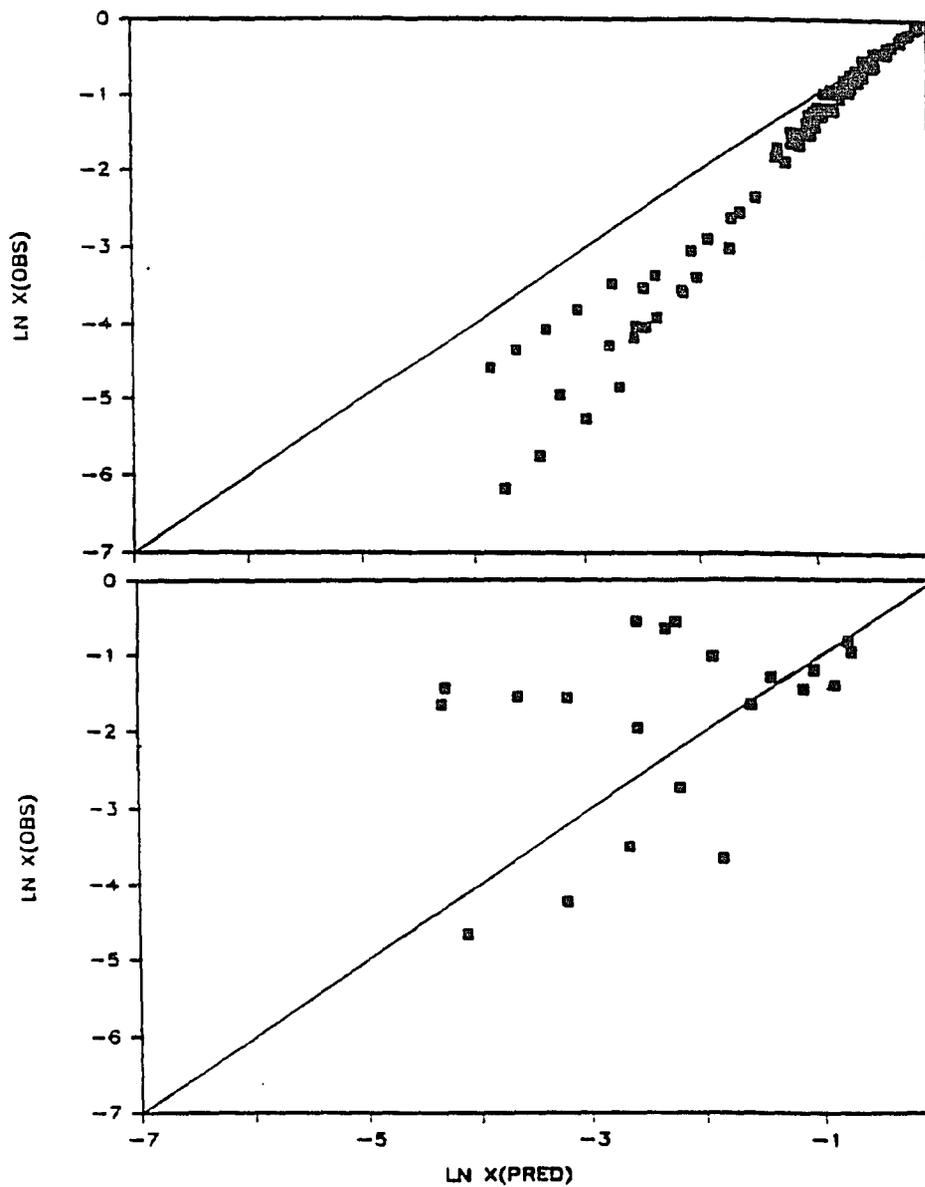


Figure 5.17: solubility predictions from model 5 for solutes in benzene (top) and n-octanol (bottom).

