EFFECTS OF NON-LINEAR
PARTITIONING BEHAVIOR ON
NAPL CHARACTERIZATION VIA
PARTITIONING TRACER TESTS

by

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Abstract

EFFECTS OF NON-LINEAR PARTITIONING BEHAVIOR ON NAPL CHARACTERIZATION VIA PARTITIONING TRACER TESTS

by Elizabeth A. Fitzpatrick

Chairperson of the Supervisory Committee: Professor William R. Wise
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This report focuses on the non-linearities involved between tracer/non-aqueous phase liquid (NAPL) pairs and their subsequent effects on subsurface contaminant characterization. Two computer models were utilized; one model predicted the extent of the non-linear behavior between selected tracer/NAPL pairs. The second model utilized Freundlich and linear isotherm data fits to the non-linearities and predicted effluent response curves based on model conditions. Accepted methods for NAPL quantification in the subsurface were applied to the linear and non-linear effluent response curves and the differences were compared.

The analyzed tracers include methanol, 2-methyl-2-hexanol, and 3-methyl-2-hexanol. Trichloroethylene (TCE) served as the NAPL for the computer simulations.

The simulation results show that NAPL saturation calculations are systematically underestimated when linear tracer partitioning is assumed. The NAPL saturation was underestimated by as much as forty percent for the specific interactions and model conditions used during this investigation.

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CHAPTER 1
OVERVIEW

Introduction

Organic contaminants have become a problem in many locations throughout the country and the world. Over the past several decades, many sites have experienced leaks, spills, and the disposal of organic wastes. Many of the organic contaminants which exist at these sites are "non-aqueous phase liquids (NAPLs)." NAPL infiltration into the subsurface and contaminant transport via groundwater have caused vast expanses of hazardous waste sites. Efforts to remediate NAPLs from the subsurface are often hampered by the fact that it is difficult to characterize the amount and extent of the contaminant distribution in the ground. Conventional techniques have proven to be relatively ineffective for this purpose (Pope *et. al.*, 1994). A recently developed technique to characterize NAPL distributions and amounts utilizes a technique which is typically used in oil field applications; this method involves the use of partitioning tracers. These tracers, when injected into the subsurface, partition into the NAPL phase; the amount of NAPL can be determined by measuring the tracer concentration downgradient from the tracer injection point. Several field demonstrations have already been completed to quantify residual NAPLs in the saturated zones of contaminated sites (Annable *et al.*, 1994). Thus far, these demonstrations have assumed that a linear relationship exists between tracer/NAPL interactions. Specifically, the amount of tracer which partitions into the NAPL is determined by a single partition coefficient regardless of the relative amounts of tracer and NAPL present. This paper examines the combination of several already established computer modeling techniques to accomplish the following: (1) determine the extent of tracer/NAPL non-linearities, and (2) estimate the non-linear effects on NAPL volume calculations using simulation techniques. The modeling programs used during this study include the UNIFAC (Chen, 1992) and COMBALL (Wise, 1985) models.

Background

Current methods used to characterize subsurface NAPL concentrations include well installation, core sampling and analysis, and borehole geophysical techniques (Pope *et al.*, 1994). These technologies are often costly, time consuming, and cause soil disturbance.

In addition, they cannot accurately predict NAPL distributions because samples are evaluated at distinct locations throughout the site. The presence of both soil heterogeneities and anisotropic conditions often lead to inaccurate NAPL characterization. As a result, remediation technologies employed at many sites cannot effectively remove the targeted contaminants. Thus, costs and remediation times are often underestimated.

A recently developed technique to characterize NAPL concentrations and distributions employs the use of partitioning tracers. Partitioning tracers have been used successfully in oil field applications (Pope *et al.*, 1994). In NAPL characterization, laboratory experiments and field demonstrations have already been conducted to determine partitioning tracer effectiveness (Annable *et al.*, 1994; Pope *et al.*, 1994). These applications are based on the knowledge that injected tracers partition into and out of the oil (NAPL) phase as they move through an aquifer; consequently, these tracers experience retardation. If the relationship between each tracer and the NAPL is known, then the amount of NAPL present along a streamline in an aquifer can be estimated based on the retardation of each tracer. Previous studies to determine NAPL presence in saturated media have included the use of a "non-partitioning" tracer and several alcohols for partitioning tracers (Annable *et al.*, 1994; Pope *et al.*, 1994). The difference between the first moment of the non-partitioning and the partitioning tracer effluent curves can then be used to quantify certain NAPLS in the aquifer.

Several advantages exist with the use of tracers. First, they only disturb the soil at tracer injection and extraction points. Second, they account for soil heterogeneities and anisotropic conditions by moving with the groundwater through the aquifer. Finally, only small amounts of tracers are required to adequately characterize the NAPL profiles. However, several limitations exist. One major limitation is that non-linearities exist between tracer/NAPL interactions. The amount of non-linearity depends on the mole fraction ratio between the tracer/NAPL pair. Therefore, the amount of retardation experienced by the partitioning tracer varies with the tracer/NAPL composition.

The laboratory and field experiments thus far have been analyzed under the assumption that the tracer/NAPL interactions are linear. However, additional information is required to fully understand the effects of non-linearities on tracer/NAPL interactions. The initial use of computer modeling techniques can predict the magnitude of non-linearities between tracer/NAPL pairs. This modeling may ultimately allow for more accurate contaminant level predictions by understanding the deviations from ideal conditions. There are, however, several disadvantages which exist to computer modeling techniques. First, the tracer/NAPL non-linearities are predicted by a computer model. Thus, these predictions may not be completely accurate. Second, the type of NAPL contaminant is not always known prior to characterization. The established computer modeling techniques can only predict non-linearities if the NAPL type is already known.

Purpose

This paper examines the extent of non-linearities involved between tracer/NAPL pairs and their effect on NAPL characterization. To accomplish this objective, tracer/NAPL non-linearities were predicted using the UNIFAC model (Chen, 1992). Established isotherm relationships were then "fit" to the UNIFAC predicted tracer/NAPL relationships. The isotherm fits, combined with hydraulic data, were used to determine partitioning tracer effluent curves through the use of the COMBALL model (Wise, 1985). Finally, the COMBALL effluent curve data was utilized to compare accepted linear methods for NAPL quantification to the actual non-linear behavior which actually exists.

CHAPTER 2
MODELING PROCEDURE

Model Parameters

Three tracers were analyzed with one NAPL during this investigation. The analyzed

tracers include methanol, 2-methyl-2-hexanol, and 3-methyl-2-hexanol. Methanol has

often been used as a "non-reactive" tracer, while the other two represent typical

partitioning tracers (Pope *et al.*, 1994). These tracers interacted with the NAPL

trichloroethylene (TCE) for the purposes of this study. Table I provides the structural

chemical makeup for each tracer and TCE..

Table I. Structural Formulas of Analyzed Compounds

Compound	Structural Formula
Trichloroethylene	$ClHC=CCl_2$
Methanol	CH_3OH
2-Methyl-2-Hexanol	$CH_3\text{-}CCH_3OH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$
3-Methyl-2-Hexanol	$CH_3\text{-}CHCH_3\text{-}CHOH\text{-}CH_2CH_2\text{-}CH_3$

The simulations were only conducted between binary systems; i.e., the interactions

between one tracer and TCE were observed for each model simulation. In addition, the

equations used in the model simulations were conducted with several dimensionless

variables. These variables include the following: (1) Concentration, c; (2) Time, t; (3)

Velocity, v; (4) Distance, x_L, and (5) the Dispersion Coefficient, D_L. The models simulate

a theoretical soil column in which no gas phase exists. Table II summarizes the

parameters which were used throughout all model simulations.

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Table II. Parameters Used for UNIFAC and COMBALL Simulations

PORE VOLUME (PV)	POROSITY (η)	DISPERSION COEFF. (D_L)	TEMP (T)	WATER SAT. (s_w)	NAPL SAT (s_n)	INJECTION TIME (Δt)*
1.0	30%	0.01	298K	95%	5%	0.5

*Injection time is expressed in terms of pore volumes for model simulations.

Assumptions

The UNIFAC and COMBALL runs were conducted under several general assumptions. First, the system is assumed to be at equilibrium. Second, the tracer only interacts with the NAPL in the column; i.e., no other tracer reactions such as biological or radioactive decay occur within the column. Third, no water phase exists within the tracer/NAPL body. Finally, the NAPL component is sparingly soluble in H_2O. In other words, the entire NAPL volume in "the column" is available for tracer partitioning and accurate NAPL quantification.

The UNIFAC Model

The UNIFAC model predicts the interactions between each tracer/NAPL pair. Formally termed "The UNIFAC Group-Contribution Method," this model was originally developed for chemical engineering purposes (Chen, 1992). The "group contribution" method assumes that compounds may be broken down into functional groups which have a unique contribution toward the compound property. By using this method, the UNIFAC model can predict liquid-phase activity coefficients. These activity coefficients represent the non-ideal behavior of a solution. The activity coefficient calculations for each molecule, i, are based on the following equation:

(1) $\ln\gamma_i = \ln\gamma^C_i + \ln\gamma^R_i$

where γ_i is the activity coefficient for the component, i, γ_i^C is the combinatorial part, and γ_i^R is the is the residual part. The combinatorial portion takes into account the entropy effects and depends on the size and the shape of the molecule i. In the combinatorial part, the group surface volume and area of each functional group are used as model parameters. Chen (1992) presents the equations used to determine the ultimate activity coefficients for mixtures.

The UNIFAC model was specifically utilized during this investigation to determine the activities between each tracer/TCE pair at varying tracer mole fractions between 0 and 1.0. The proper use of UNIFAC requires user identification of the functional subgroups for each compound. The chemical configuration of each compound determines the functional subgroup types and subgroup quantities for that compound. The subgroup information for each compound must be entered at a specified reaction temperature and mole fraction. The UNIFAC program, with this information, calculates activity coefficients for each tracer/NAPL interaction between mole fractions of 0 to 1.0. Chen (1992) provides a table of functional subgroups and their "assigned" UNIFAC subgroup numbers. Table III provides the functional subgroup information for each tracer/TCE pair.

Table III. UNIFAC Functional Subgroup Information for Tracers and NAPL

COMPOUND	FUNC. GROUP	MAIN GROUP #	SUB-GROUP#	TOTAL GROUPS
Trichloroethylene	H-C=C	2	8	1
	Cl-(C=C)	37	70	3
Methanol	CH_3OH	6	16	1
2-Methyl-2-Hexanol	CH_3	1	1	3
	CH_2	1	2	3
	C	1	4	1
	OH	5	15	1
3-Methyl-2-Hexanol	CH_3	1	1	3
	CH_2	1	2	2
	CH	1	3	2
	OH	5	15	1

Appendix (A) includes an example UNIFAC input and output data file for the 2-methyl-2-hexanol/TCE system. The input file varies tracer mole fractions from 0 to 1.0 with an increasing mole fraction interval of 0.1. The corresponding TCE mole fractions range from 1.0 to 0 with a decreasing mole fraction interval of 0.1. Additional input parameters are further explained in Appendix (A).

The UNIFAC output data files were then used to calculate the tracer and TCE activities; each activity coefficient multiplied by it's corresponding mole fraction yields that mole fraction's activity. Figures (1), (2), and (3) display the results for methanol/TCE, 2-methyl-2-hexanol/TCE, and 3-methyl-2-hexanol/TCE combinations. The lower "X" axis represents the tracer mole fraction, while the upper "X" axis represents the TCE mole fraction.

METHANOL/TRICHLOROETHYLENE SYSTEM
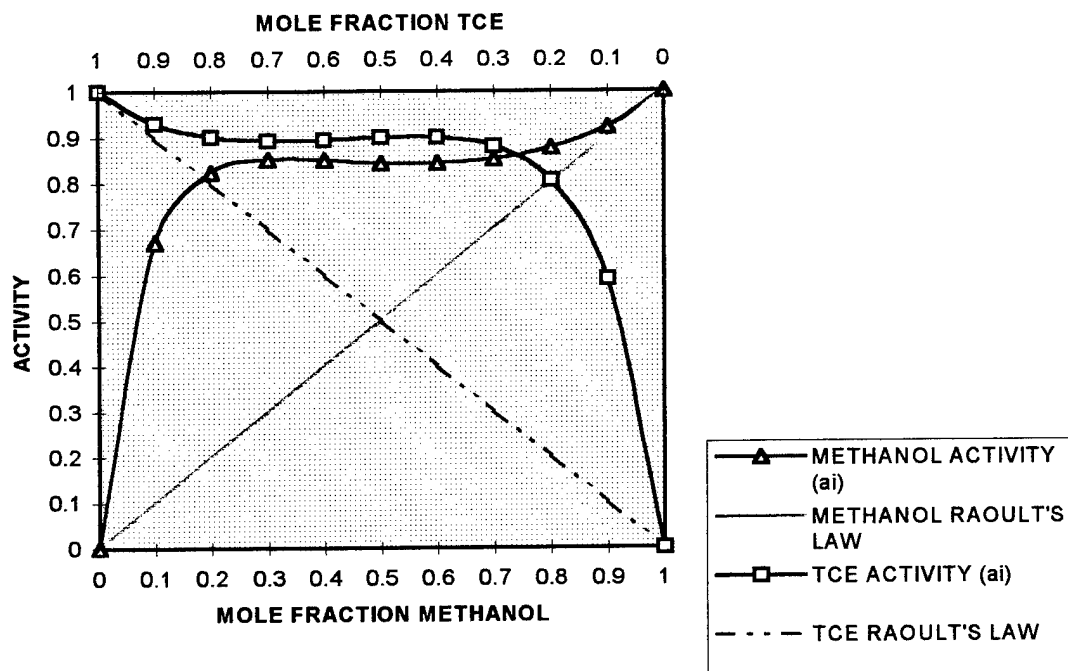
Figure 1.

2-METHYL-2-HEXANOL/TRICHLOROETHYLENE SYSTEM

Figure 2.