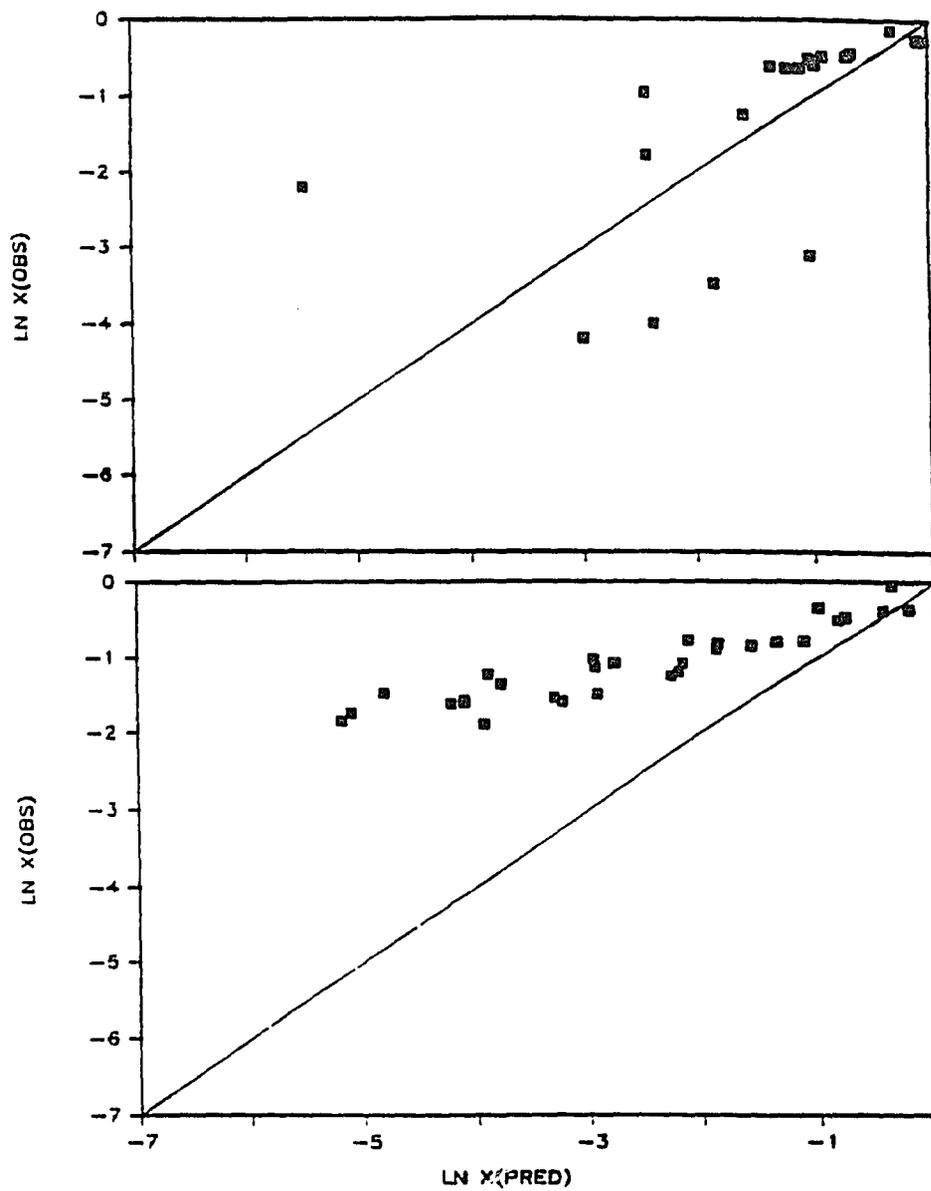


Figure 5.18: Solubility predictions from model 5 in triolein for non H-bonding (top) and H-bonding solutes (bottom).

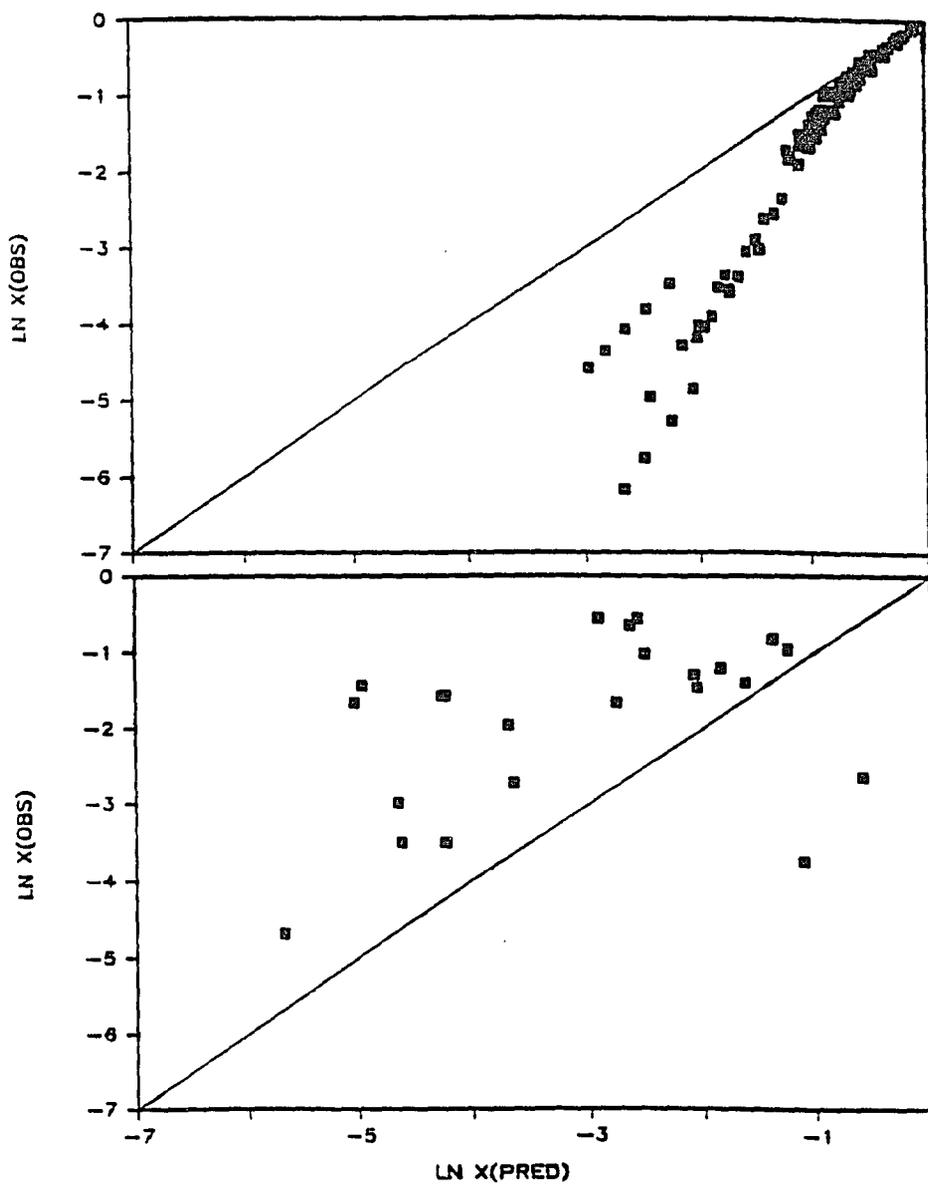


Figure 5.19: Solubility predictions from model 6 for solutes in benzene (top) and n-octanol (bottom).