3-METHYL-2-HEXANOL/TRICHLOROETHYLENE SYSTEM
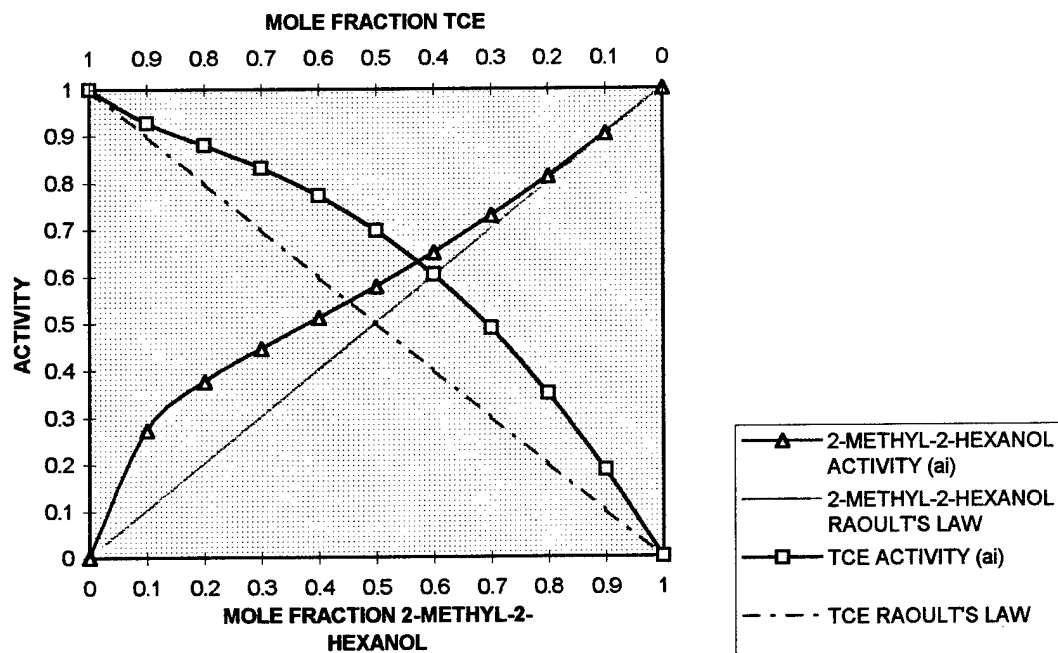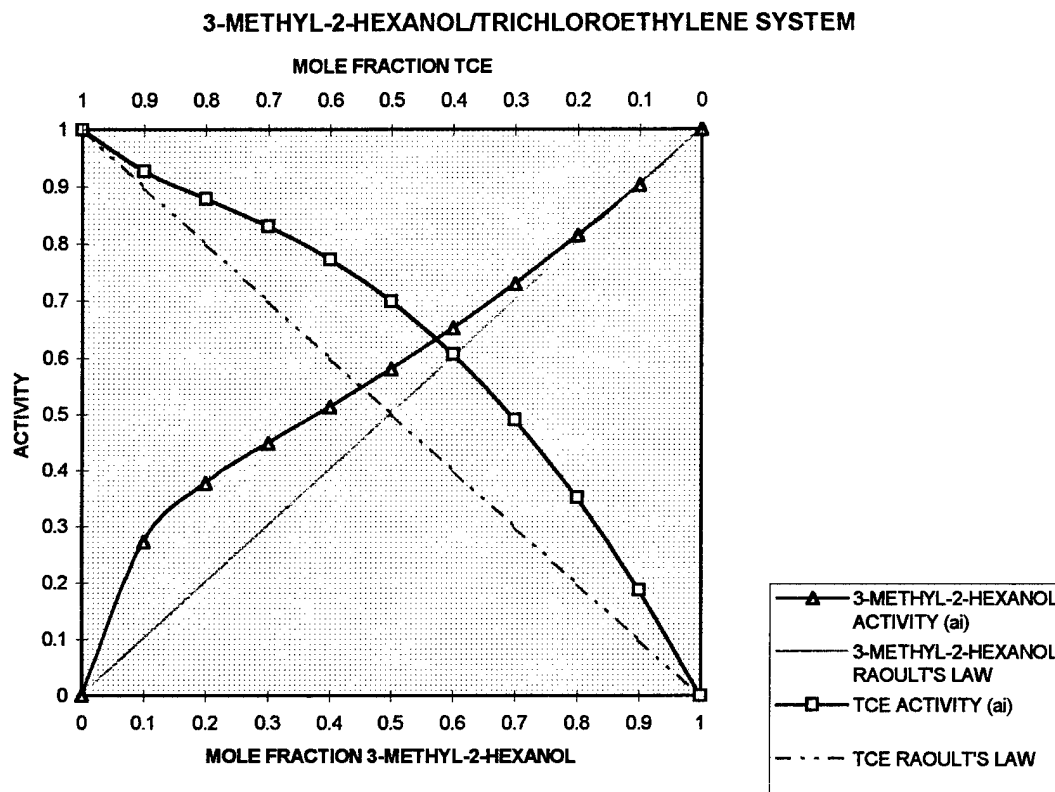
Figure 3.

The UNIFAC simulations represented by figures (1), (2), and (3) were conducted under the assumption that Henry's Law is valid for both the tracer constituent and TCE; therefore, the activity in each figure represents the aqueous phase concentration of the tracer or TCE. Here, the aqueous phase concentration is defined as the compound's actual concentration divided by the compound's solubility. Figure (1), which represents the methanol/TCE interactions, displays highly "non-linear" results. Since methanol is highly soluble in water, it may not follow the Henry's Law assumption. Thus, the methanol/TCE system requires further investigation to accurately quantify the portion of the non-linearities which result from TCE interactions.

Figures (1), (2), and (3) also depict Raoult's Law for these tracer/TCE systems; the aqueous phase concentration of the specified compound is given by its mole fraction since γ_i (the activity coefficient) equals 1.0. The "non-ideal" behavior of each tracer/NAPL pair

can be easily seen by examining the UNIFAC results against Raoult's Law. In all three cases, the non-idealities result in higher aqueous phase tracer concentrations than those predicted by Raoult's Law. As mandated by thermodynamics, the compounds obey Raoult's Law at mole fractions close to 1.0.

Recent experiments have used relatively small concentrations of tracer to characterize NAPL concentrations (Annable *et al.*, 1994; Pope *et al.*, 1994). Therefore, the lower left portion of each of the preceding figures represents the primary region of interest; the non-linearities which exist in the lower left region must be further analyzed. For this reason, more detailed UNIFAC runs were conducted on smaller tracer mole fraction intervals; these tracer mole fraction intervals first ranged from 0 to 0.2 and then from 0 to 0.05. The activity (aqueous phase concentration) vs. tracer mole fraction in each case was plotted for analysis in figures (4) through (9).

*Note: The notation "c" used in the text is represented by "c_w" in the UNIFAC figures.

TRACER ACTIVITY VS. MOLE FRACTION FOR METHANOL/TCE
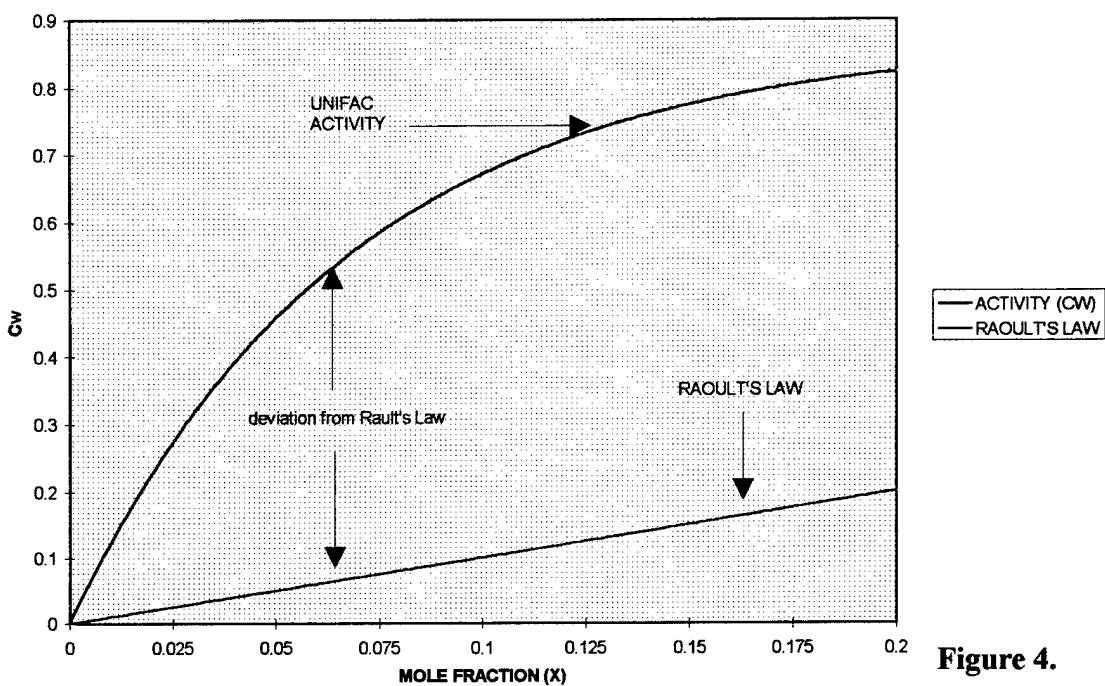
Figure 4.

TRACER ACTIVITY VS. MOLE FRACTION FOR METHANOL/TCE
(WHEN USED AS A TRACER FOR TCE NAPL)
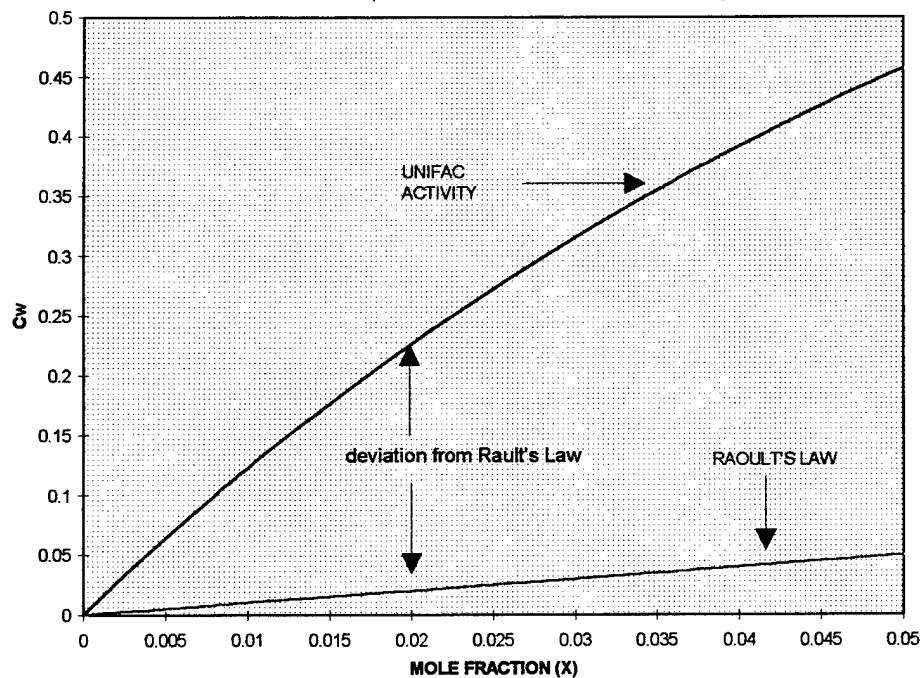
Figure 5.

TRACER ACTIVITY VS. MOLE FRACTION FOR 2-METHYL-2-HEXANOL/TCE
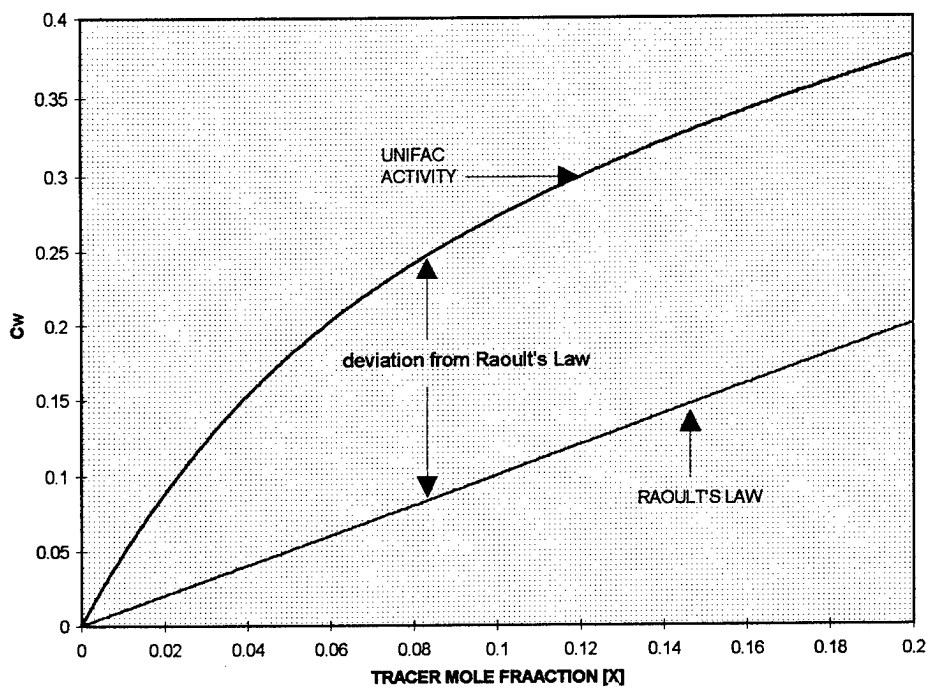
Figure 6.

UNIFAC ACTIVITY VS. MOLE FRACTION FOR 2-METHYL-2-HEXANOL/TCE
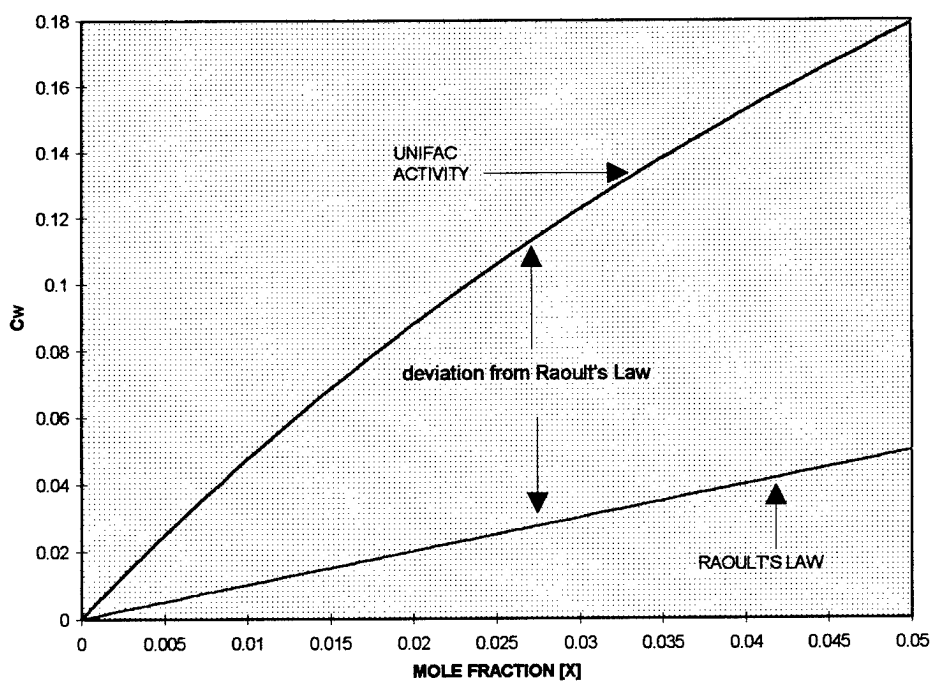
Figure 7.

UNIFAC ACTIVITY VS. MOLE FRACTION FOR 3-METHYL-2-HEXANOL/TCE
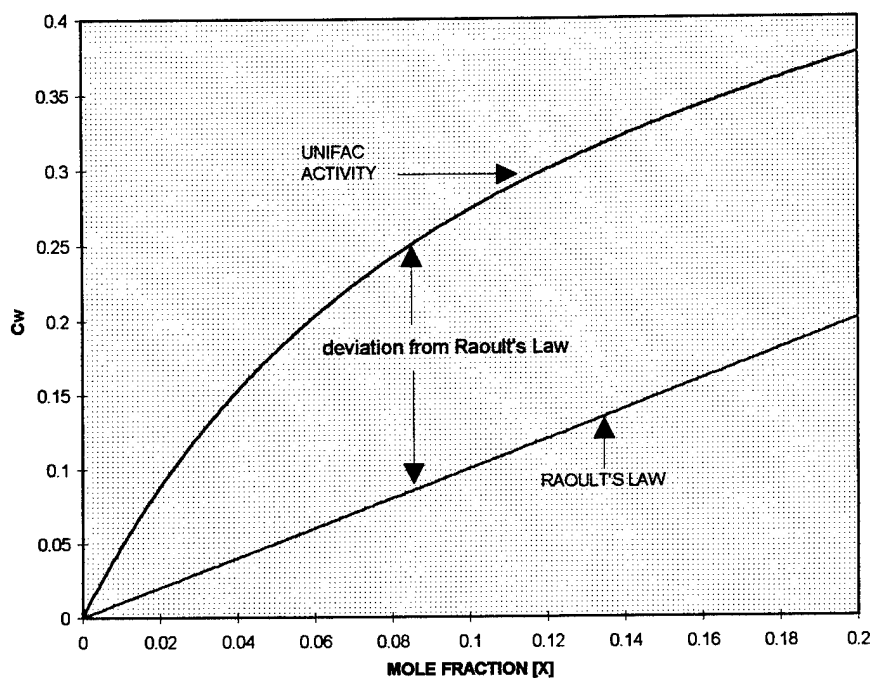
Figure 8.