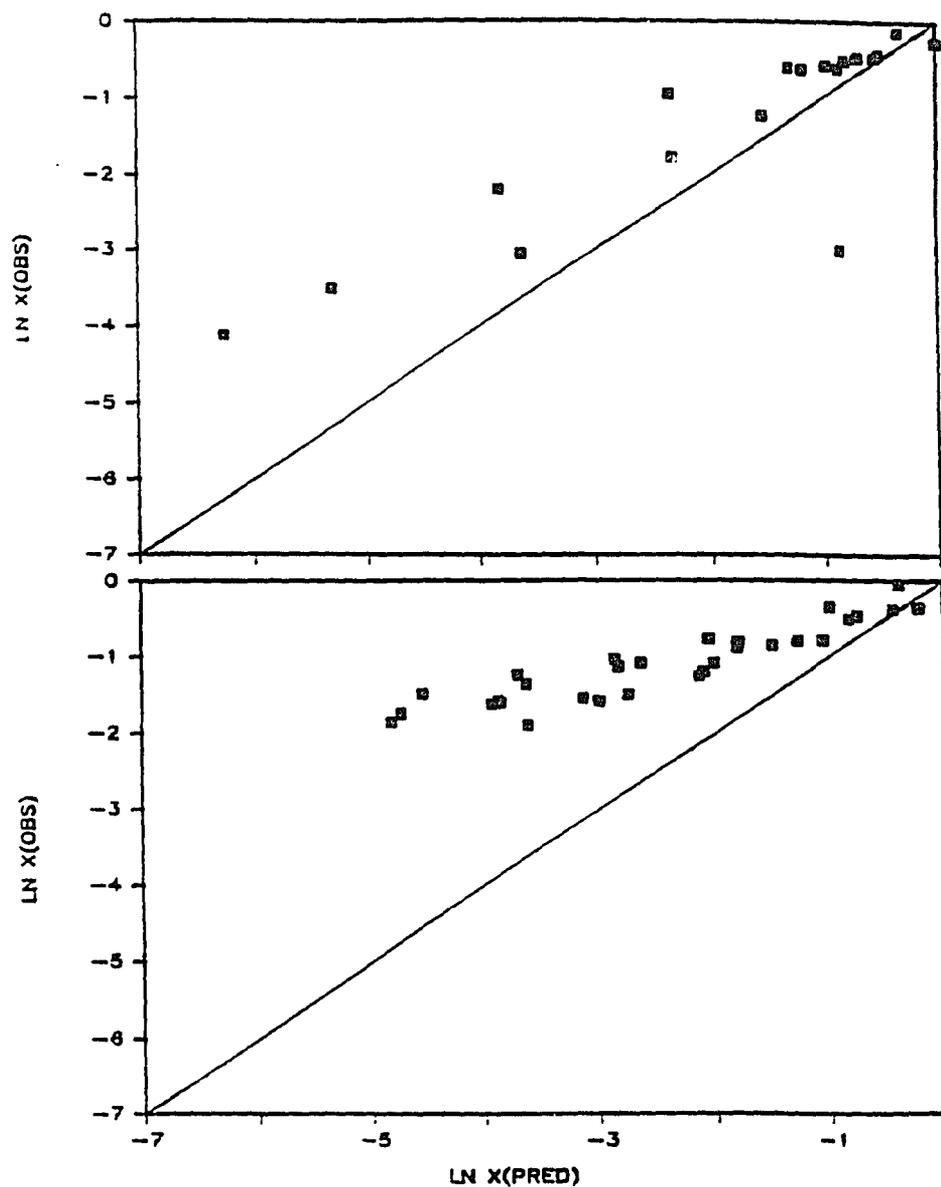


Figure 5.20: Solubility predictions from model 6 in triolein for non H-bonding (top) and H-bonding solutes (bottom).

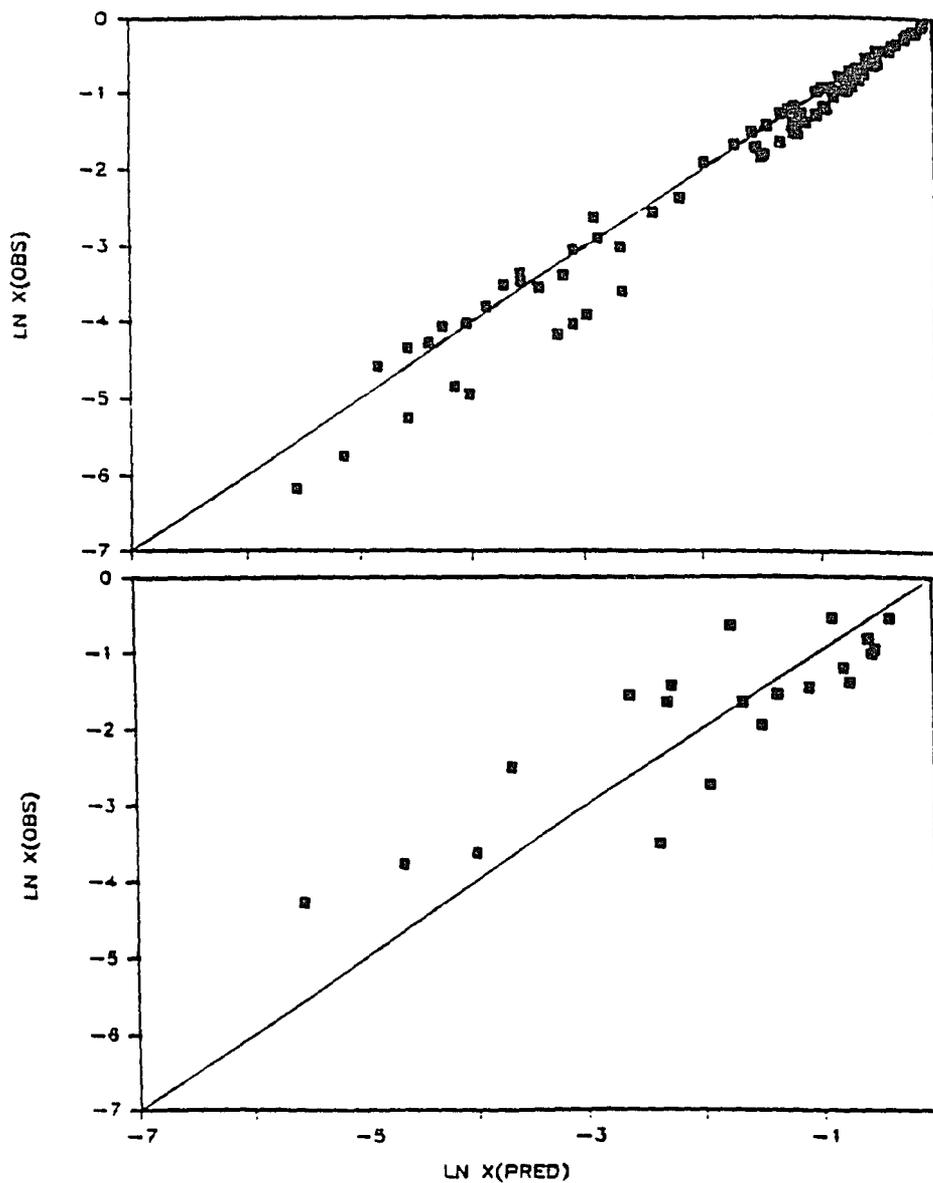


Figure 5.21: Solubility predictions from model 7 for solutes in benzene (top) and n-octanol (bottom).