UNIFAC ACTIVITY VS. MOLE FRACTION FOR 3-METHYL-2-HEXANOL/TCE
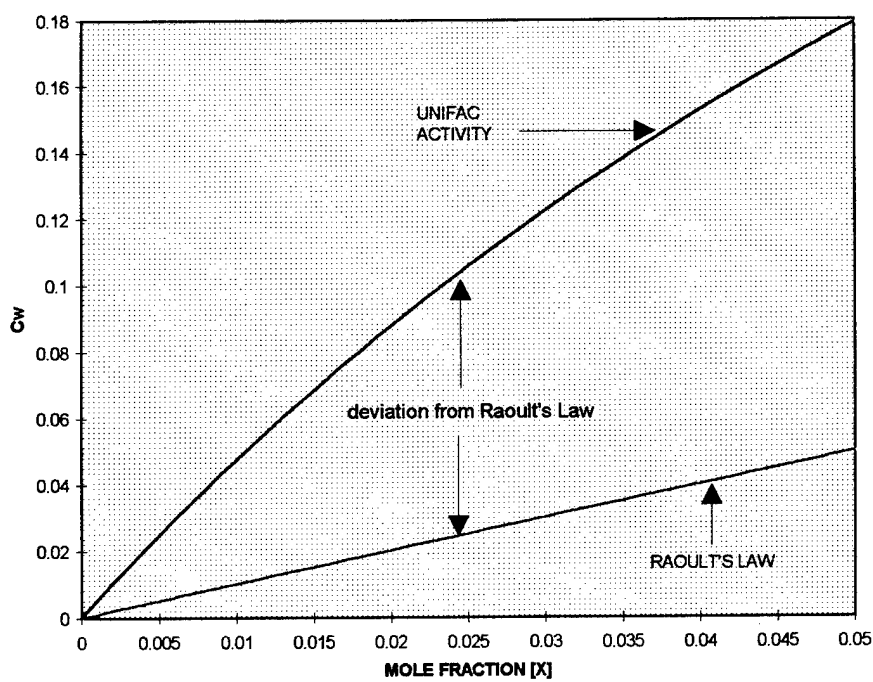
Figure 9.

Figures (4), (6), and (8) demonstrate that tracer mole fraction intervals between 0 and 0.2 display significantly non-linear behavior. The non-linear behavior is also evident between mole fraction intervals of 0 and 0.05. However, the non-linearities are not as pronounced within this smaller interval.

Freundlich Relationship

Each of the six "Aqueous Phase Concentration vs. Tracer Mole Fraction" plots was modeled to fit a Freundlich isotherm type relationship. For each tracer/TCE pair, the mole fraction interval which demonstrated a closer fit to the Freundlich model was chosen for further investigation. The following expression was approximated using data points from the UNIFAC-generated c-x relationship:

(2) $x = \beta c^{\alpha}$

$\quad$ x represents the tracer mole fraction $\left[\dfrac{moles\_tracer}{moles\_tracer + moles\_TCE}\right]$

$\quad$ c represents the aqueous phase concentration (mass in solution/solution volume)
$\qquad$ $[ML^{-3}]$

$\quad$ α represents the Freundlich exponent

$\quad$ β represents the Freundlich coefficient

The Freundlich parameters α and β were determined by minimizing the error between the UNIFAC calculated "x-c" relationship and the Freundlich approximated "x-c" relationship; a spreadsheet solver routine (Microsoft® Excel Solver) was used to vary α and β until the error between the data and the Freundlich approximation was minimized. Figures (10) through (15) display the Freundlich fits for each tracer/TCE pair for mole fraction intervals between 0 to 0.2 and 0 to 0.05. These figures plot the dependent variable, c, as the abscissa so that the shape of the approximated Freundlich relation can be easily recognized.

METHANOL/TCE UNIFAC RESULTS COMPARED WITH FREUNDLICH APPROXIMATION

MOLE FRACTION TRACER
CALC. FREUND. MOLE FRACTION

FOR MOLE FRACTIONS
BETWEEN
    0—— > 0.2
BETA= 0.29323377
ALPHA=2.50636922

X = BETA*Cw^ALPHA
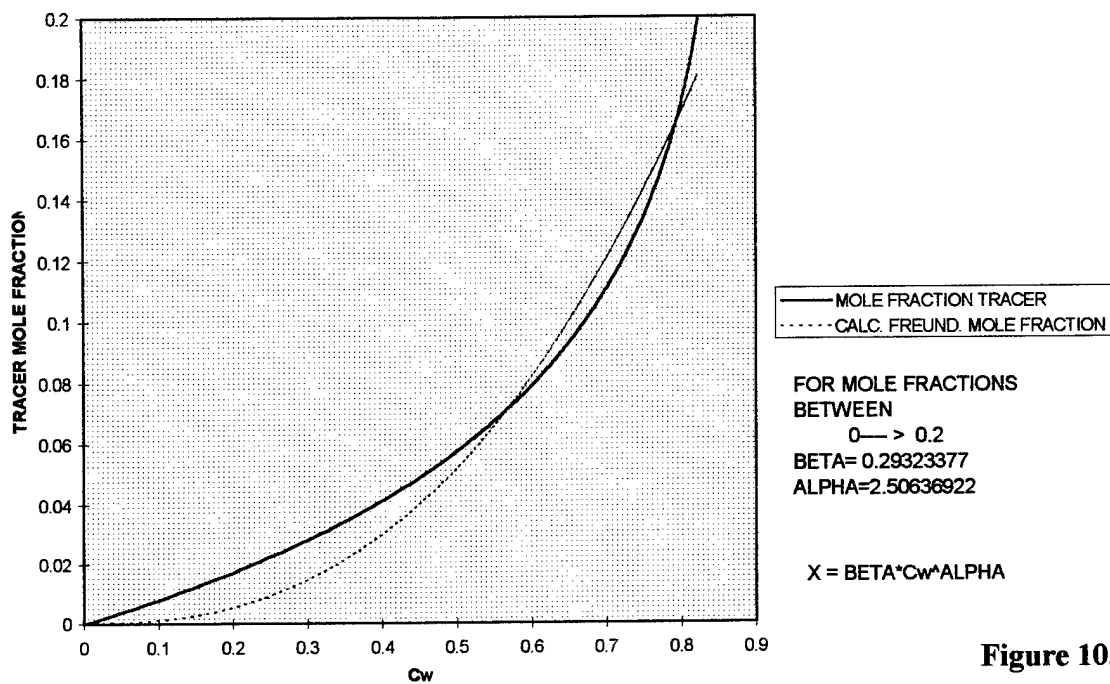
Figure 10.

METHANOL/TCE UNIFAC RESULTS COMPARED WITH FREUNDLICH APPROXIMATION

MOLE FRACTION TRACER
CALC. FREUND. MOLE FRACTION

FOR MOLE FRACTIONS
BETWEEN
    0—— > 0.05
BETA= 0.13059633
ALPHA=1.25733495

X = BETA*Cw^ALPHA
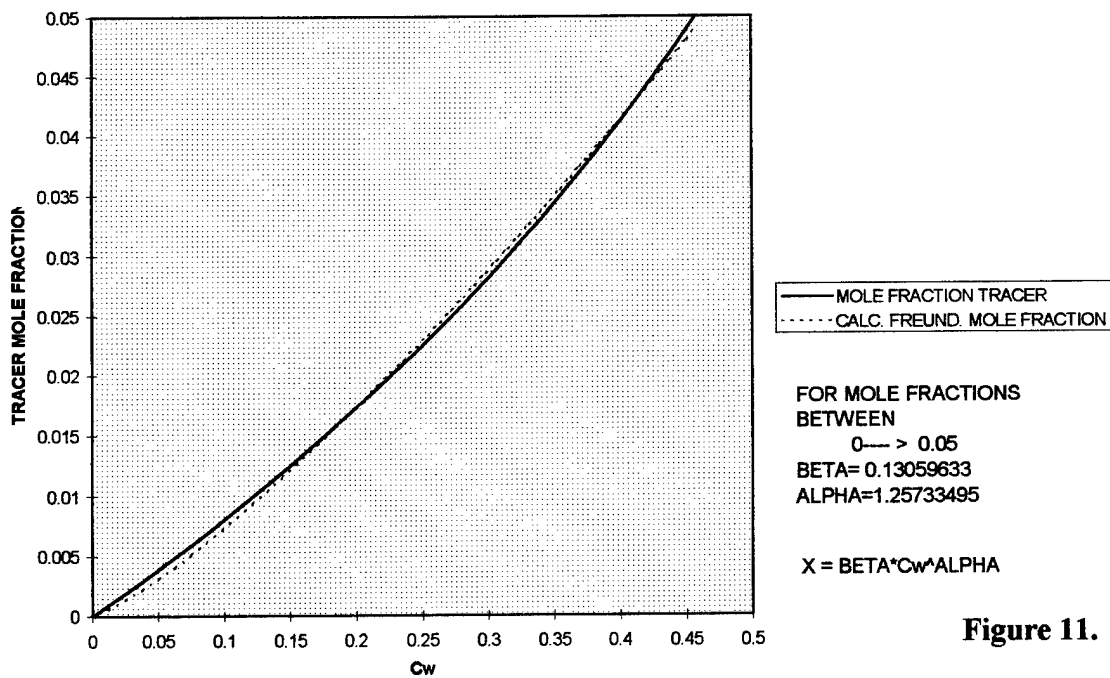
Figure 11.

**2-METHYL-2-HEXANOL/TCE UNIFAC RESULTS COMPARED WITH FREUNDLICH
APPROXIMATION**

FOR MOLE FRACTIONS
BETWEEN
        0—— > 0.2
BETA= 1.26225144
ALPA=1.92063211

X = BETA*Cw^ALPHA
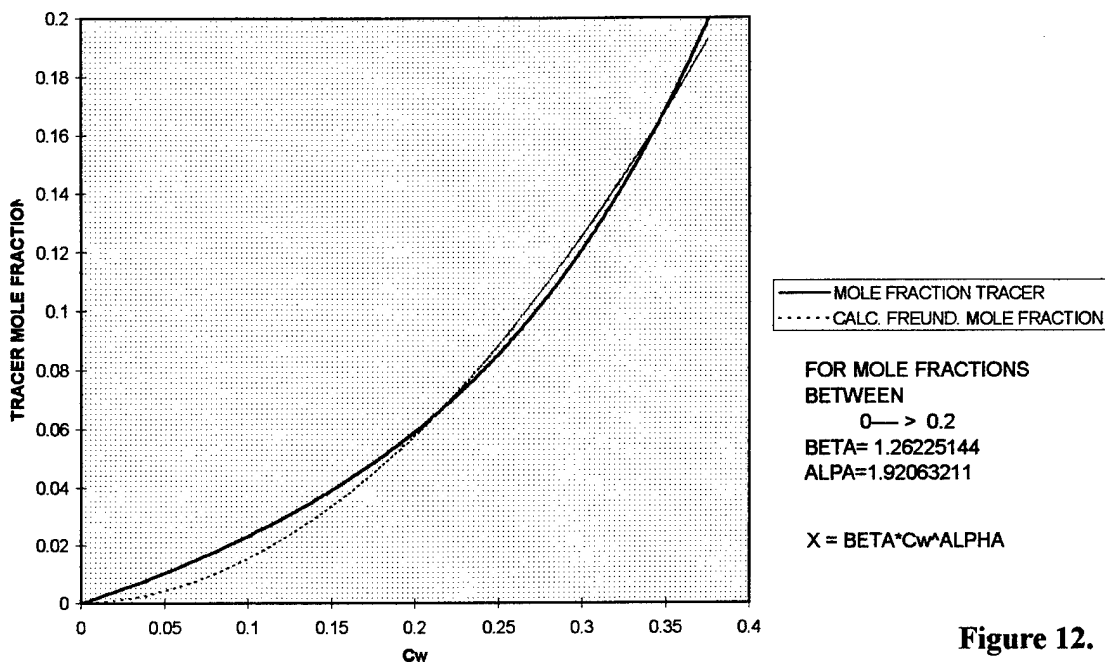
Figure 12.

**2-METHYL-2-HEXANOL/TCE UNIFAC RESULTS COMPARED WITH FREUNDLICH
APPROXIMATION**

FOR MOLE FRACTIONS
BETWEEN
        0—— > 0.05
BETA= 0.41835494
ALPHA=1.24654054

X = BETA*Cw^ALPHA
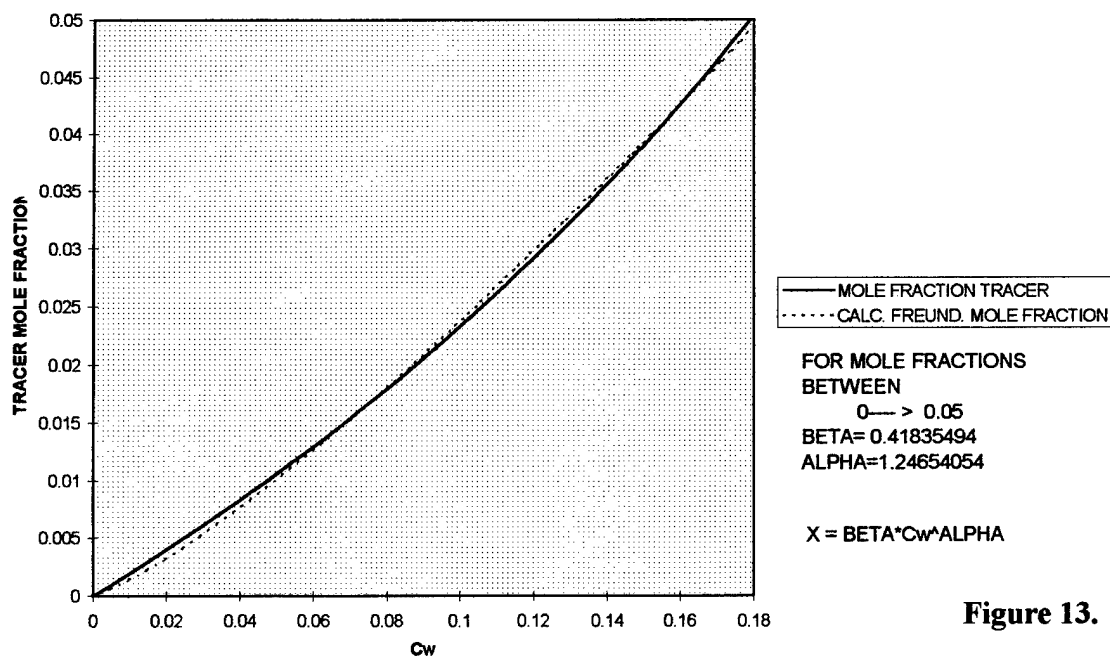
Figure 13.

3-METHYL-2-HEXANOL/TCE UNIFAC RESULTS COMPARED WITH FREUNDLICH APPROXIMATION

MOLE FRACTION TRACER
CALC. FREUND. MOLE FRACTION

FOR MOLE FRACTIONS
BETWEEN
 0—— > 0.2
BETA= 1.24395432
ALPHA=1.91242923

X = BETA*Cw^ALPHA
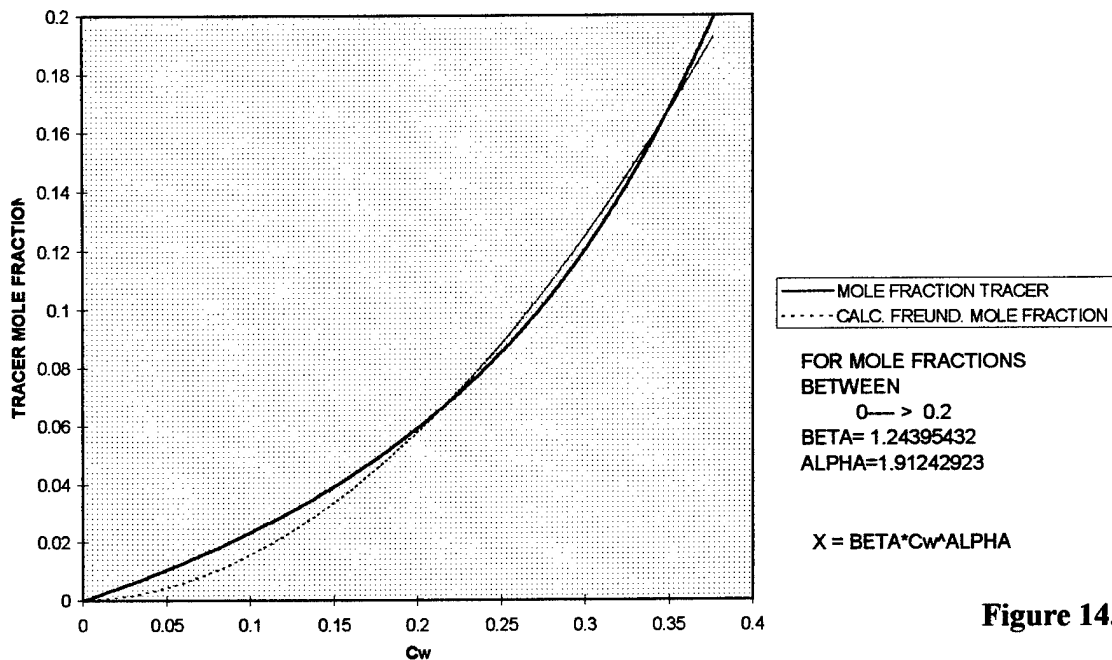
Figure 14.

3-METHYL-2-HEXANOL/TCE UNIFAC RESULTS COMPARED WITH FREUNDLICH APPROXIMATION

MOLE FRACTION TRACER
CALC. FREUND. MOLE FRACTION

FOR MOLE FRACTIONS
BETWEEN
 0—— > 0.05
BETA= 0.41668518
ALPHA=1.24437431

X = BETA*Cw^ALPHA
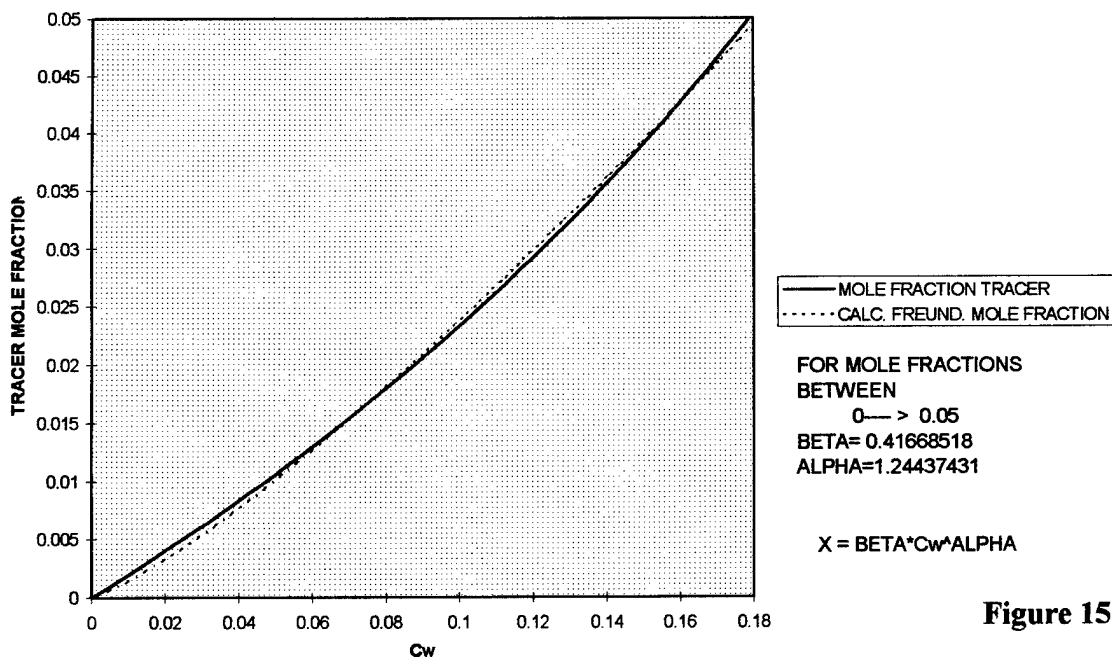
Figure 15.

In all three tracer cases, the Freundlich isotherms fit the UNIFAC data better at lower mole fraction intervals (x=0 to 0.05). The root mean-squared (RMS) approximation errors ranged from 5.112×10^{-4} to 5.683×10^{-4} for the tracers analyzed within the x=0 to 0.05 interval (see Table IV). The higher mole fraction intervals (x=0 to 0.20) did not display a UNIFAC/Freundlich correlation as favorable as that for the lower mole fraction intervals. The RMS error ranged from 4.330×10^{-3} to 8.846×10^{-3} for the tracers analyzed within the x=0 to 0.20 interval. Generally, the Freundlich calculated mole fractions fell below the UNIFAC fits at the lower portion of the mole fraction interval analyzed, while the Freundlich approximation resided above the UNIFAC results for the upper end of the analyzed mole fraction interval. The Freundlich approximation for the mole fraction interval x=0 to 0.05 was chosen for further analysis because of its close approximation to the UNIFAC results within this interval. Appendix (B) includes a sample spreadsheet solution for 2-methyl-2-hexanol/TCE (for x=0 to 0.05) and the method used to calculate the RMS error.

Table IV. Tracer "β" and "α" Values With Error Approximations With Associated RMS Errors

Tracer/TCE Pair	x Interval	β	α	RMS Error
Methanol	0 → 0.2	.29324	2.50637	8.8458×10^{-3}
	0 → 0.05	.13060	1.25733	5.6830×10^{-4}
2-Methyl-2-Hexanol	0 → 0.2	1.26225	1.92063	4.3418×10^{-3}
	0 → 0.05	.41836	1.24654	5.1531×10^{-4}
3-Methyl-2-Hexanol	0 → 0.2	1.24395	1.91243	4.3298×10^{-3}
	0 → 0.05	.41669	1.24437	5.1122×10^{-4}

Relation Between Mole Fraction (x) and Sorbed Concentration (q)

Although the equation $x=\beta c^{\alpha}$ represents a Freundlich type equation, it must be related to the "classic" Freundlich isotherm so that its meaning can be fully understood. The "classic" Freundlich isotherm may be expressed in terms of sorbed concentrations:

(3) $q = Bc^A$

> q represents the sorbed concentration (mass sorbed/solution volume) $[ML^{-3}]$.
>
> c represents the aqueous phase concentration (mass in solution/solution volume) $[ML^{-3}]$.
>
> "B" and "A" represent Freundlich parameters.

The relationship between the "classic" Freundlich isotherm and that which was solved during this investigation can be expressed using the following general analysis:

(4) $x = \beta c^\alpha$

> as determined by the approximations to the UNIFAC results (same as equation (2), but repeated here for complete analysis). Assuming that only one tracer exists in the "column,"

$$(5) \quad x = \frac{moles\_tracer}{moles\_tracer + moles\_NAPL}.$$

> Further, assuming no gas phase is present,

(6) $s_n + s_w = 1$

> where s_n and s_w represent the NAPL (oil) and aqueous phase saturations, respectively. The tracer mass may be related to the water volume present with the following equation:

$$(7) \quad q = \frac{mass\_tracer\_in\_oil\_per\_bulk\_volume}{s_w},$$

> where q $[ML^{-3}]$ represents the local storage of the tracer in the oil (NAPL) phase.

Assuming that the tracer's presence does not significantly affect the water saturation, equation (7) may be written using equation (5):

$$(8) \quad q= \left\{ \frac{M.W._T}{s_w}(moles\_NAPL\_per\_bulk\_volume) \right\} \left\{ \frac{x}{1-x} \right\},$$

where M.W.$_T$ represents the molecular weight of the tracer [M/mole].

The tracer's presence should not significantly affect the water saturation, s_w, since s_w is significantly higher than s_n (95% compared to 5%). Thus, even a significant change in s_n (i.e., 20%) will only result in a minute change in s_w (1.05%).

$$(9) \quad moles\_NAPL\_per\_bulk\_volume = \frac{\eta s_n \rho_n}{M.W._n}.$$

η represents porosity $\left[\dfrac{void\_volume}{bulk\_volume} \right]$.

ρ_n represents the NAPL density [ML^{-3}].

M.W.$_n$ represents the molecular weight of the NAPL [M/mole] .

Letting

$$(10) \quad \xi = \frac{M.W._T}{s_w}(moles\_NAPL\_per\_bulk\_volume),$$

$$(11) \quad q= \xi \left(\frac{x}{1-x} \right).$$

Combining equations (4) and (11),

$$(12) \quad q= \xi \frac{\beta c^\alpha}{1 - \beta c^\alpha}.$$

The solution represented by equation (12) does not yield a "simple" Freundlich relationship which correlates "B" and "β" or "A" and "α." Therefore, the spreadsheet solver routine was used to solve for B and A based upon equations (3) and (11).

$$(13) \quad Bc^A = \xi \frac{x}{1-x}.$$

Letting

(14) $B' = \dfrac{B}{\xi}$,

(15) $B'c^A = \dfrac{x}{1-x}$.

Letting $\psi = B'c^A$, the Microsoft® Excel spreadsheet solver routine was used to calculate a "ψ" value for each x. Specifically, the routine varied the values of B' and A until the minimum error was reached between ψ and $\dfrac{x}{1-x}$. Finally, "B" was found by evaluating B' with appropriate values of ξ for each tracer/TCE pair. The TCE molecular weight and density used for the ξ calculations were 131.5 g/mole and 1.46 g/ml, respectively. Table V provides the values used to determine the Freundlich parameters for each tracer/TCE pair.

Table V. Values Used to Determine Freundlich Isotherm Parameters

Tracer	M.W._T (g/mole)	ξ (g/ml)	B'	B	A	RMS Error
Methanol	32	.0058622	.14143	.82911	1.29760	6.67×10^{-4}
2-Methyl-2-Hexanol	116	.0212505	.47007	9.98927	1.28623	6.14×10^{-4}
3-Methyl-2-Hexanol	116	.0212505	.46806	9.94644	1.28392	6.10×10^{-4}

Appendix (C) contains a sample spreadsheet solution for 2-methyl-2-hexanol/TCE which solves for B and A based on β, α, and ξ.

CHAPTER 3
COMBALL MODEL

Overview

The COMBALL program, which is written in FORTRAN, determines the effluent
response curve for general multi-well injection tests (Wise, 1985). For the purposes of
this investigation, the model solved the streamline advective transport equation for a soil
column into which a pulse input of a sorbing tracer was injected at one end. Although
COMBALL can determine the effluent response curves for sorption which follows either
the Langmuir or Freundlich isotherm, the routine only modeled the effluent response curve
for the unfavorable Freundlich isotherm during this investigation. COMBALL solves the
streamline advective transport equation which corresponds to the Freundlich isotherm
using the method of characteristics. This solution, coupled with an appropriate
description of the system's hydraulics, is utilized by the COMBALL model to determine
the effluent concentration through time. The COMBALL program is attached as
Appendix (D).

Advective Transport Equation

The advective transport equation is critical in the determination of the effluent response
curve for a given tracer/NAPL pair. For an arbitrary partitioning tracer, the general form
of the transport equation is represented by the following (after Wise, 1985; Rainwater *et
al.*, 1987; Wise and Charbeneau, 1994):

$$(16) \quad \frac{\partial q}{\partial t} + \frac{\partial c}{\partial t} + \frac{\partial c}{\partial \tau} = 0$$

$\partial q/\partial t$ represents the temporal change in tracer storage in the NAPL (immobile)
phase $[ML^{-3}T^{-1}]$.

$\partial c/\partial t$ represents the temporal change in tracer storage in water $[ML^{-3}T^{-1}]$.

$\partial c/\partial \tau$ represents the divergence of the tracer advective flux through the colum. τ
represents travel time $[T]$ and expresses distance in the form of time
$(\tau = x_L/v_p)$; it relates the pore water velocity, v_p $[LT^{-1}]$, and the time it takes
the tracer to travel along a streamline to a distance "x_L" along the
streamline $[L]$. τ is used so that the hydraulics and chemistry of the

advective transport equation can be treated in an efficient and consistent manner.

COMBALL is predicated on the local equilibrium assumption (LEA) and on steady hydraulics throughout the test. Based on the LEA,

$$(17) \quad \frac{\partial q}{\partial t} = \left(\frac{\partial q}{\partial c}\right)\left(\frac{\partial c}{\partial t}\right)$$

and

$$(18) \quad \left(1 + \frac{\partial q}{\partial c}\right)\frac{\partial c}{\partial t} + \frac{\partial c}{\partial \tau} = 0.$$

This version of the transport equation demonstrates its quasi-linear, hyperbolic nature.

Characteristic Solution to the Advective Transport Equation

Utilizing the Method of Characteristics, the following base characteristics apply at the extraction well, and can be represented mathematically in the τ-t plane (Wise, 1985):

$$(19) \quad \frac{dt}{d\tau}\bigg|_c = 1 + \frac{dq}{dc} \qquad \text{isochore.}$$

The "isochore" characteristic equation applies for paths of constant concentration leaving the t and τ axes. Since characteristics are not allowed to cross, a "shock" condition results whenever characteristics meet. These concentration "jumps" in the τ-t plane satisfy the following:

$$(20) \quad \frac{dt}{d\tau}\bigg|_{STEP} = 1 + \frac{\Delta q}{\Delta c} \qquad \text{shock.}$$

Using the Freundlich relation in equation (3), equations (19) and (20) become:

(21) $\left.\dfrac{dt}{d\tau}\right|_{c} = 1 + ABc^{(A-1)}$ isochore.

(22) $\left.\dfrac{dt}{d\tau}\right|_{STEP} = 1 + Bc^{(A-1)}$ shock

The shock equation represents the curve in the τ-t plane in which the wave steps from a composition of (c, Bc^{A}) to $(0, 0)$. This condition will be met for all effluent results presented in this investigation.