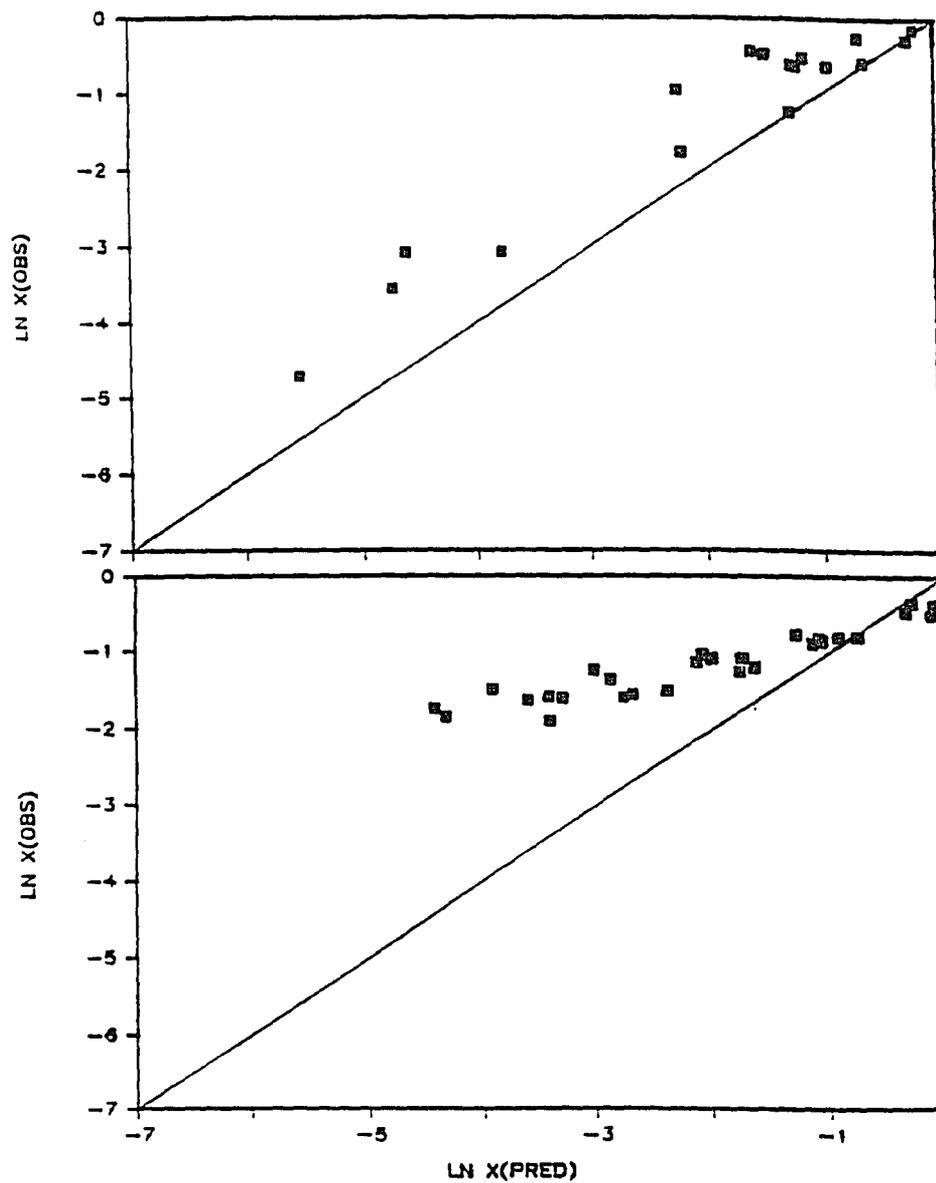


Figure 5.22: Solubility predictions from model 7 in triolein for non-H-bonding (top) and H-bonding solutes (bottom).

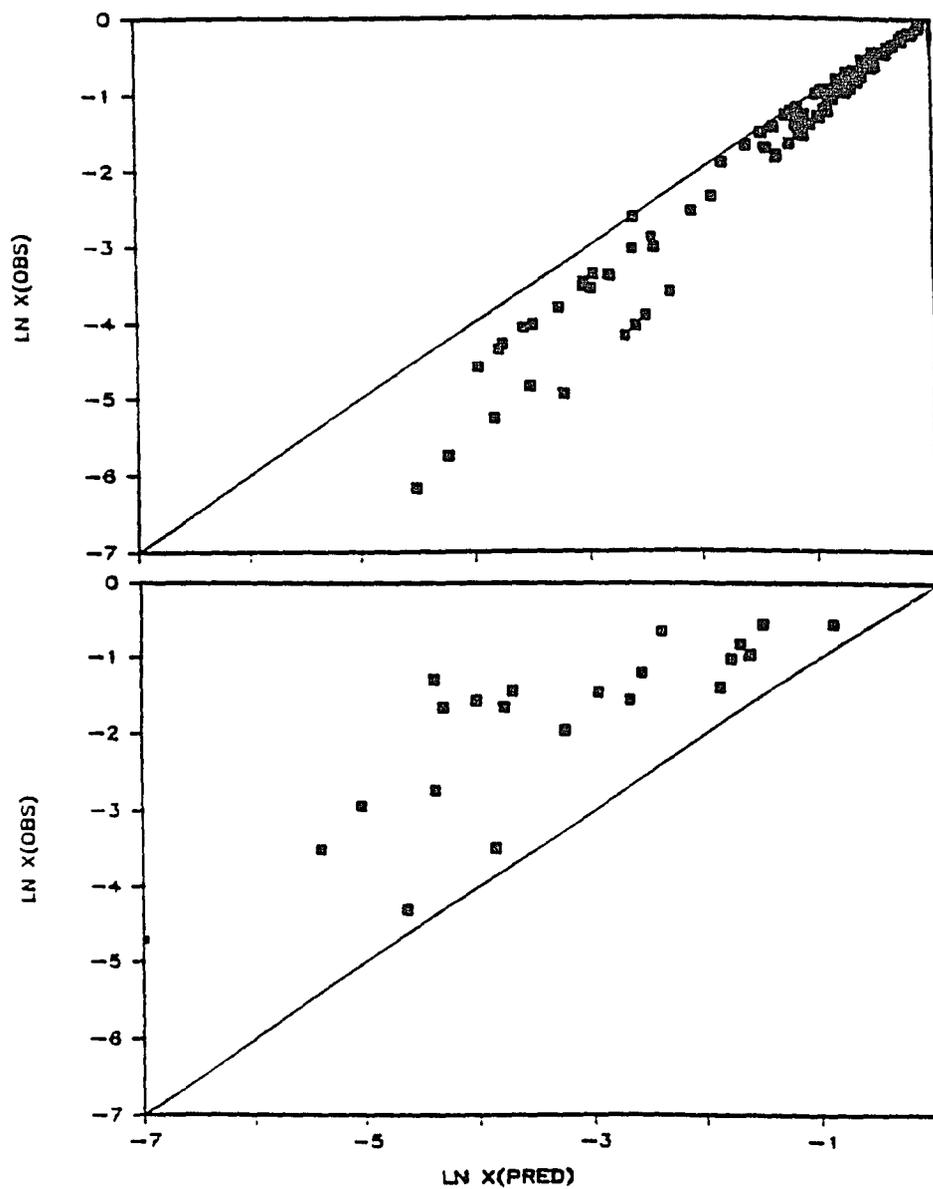


Figure 5.23: Solubility predictions from model 8 for solutes in benzene (top) and n-octanol (bottom).