Application of Characteristic Solution to Streamline Transport Problem

The three tracers which were analyzed in this investigation were fitted to unfavorable Freundlich isotherms. Therefore, this investigation made use of the method of characteristics solution through the COMBALL subroutine for an unfavorable isotherm (see Appendix (D)). For an injection time of Δt, the shape of the characteristic curve for an unfavorable isotherm (A>1) resembles figure (16):
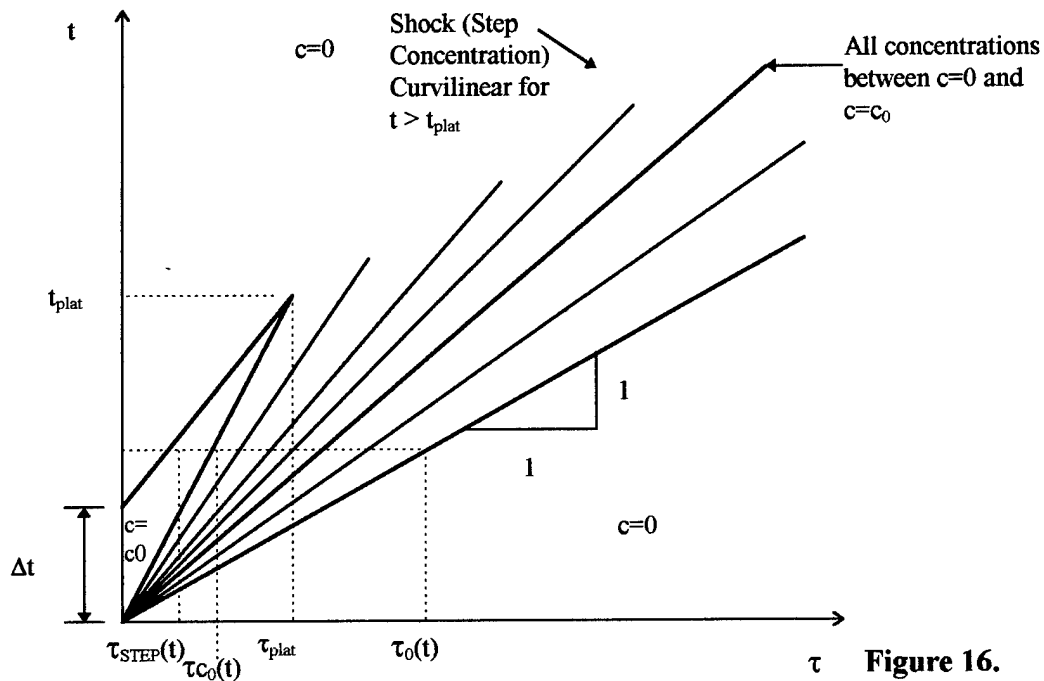
Figure 16.

For A>1, seven equations govern the characteristic solution. A description of the equations and the areas to which they apply are the following:

As can be seen in figure (16), the endpoint (τ_{plat}, t_{plat}) represents the intersection of the shock wave of the c_0 and $c=c_0$ isochores. These points are described by equations (23) and (24):

$$(23) \quad \tau_{plat} = \frac{\Delta t}{Bc_0^{(A-1)}(A-1)}$$

$$(24) \quad t_{plat} = \frac{\left(1 + ABc_0^{(A-1)}\right)\Delta t}{Bc_0^{(A-1)}(A-1)}$$

Between the c=0 and the $c=c_0$ isochores, the following equation provides the concentration at any point (τ, t):

$$(25) \quad c = \left(\frac{t-\tau}{AB\tau}\right)^{\left(\frac{1}{A-1}\right)}$$

The following equations determine the τ values at which an isochrone (line of constant time) passes the $c=c_0$ and the c=0 isochores, respectively:

$$(26) \quad \tau_0(t) = t$$

$$(27) \quad \tau_{c_0}(t) = \frac{t}{\left(1 + ABc_0^{(A-1)}\right)}$$

$\tau_{STEP}(t)$ is defined as the τ value at which an isochrone, t, crosses the step concentration and can be found by the following:

(28) For $t \leq t_{plat}$: $\tau_{STEP}(t) = \dfrac{(t - \Delta t)}{1 + Bc_0^{(A-1)}}$

(29) For $t > t_{plat}$: $\tau_{STEP}(t)$ results from solving equation (29.a) using Newton's Method. Equation (29.b) results.

(29.a) $G(\tau) = \tau^{\left(\frac{A-1}{A}\right)} - t\tau^{\left(\frac{-1}{A}\right)} + I^{\left(\frac{A-1}{A}\right)}$

(29.b) $G'(\tau) = \left(\dfrac{A-1}{A}\right)\tau^{\left(\frac{-1}{A}\right)} + \dfrac{1}{A}t\tau^{-\left(\frac{A+1}{A}\right)}$

(29.c) $I = \dfrac{\Delta t c_0}{(A-1)} A^{\left(\frac{A}{A-1}\right)} B^{\left(\frac{1}{A-1}\right)}$

Again, the preceding equations are those which are utilized in the COMBALL model for an unfavorable Freundlich isotherm.

Fractional Breakthrough Curve

A "theoretical" fractional breakthrough curve was used to determine the effluent results from the COMBALL routine. The solution to the advection-dispersion (A-D) equation was used to generate the fractional breakthrough curve for the simulated, one-dimensional, laboratory column experiment. The A-D equation for a pulse input of time Δt is the following:

(30) $F = \dfrac{1}{2}\left[erfc\left(\dfrac{L - v_x t}{2\sqrt{D_L t}}\right) + \exp\left(\dfrac{v_x L}{D_L}\right)erfc\left(\dfrac{L + v_x t}{2\sqrt{D_L t}}\right)\right]$ (Fetter, p.458).

F represents the decimal fraction of the injected tracer concentration observed at the end of the column.

L represents the column length [L].

v_x represents the average linear pore water velocity [LT^{-1}].

t represents the time after tracer injection [T].

D_L represents the dispersion coefficient $[L^2 T^{-1}]$.

Since the second "erfc" term quickly approaches zero through time, the A-D equation can be approximated as the following:

(31) $\quad F = \dfrac{1}{2} \, [\, erfc(\dfrac{L - v_x t}{2 * \sqrt{D_L t}})\,]$.

Equation (31) describes the system hydraulics for a column of length "L." Any distance which is less than L can now be expressed in terms of pore volume; the length of the column equals 1 pore volume. Remembering that $x_L = v_x \tau$, the term τ replaces the "$v_x t$" term by taking the velocity through the column as one pore volume per pore volume injected. Thus, equation (31) can be expressed as the following:

(32) $\quad F = \dfrac{1}{2} \, erfc\left(\dfrac{1 - \tau}{2\sqrt{D_L \tau}}\right)$.

For a dispersion coefficient of .01 $\left[\dfrac{pore\_volumes^2}{pore\_volume}\right]$, the fractional breakthrough curve shown in figure (17) results.

A-D SOLUTION FOR FRACTIONAL BREAKTHROUGH CURVE
PORE VOLUME=1, D=.01
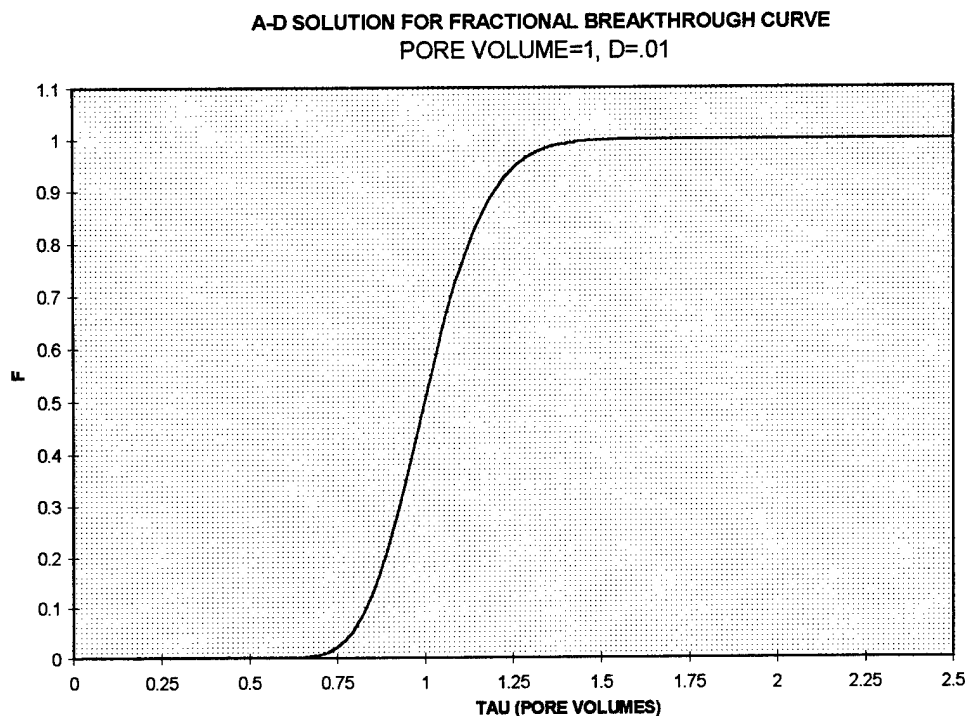
Figure 17.

COMBALL Simulations

Simulations were conducted for methanol, 2-methyl-2-hexanol, and 3-methyl-2-hexanol.

TCE was again used as the NAPL. The Freundlich coefficients based on the UNIFAC

results were used as model inputs. As was stated in the "UNIFAC" portion of this paper,

the tracer mole fraction interval between 0 and 0.05 was used for each simulation since

there was minimal error between the UNIFAC results and the Freundlich solution.

Simulations were completed with a maximum time of 10 and a time interval of .025

between data points. In addition, all COMBALL simulations utilized the same fractional

breakthrough curve shown in figure (17). Linear approximations and sensitivity analyses

were then conducted for the tracers. A sample COMBALL input and output file for 2-

methyl-2-hexanol/TCE is attached as Appendix (E).

The initial runs were conducted using c_0 values corresponding to mole fractions of 0.025

(as determined by UNIFAC). Figure (18) displays the results for the three tracers plus a

theoretical "non-reactive" tracer. Table VI provides a summary of the parameters which

were entered into the COMBALL data file for a tracer mole fraction of 0.025.

TRACER EFFLUENT CURVES USING FREUNDLICH APPROXIMATION
FRACTIONAL BREAKTHROUGH CURVE GENERATED BY THE A-D EQUATION
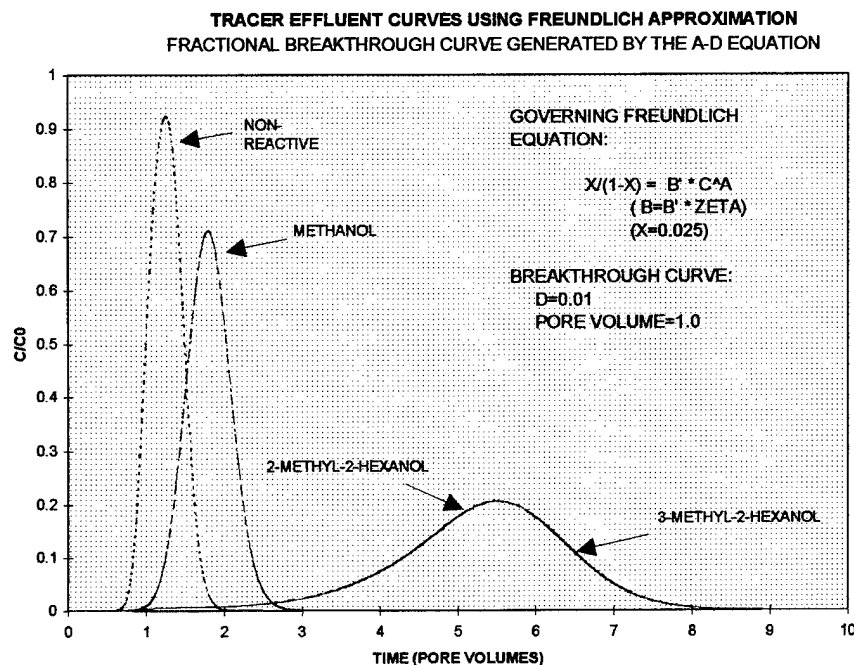
Figure 18.

Table VI. Freundlich Parameters for Tracer/NAPL Mole Fraction = 0.025

Tracer/TCE Pair	B	A	c_0
Non-Reactive	0	1	1
Methanol	.82911	1.29760	.27262
2-Methyl-2-Hexanol	9.98927	1.28623	.10581
3-Methyl-2-Hexanol	9.94644	1.28392	.10572

The tracer effluent curves demonstrate that 2-methyl-2-hexanol and 3-methyl-2-hexanol are significantly retarded by the TCE as compared to the methanol. Since the only structural difference between 2-methyl-2-hexanol and 3-methyl-2-hexanol is the location of the methyl group, they perform almost identically in the presence of TCE. The fact that their curves are indistinguishable in Figure (18) verifies this fact. As was stated in the "Procedure" portion of this paper, methanol is often used as the "non-reactive" tracer.

Compounds which are highly polar are often used as non-reactive tracers since they do not tend to partition into the NAPL. Non-polar tracers, however, partition into the NAPL more easily and have higher retardation factors. Figure (18) demonstrates that although methanol is highly polar and is typically used as the non-reactive tracer, some partitioning into TCE takes place. This occurrence ultimately affects the TCE saturation calculation. (The effect of this occurrence will be further discussed in Chapter 4 of this paper.)

CHAPTER 4
ANALYSIS OF RESULTS

Moment Analysis

As described in Pope *et al*. (1994) the "Method of First Moment" theory is typically used to determine NAPL saturation in partitioning interwell tracer tests. The retardation factor, R_f, and average NAPL saturation, s_n, in the subsurface (or "column" during this investigation) are both based on the first moments of the partitioning and non-partitioning tracers:

$$(33) \quad R_f = 1 + \frac{Ks_n}{1-s_n} = \frac{\bar{t}_p}{\bar{t}_{nr}}.$$

$\bar{t}_{nr}$ represents the first moment of the non-partitioning tracer [T].

$\bar{t}_p$ represents the first moment of the partitioning tracer [T].

K represents the partition coefficient of the partitioning tracer into the NAPL.

Since figure (18) demonstrates that methanol does not truly represent a "non-reactive" tracer, the retardation factor will not reflect the actual retardation which takes place in the column or aquifer. The predicted TCE saturation, in turn, will reflect a lower value than that which actually exists; this is demonstrated by the analysis described below.

The first moments of the theoretical non-reactive tracer, methanol, 2-methyl-2-hexanol, and 3-methyl-2-hexanol were calculated during this investigation to compare the effects of differing moments on the TCE saturation calculation.

The *i*th moment, m_i, of the effluent response curve is given by the following equation:

$$(34) \quad m_i = \int_0^\infty t^i \left(\frac{c(t)}{c_0} \right) dt.$$

For this investigation, the 0th moment represents the total amount of mass which exits the column for the case in which the injected mass equals Δt pore volumes. The 1st moment represents the time that the center of mass exits the column.

For an injection time of 0.5 pore volumes, the theoretical non-reactive tracer should result in a 0th moment of .5 pore volumes and a 1st moment of 1.25 pore volumes. The trapezoidal rule was used to perform the effluent curve integration; thus some error results from this approximation. Table VII represents a compilation of each tracer's 0th and 1st moments and their associated errors (when they could be quantified).

Table VII. Tracer/TCE Effluent Moment Approximations

Tracer	Moment #	Value	% Error
Non-Reactive	M_0	0.5	0%
	M_1	1.259999	0.8%
Methanol	M_0	.500454	0.0908%
	M_1	1.811421	---
2-Methyl-2-Hexanol	M_0	.512428	2.4856%
	M_1	5.418368	---
3-Methyl-2-Hexanol	M_0	.512498	2.4996%
	M_1	5.432651	---

Effect of Using the "Non-Partitioning" Methanol Assumption

This portion of the investigation focused on the potential error which results from the assumption that methanol acts as a non-partitioning tracer. The method as described below was used to quantify the effect on the TCE saturation calculation using methanol as the non-reactive tracer.

First, the retardation factor, R_f, was evaluated using the respective $\bar{t}_p$ and $\bar{t}_{nr}$ values for one partitioning tracer/ideal non-reactive tracer pair. Because all moment calculations resulted in systematic moment overestimations, these calculated values were used to maintain consistency throughout the error determination. Since the model conditions assumed a TCE saturation, s_n, of 5% this value was used to calculate a partition coefficient, K. The partition coefficient is constant under the linear partitioning

assumption and thus can be used in subsequent calculations. Next, the retardation factor for each partitioning tracer/methanol pair was calculated. The corresponding TCE saturation was then determined by utilizing the partition coefficient found with the theoretical tracer and the retardation factor for the tracer/methanol comparison. Finally, the error between the "simulated" TCE saturation and that found with methanol was calculated. Tables VIII and IX present the results.

Table VIII. NAPL Saturation Error When Using Methanol as the "Non-Reactive" Tracer with 2-Methyl-2-Hexanol

Non-Reactive Tracer	$\bar{t}_p$	$\bar{t}_{nr}$	K	R_f	S_n
Ideal	5.418368	1.259999	62.7	4.30	.05
Methanol	5.418368	1.811421	62.7	2.991	.0303119
				S_n ERROR	39.38%

Table IX. NAPL Saturation Error When Using Methanol as the "Non-Reactive" Tracer with 3-Methyl-2-Hexanol

Non-Reactive Tracer	$\bar{t}_p$	$\bar{t}_{nr}$	K	R_f	S_n
Ideal	5.432651	1.259999	81.9	4.31	.05
Methanol	5.432651	1.811421	81.9	2.999	.0353263
				S_n ERROR	29.35%

These results demonstrate that the TCE saturation can be underestimated by almost 40% under the given model conditions; thus, small differences in the first moments of an ideal non-reactive tracer and actual tracers used for non-reactive tracers may possibly result in significant errors. This area deserves further investigation, however, since methanol is soluble in water and may not completely follow the investigation assumptions.

Effect of Linear Partitioning Assumption

Another assumption which is typically used in interwell partitioning tracer tests is that the tracer/NAPL pair interacts linearly. To analyze this assumption, the Freundlich approximation to the UNIFAC-calculated activities was compared to a linear approximation to the UNIFAC-calculated activities. The linear approximation was determined by solving the equation $B'c_0 = \dfrac{x}{1-x}$ for B'. This equation is similar to equation (15); the only difference is that the Freundlich exponent, A, is set to 1.0. The same c_0 which was determined for each Freundlich run was used for consistency with the previously discussed observations. Again, B' was converted to B using $B = B'\xi$. The same ξ values (see Table V) were used to convert B' to B as were used when calculating the Freundlich coefficient. The linear parameters determined using the method described above are printed in Table X.

Table X. Linear Approximations to UNIFAC-Calculated Tracer/TCE Interactions

Tracer/TCE Pair	A	B'	B	c_0
Methanol	1.0	.09405	.55136	.27262
2-Methyl-2-Hexanol	1.0	.24233	5.14963	.10581
3-Methyl-2-Hexanol	1.0	.24254	5.15404	.10572

Figures (19), (20), and (21) display the results of each tracer when compared with its linear approximation. Each comparison also includes a plot of the theoretical "non-reactive" tracer.

COMPARISON BETWEEN FREUNDLICH AND LINEAR APPROXIMATIONS FOR
METHANOL/TCE
FRACTIONAL BREAKTHROUGH CURVE GENERATED BY THE A-D EQUATION

Figure 19.

FREUNDLICH VS. LINEAR APPROXIMATIONS FOR 2-METHYL-2-HEXANOL/TCE
FRACTIONAL BREAKTHROUGH CURVE GENERATED BY THE A-D EQUATION

Figure 20.

**FREUNDLICH VS. LINEAR APPROXIMATIONS FOR 3-METHYL-2-HEXANOL
FRACTIONAL BREAKTHROUGH CURVE GENERATED BY THE A-D EQUATION**
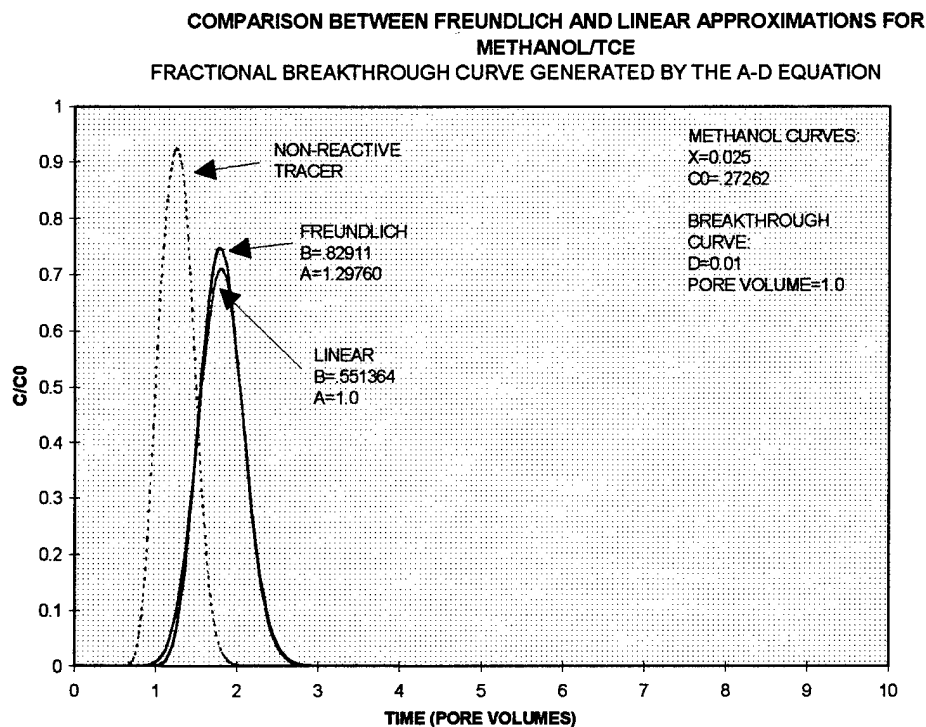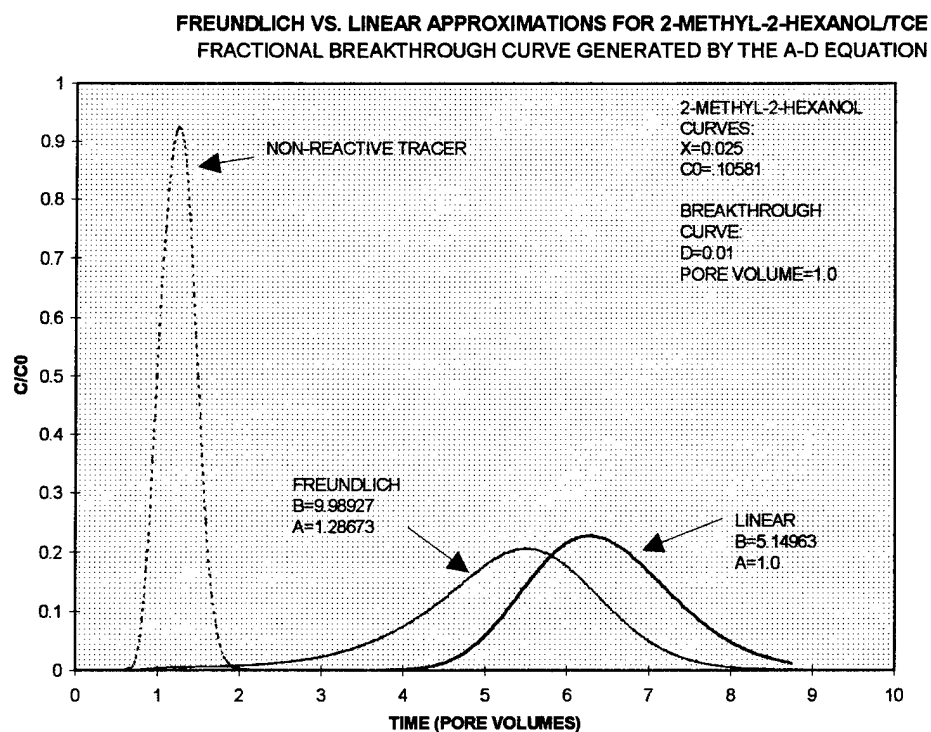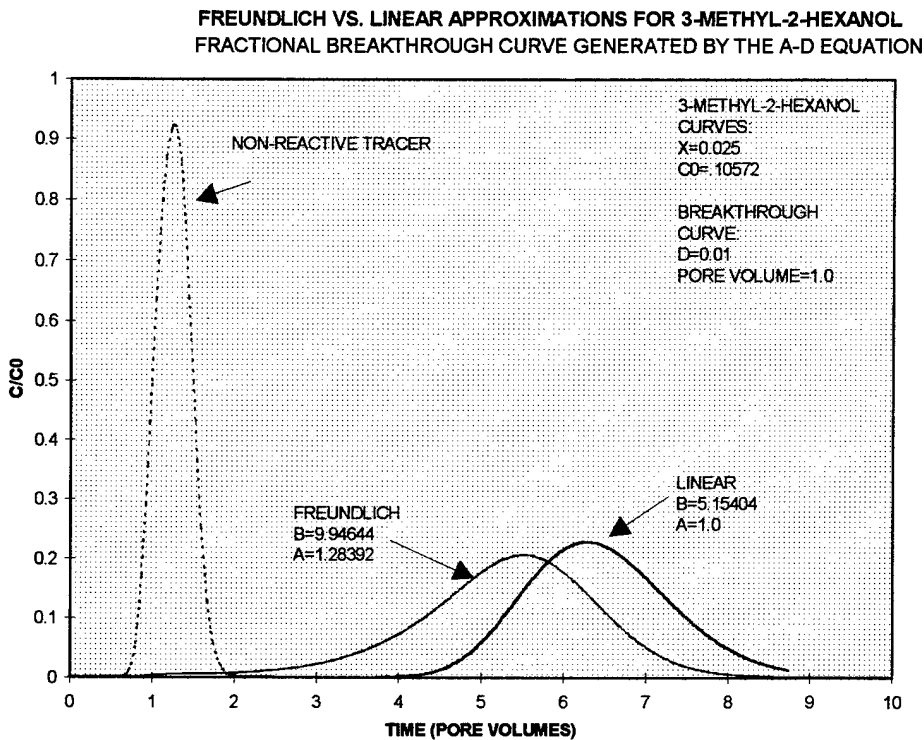
Figure 21.

Figures (19), (20), and (21) show that the linear approximations do not yield the same effluent response curves as the Freundlich approximations. The 1st moment calculations demonstrate the differences between the time of the center of mass between each tracer comparison (see Table XI).

Table XI: 1st Moment Differences Between Freundlich and Linear Approximations

Tracer	Freundlich M_1	Linear M_1	ΔM_1
Methanol	1.811421	1.816846	.005425
2-Methyl-2-Hexanol	5.418368	6.359433	.941065
3-Methyl-2-Hexanol	5.432651	6.362715	.930064

Figures (19), (20), and (21) simply demonstrate that a linear approximation does not yield the same effluent curve as the Freundlich approximation. These results, however, cannot

be used to determine the "linear assumption" effects on TCE saturation calculations. To correctly quantify the error between TCE saturation calculations, the method as described below was used.

First, each Freundlich effluent curve was treated as the "simulated" column test result. Therefore, a linear isotherm must be deduced which will provide the same first moment (M_1 or $\bar{t}_p$) as that produced by the simulated (Freundlich) effluent curve. The corresponding linear coefficient, B, was determined by subtracting the first moment of the non-reactive tracer from the first moment of the tracer effluent response curve. Mathematically, this is represented by the following equation:

(35) $B_{linear} = M_{1(Freundlich)} - M_{1(non-reactive)}$.

A corresponding ξ value was then obtained using the B obtained by equation (35) and B' obtained by the original linear spreadsheet solver solution. Finally, a corresponding NAPL saturation, s_n, was determined by solving the following equation:

(36) $s_n = \dfrac{\xi M.W._n}{M.W._T \, \eta \rho_n + \xi M.W._n}$.

This equation is a combination of equations (6) through (9) and is expressed to solve for s_n. Table XII presents the difference in TCE saturation determinations:

Table XII. Linear Assumption Effects on TCE Saturation Calculations For Tracer/TCE Pairs

(a) Methanol:

Effluent Curve	B	A	B'	ξ (g/ml)	s_n
Simulated	.82911	1.25733	.14143	.0058622	.05
Equivalent Linear	.56142	1.0	.094054	.0059694	.04845
				s_n Error:	3.10%

**Table XII (cont.). Linear Assumption Effects on TCE Saturation
Calculations For Tracer/NAPL Pairs**

(b) 2-Methyl-2-Hexanol:

Effluent Curve	B	A	B'	ε(g/ml)	s_n
Simulated	9.98927	1.28623	.47007	.0212505	.05
Equivalent Linear	4.16837	1.0	.24233	.172012	.03890
				s_n Error:	22.20%

(c) 3-Methyl-2-Hexanol

Effluent Curve	B	A	B'	ε(g/ml)	s_n
Simulated	9.94644	1.28392	.46806	.0212505	.05
Equivalent Linear	4.18265	1.0	.24254	.0172452	.03899
				s_n Error:	22.02%

Figures (22), (23), and (24) compare the "simulated" (Freundlich) effluent curves to the linear approximations for the tracer/TCE pairs. In addition, comparisons between the 1st moments are also shown. In each comparison, the 1st moment of the linear approximations do not match that of the Freundlich simulated effluent curve exactly. These disparities can be attributed to the fact that the calculations utilized the trapezoidal approximation to determine the 1st moments. The errors between the two approximations, however, are all within 0.5 %. Thus, the s_n comparisons between the tracer effluent curves compared with their linear approximations represent the expected errors which result from a linear analysis of partitioning tracer data.