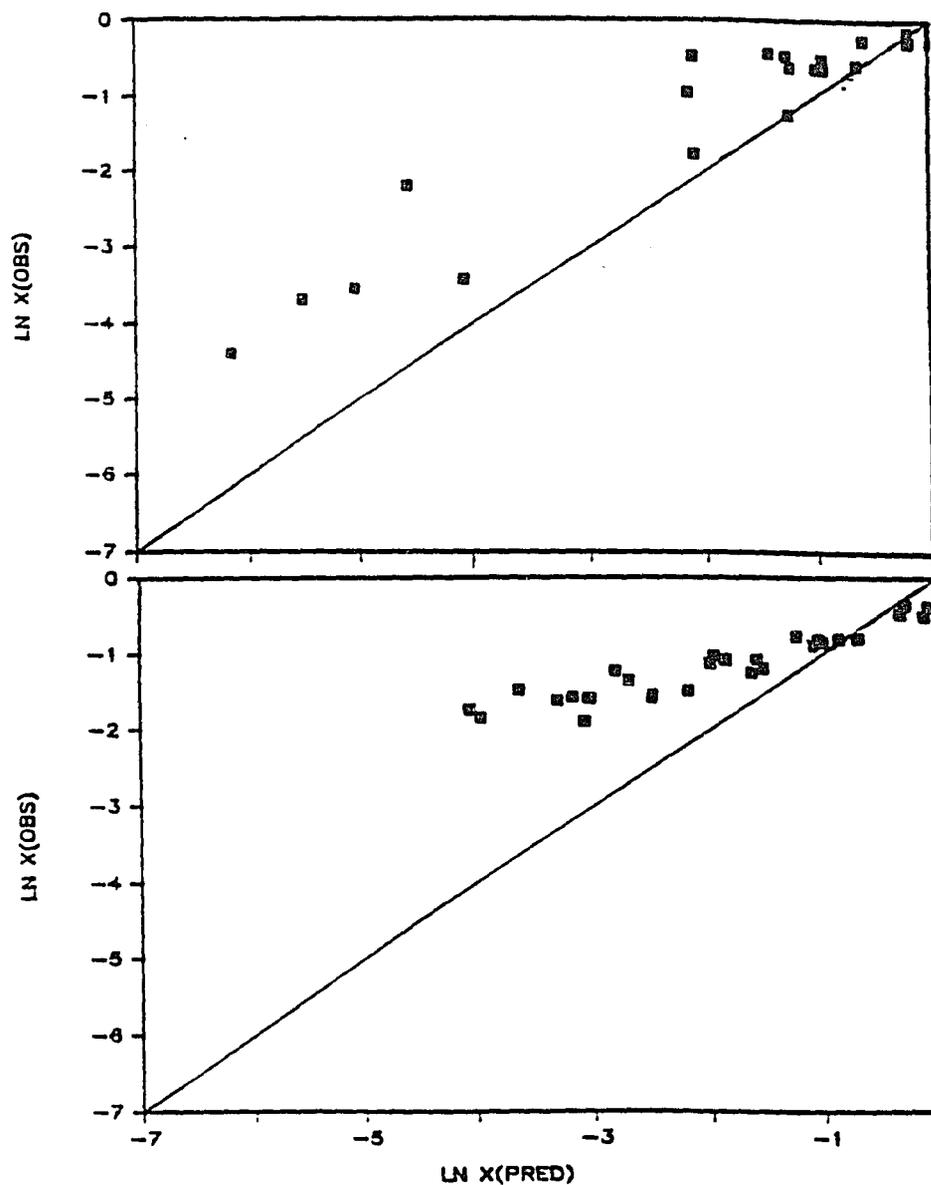


Figure 5.24: Solubility predictions from model 8 in triolein for non H-bonding (top) and H-bonding solutes (bottom).

CHAPTER 6

SUMMARY

The solubility of a solid solute can be estimated from the following general equation:

$$\ln X = \ln X^i + \ln \gamma (\text{comb.}) + \ln \gamma (\text{resid.}) \quad (6.1)$$

where $\ln X^i$ is the ideal solubility, $\ln \gamma$ is the activity coefficient, which is separated into two parts: combinatorial (entropic) and residual (enthalpic).

There are several theories which can be used to calculate the activity coefficients. In the present study two models were chosen for the combinatorial and the residual activity coefficient. The models chosen are as follows:

Combinatorial activity coefficient

Flory-Huggins

UNIFAC combinatorial

Residual activity coefficient

Scatchard-Hildebrand

UNIFAC residual

These equations for the activity coefficient were used in the present study to estimate the solubility of organic compounds in benzene, triolein and octanol.

The activity coefficients were calculated for the solutes in all the three systems. The combinatorial activity coefficient calculated from Flory-Huggins and UNIFAC models were found to be identical in most cases. Both the models predict combinatorial activity coefficient value of unity in the case of solutes in octanol. This is expected as the volume of the solute and the solvent are very close. The UNIFAC model has an additional term to the Flory-Huggins theory for activity coefficient. This term however is very close to zero in almost all the cases. Thus the two models are equivalent and UNIFAC combinatorial does not offer any advantage over the simple model of Flory and Huggins.

The residual activity coefficient was calculated for all the solutes in all the systems. The two models i.e. Scatchard-Hildebrand and the UNIFAC residual, yield activity coefficients which are very different. The UNIFAC model is a group contribution method for the calculation of activity coefficient. It requires binary interaction parameters for the groups in the molecule. In contrast the Scatchard-Hildebrand theory does not require any binary parameters. The

activity coefficient is calculated from only the pure component properties. The residual activity coefficient calculated from the two models in all the three systems are very different. In the case of benzene as a solvent the UNIFAC model predicts a activity coefficient value of unity in almost all the cases. In contrast the Scatchard-Hildebrand predicts a positive deviation from ideality and activity coefficient values greater than unity. In the case of triolein and octanol the relationship of the two activity coefficient is relatively complex.

The solubility of the solutes were predicted using equation 6.1 with different combinations of the activity coefficient and the ideal equation. All the models however have one combinatorial activity coefficient and one residual activity coefficient. The models were compared for their suitability in predicting solubility by a single parameter, the prediction coefficient. The best prediction was obtained in almost all the cases when Flory-Huggins or UNIFAC combinatorial was used with the Scatchard-Hildebrand theory.

However all the models give very poor results in the case of the H-bonding solutes in triolein. It is clear that the models give good results when there is no specific

chemical interaction between the solute and the solvent. For those molecules which have tendency to H-bond, the equations for the activity coefficient have to be modified to include these interactions. However there are very few theories available which can correctly predict the activity coefficients in solutions where H-bonding can occur. Some theories based on complex (H-bond) formation have been proposed (Coleman, 1988; Painter, 1988). However they have very little practical significance from the prediction point of view. They all require the complexation constant which cannot be predicted.

In conclusion the simple model of Flory-Huggins and Scatchard-Hildebrand successfully predicts the solubility behavior of all the solutes in the systems considered. The model does not work for H-bonding solutes in triolein.

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