LINEAR APPROXIMATION TO FREUNDLICH 1ST MOMENT FOR METHANOL/TCE SYSTEM
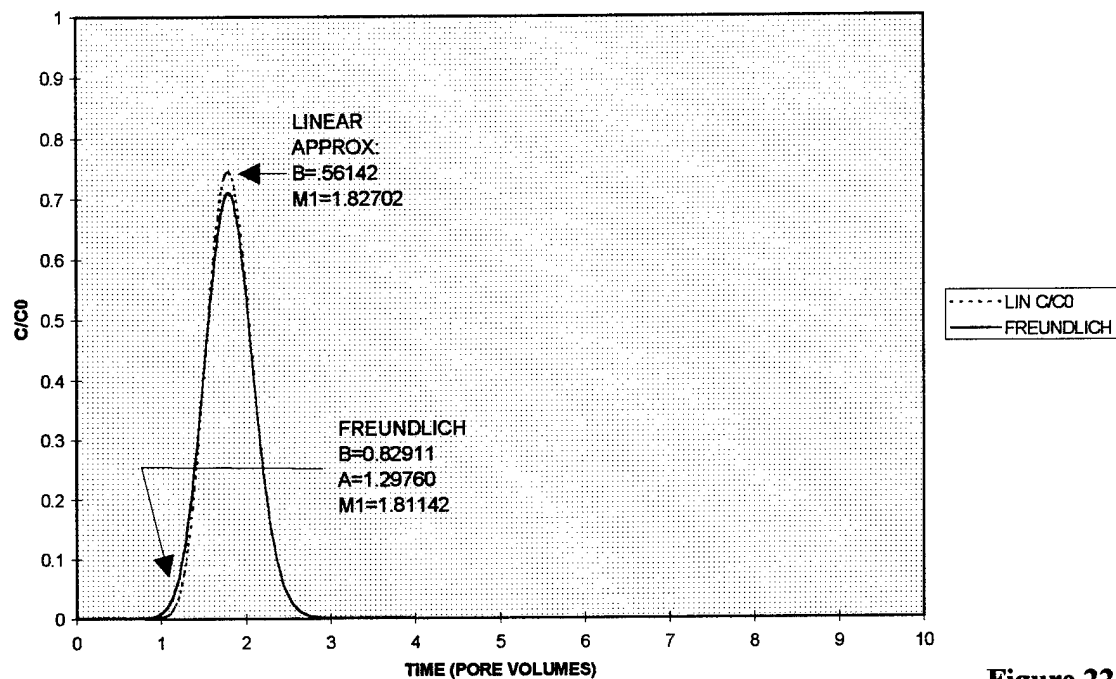
Figure 22.

LINEAR APPROXIMATION TO FREUNDLICH 1ST MOMENT FOR 2-METHYL-2-HEXANOL/TCE
SYSTEM
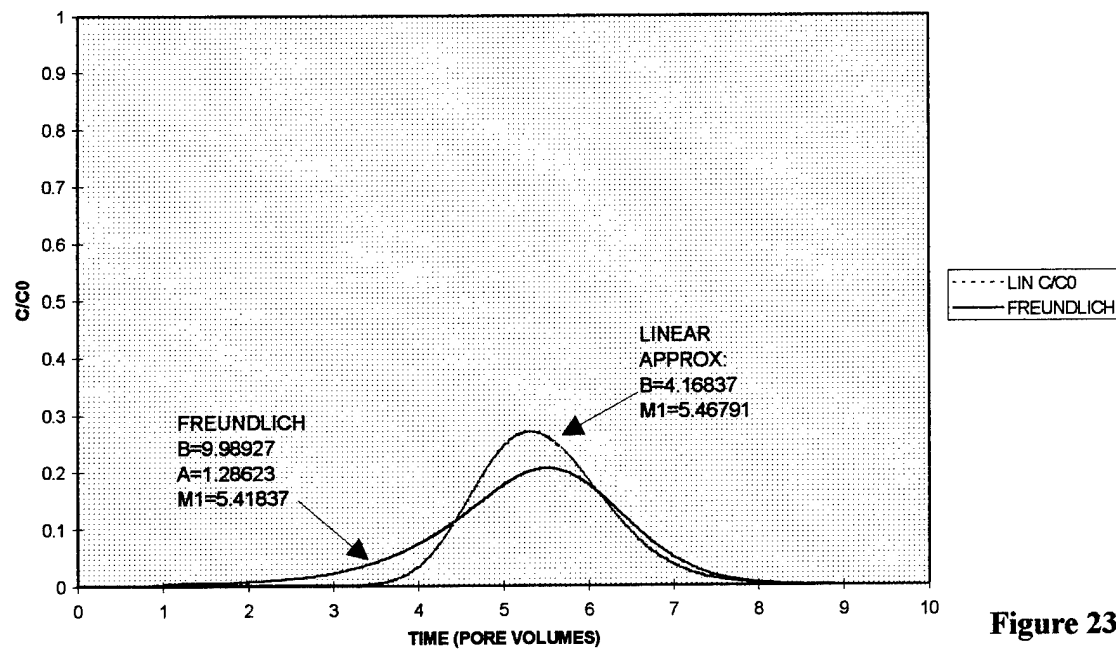
Figure 23.

LINEAR APPROXIMATION TO FREUNDLICH 1ST MOMENT FOR 3-METHYL-2-HEXANOL/TCE
SYSTEM
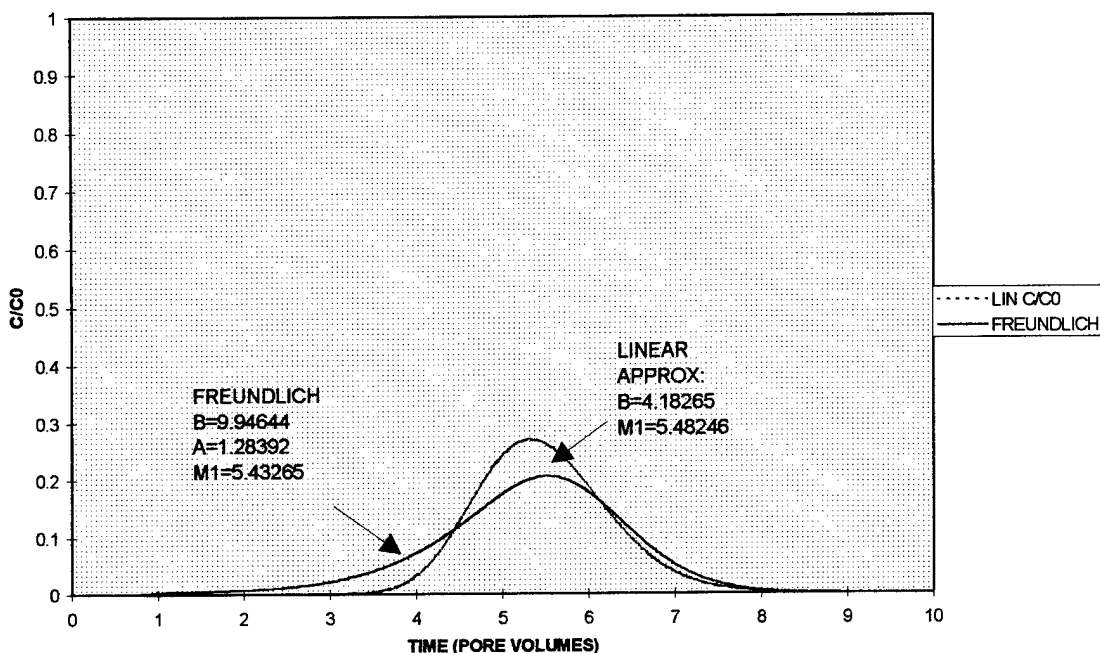
Figure 24.

Table XII combined with figures (22), (23), and (24) show that a linear approximation to non-linear tracer/NAPL interactions can lead to the systematic underestimation of oil phase saturations. For the tracers analyzed in this study, the error is as great as 22% when the "given" NAPL phase saturation (s_n) is 5%; this error applies to tracer mole fractions between 0 and 0.05. For larger mole fractions (i.e., x= 0 to 0.20), this error may be larger since the system is more non-linear at higher tracer/NAPL mole fractions. These findings suggest that a linear approximation to tracer/NAPL interactions may not be appropriate to quantify the volume of a NAPL in the subsurface.

Sensitivity Analysis

Several variables in the Freundlich approximation to the tracer/TCE interactions were modified to determine the sensitivity of changes to these variables on the effluent response curve. The tracer 2-methyl-2-hexanol was used as the partitioning tracer in all sensitivity analysis tests. First, the Freundlich exponent, A, was changed from its original value of 1.28623 to a value of 2.0 and then to a value of 3.0. For each exponent, the same

injection concentration, c_0, and the same Freundlich coefficient, B, were used as determined by the original solution. Figure (25) displays the effects of these changes.

FREUNDLICH EXPONENT COMPARISON FOR 2-METHYL-2-HEXANOL/TCE SYSTEM
FRACTIONAL BREAKTHROUGH CURVE GENERATED BY THE A-D EQUATION

Figure 25.
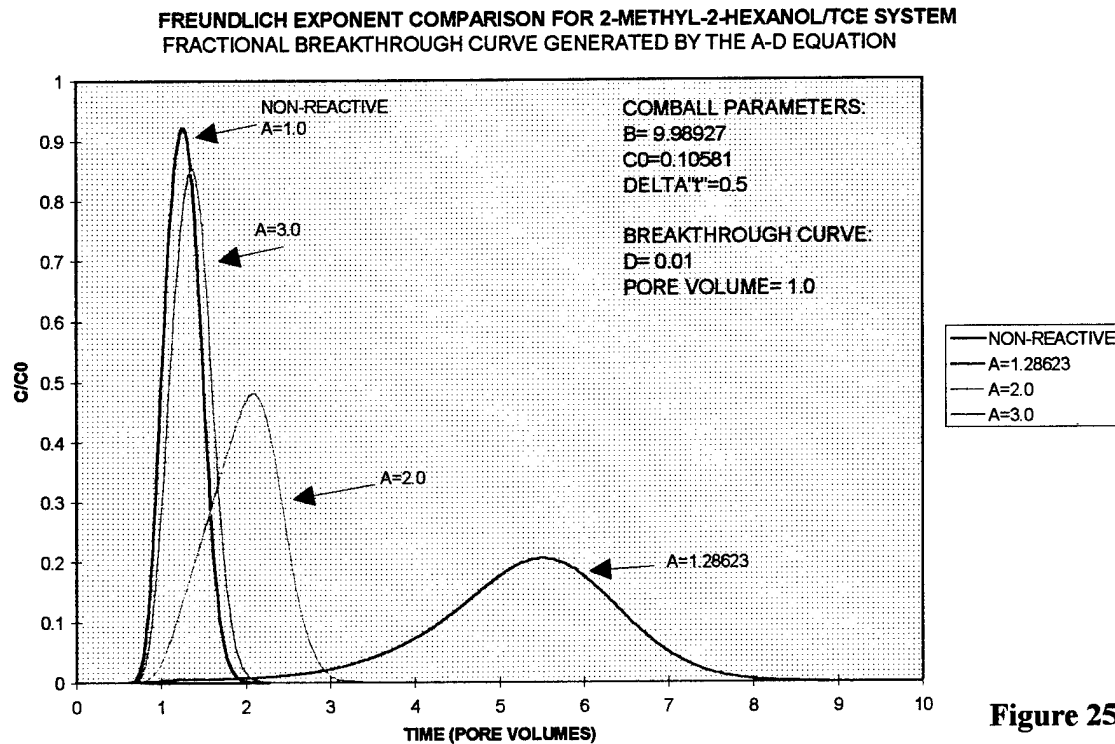
The results show that as the exponent, A, is increased, the effluent response curve becomes less retarded. A mathematical explanation for this result emanates from the characteristic solution for the unfavorable Freundlich isotherm. Equation (21) given in the "Advective Transport Equation" section represents the slope of an isochore in the τ-t plane. The slope of each characteristic curve in the τ-t plane is altered when the Freundlich exponent, A, changes. For A>1 and c_0 concentrations less than 1, $\dfrac{dt}{d\tau}$ (which represents retardation) decreases as A increases. Thus, the behavior of a more non-linear system simulates the behavior of a non-reactive tracer; these non-linear systems may not be able to correctly predict NAPL saturation since the first moment of the effluent curve decreases as the exponent increases.

The second sensitivity analysis was conducted by varying the Freundlich coefficient, B.
For 2-methyl-2-hexanol, the original Freundlich value of B was 9.98927. For the
sensitivity analysis, B was reduced to one-half its original value. The results are shown in
figure (26).

FREUNDLICH COEFF. COMPARISON FOR 2-METHYL-2-HEXANOL/TCE SYSTEM
FRACTIONAL BREAKTHROUGH CURVE GENERATED BY THE A-D EQUATION
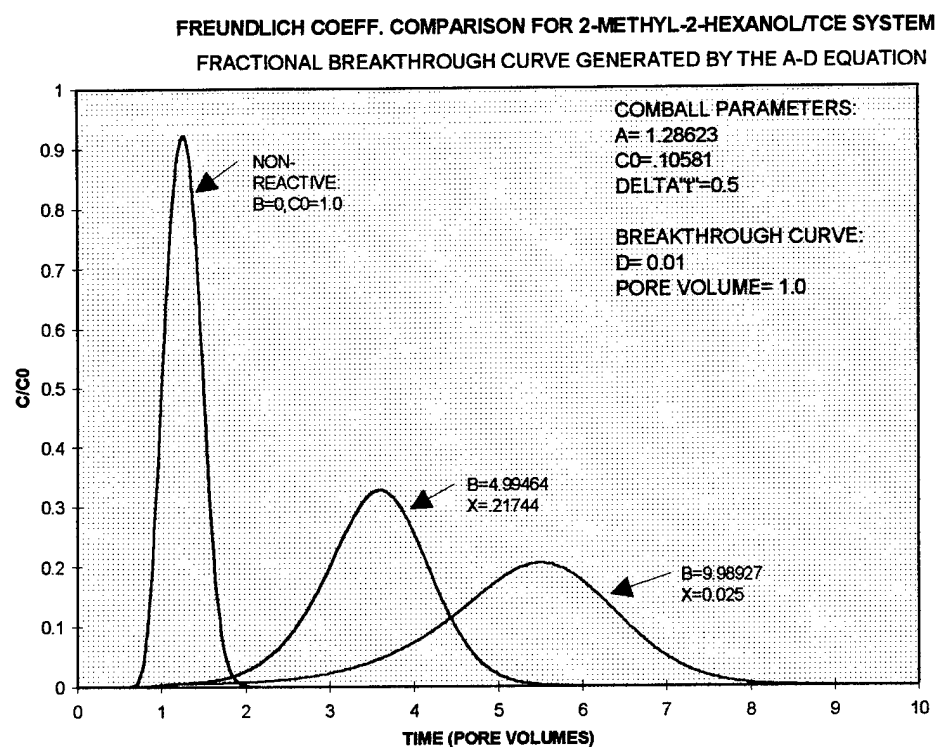
Figure 26.

Since higher values of the Freundlich coefficient, B, correspond to higher TCE amounts
present in the column (or subsurface), the effluent results display the expected behavior;
the 2-methyl-2-hexanol experiences more retardation. In addition, more "smearing" of the
tracer occurs with higher TCE amounts in the column. These results can also be
mathematically demonstrated by the characteristic solution to the unfavorable Freundlich

isotherm. As the value of B decreases, $\dfrac{dt}{d\tau}$ also decreases.

Finally, the effect of varying c_0 was analyzed using the original Freundlich parameters for
the 2-methyl-2-hexanol/TCE system. The c_0 values which correspond to tracer mole

fractions of 0.025 and 0.05 were used in the COMBALL runs. Figure (27) displays the results.

VARYING MOLE FRACTION COMPARISON, 2-METHYL-2-HEXANOL/TCE SYSTEM
FRACTIONAL BREAKTHROUGH CURVE GENERATED BY THE A-D EQUATION

COMBALL PARAMETERS:
B=9.98927
A= 1.28623
DELTA'T'=0.5

BREAKTHROUGH CURVE:
D= 0.01
PORE VOLUME= 1.0

NON-REACTIVE
TRACER
B=0, A=1;CO=1

X=.025
CO=.10581

X=.05
CO=.18226
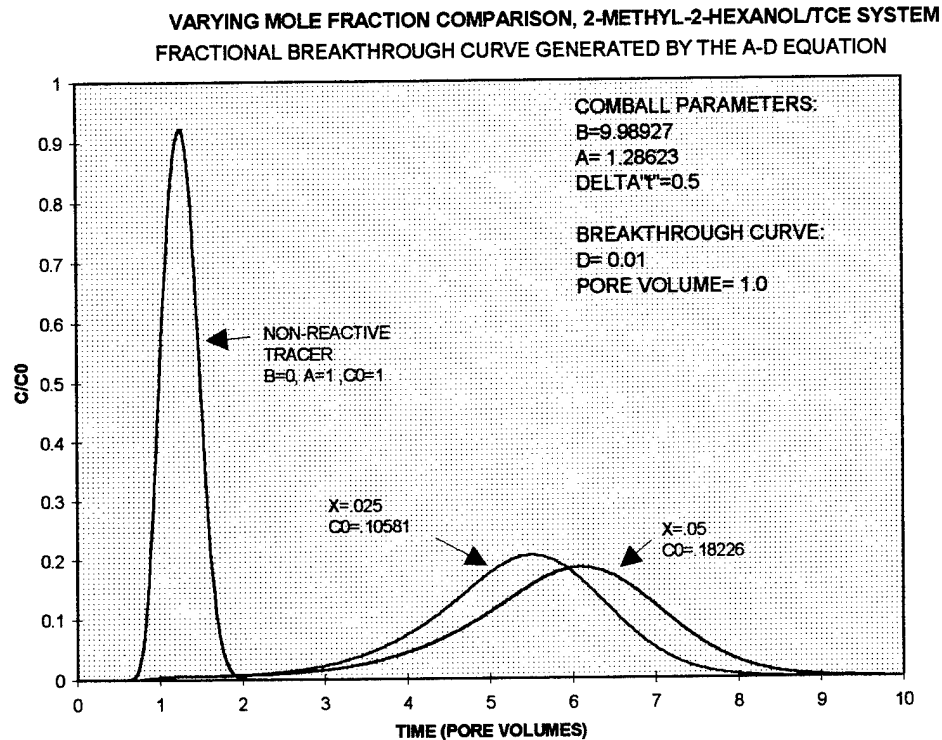
Figure 27.

As can be seen by figure (27), the effluent response curve for the higher mole fraction is retarded more than that for the base case. This is expected; if a higher c_0 is injected into the same system for the same time interval, the slope of the system's characteristic curves will be greater. These results are important in field applications since the slightly lower peak and the wider base for the higher c_0 indicates that more "smearing" occurs when the tracer mole fraction is increased. Thus, careful consideration must be taken in the c_0 determination during field applications; although a higher c_0 allows for analytic instrument detection of the effluent, the higher c_0 may result in the manifestation of more non-linear effects.

CHAPTER 5
LANGMUIR APPROXIMATION

Langmuir isotherms were also fit to the tracer/TCE UNIFAC curves. The "classic" Langmuir isotherm is often expressed in terms of sorbed concentrations:

$$(37) \quad q = \frac{Qc}{K+c}$$

        q represents the sorbed concentration (mass sorbed/solution volume) [ML^{-3}].

        c represents the aqueous phase concentration (mass in solution/solution volume) [ML^{-3}].

        Q represents the adsorption capacity (mass sorbed/solution volume) [ML^{-3}].

        K represents the selectivity coefficient (mass in solution/solution volume) [ML^{-3}].

A Langmuir type approximation was initially modeled using the UNIFAC data with equation (38):

$$(38) \quad x = \frac{Q'c}{K'+c}$$

        x represents the tracer mole fraction $\left[\frac{moles\_tracer}{moles\_tracer + moles\_TCE} \right]$.

        c represents the aqueous phase concentration (mass in solution/solution volume) [ML^{-3}].

        Q' and K' represent the Langmuir-type parameters which must be converted to Q and K in the "classic" Langmuir expression.

The Langmuir parameters Q' and K' were determined by minimizing the error between the UNIFAC calculated "x-c" relationship and the Langmuir approximated "x-c" relationship; The Microsoft® Excel Solver was used to vary the Langmuir parameters until the minimal error resulted.

Langmuir fits were first attempted using mole fraction intervals between 0 and 0.02. As can be seen with figures (28), (29), and (30), the Langmuir approximations correlate closely with the UNIFAC data. For 2-methyl-2-hexanol and 3-methyl-2-hexanol, the fits almost matched exactly. The methanol Langmuir approximation did not fit as closely as did the other two tracers; therefore, the mole fraction interval was reduced slightly to x=0 to 0.13 and is displayed as figure (31). The RMS errors associated with the Langmuir approximations are summarized in Table XIII.

METHANOL/TCE UNIFAC Cw COMPARED WITH LANGMUIR APPROXIMATION

Q'= -.07662
K'= -1.16724
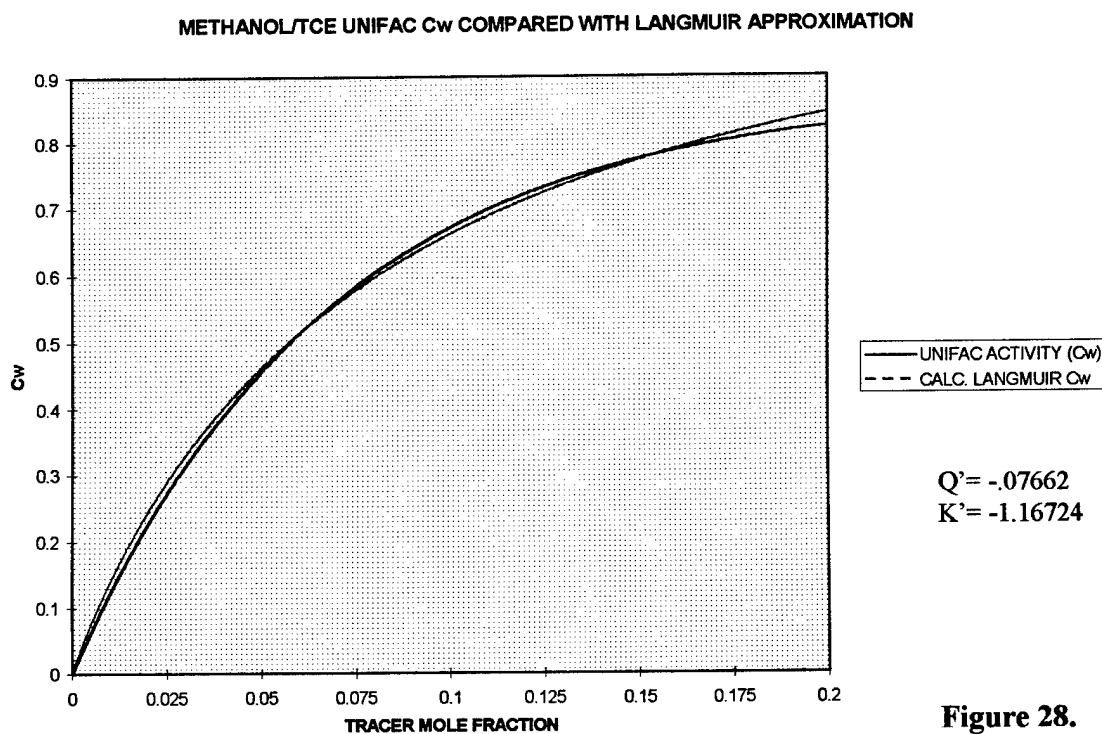
Figure 28.

2-METHYL-2-HEXANOL/TCE UNIFAC Cw COMPARED WITH LANGMUIR APPROXIMATION

$Q' = -.11485$
$K' = -.58743$
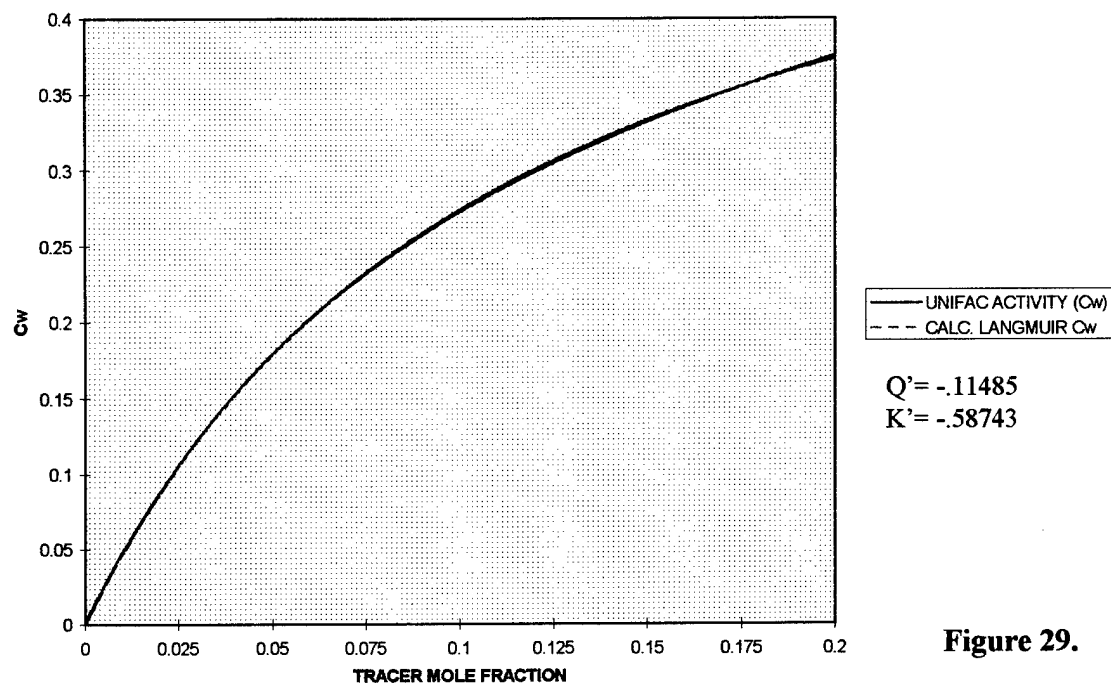
Figure 29.

3-METHYL-2-HEXANOL/TCE UNIFAC Cw COMPARED WITH LANGMUIR APPROXIMATION

$Q' = -.1159$
$K' = -.59154$

Figure 30.

METHANOL/TCE UNIFAC Cw COMPARED WITH LANGMUIR APPROXIMATION
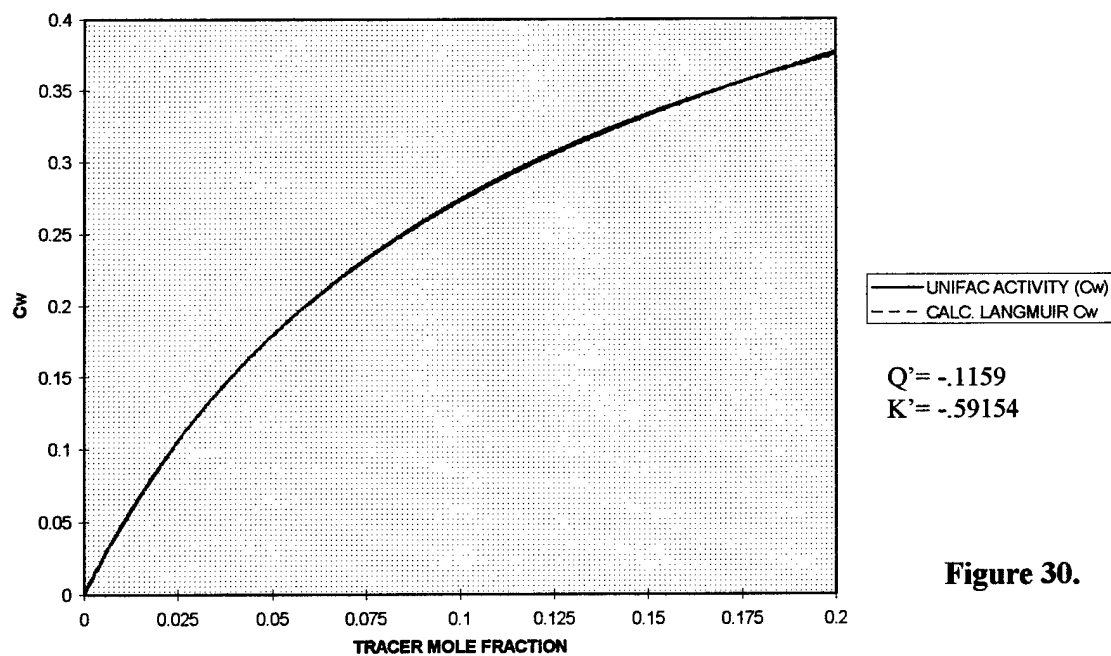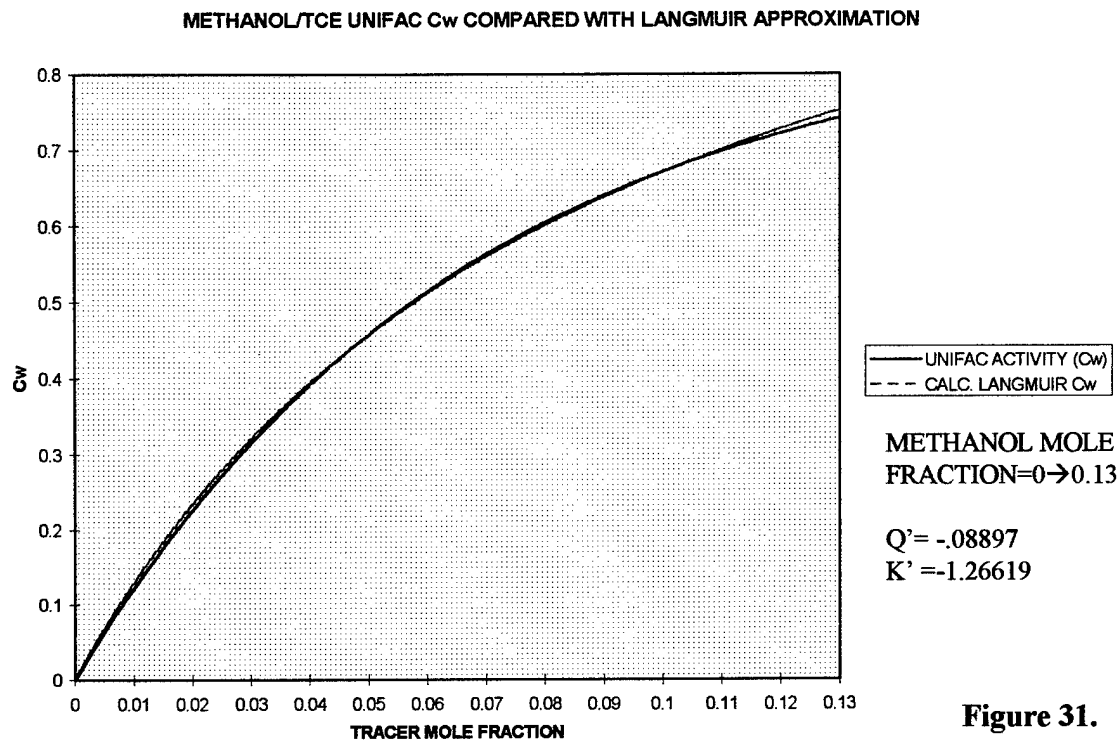
Figure 31.

Table XIII. Langmuir Values for Tracer/TCE Unifac Approximations[*]

Tracer	K'	Q'	RMS Error
Methanol (0→0.2)	-1.16724	-.076672	9.5824×10^{-3}
Methanol (0→0.13)	-1.26619	-.08897	4.2197×10^{-3}
2-Methyl-2-Hexanol	-.58743	-.11485	8.8322×10^{-4}
3-Methyl-2-Hexanol	-.59154	-.1159	8.6942×10^{-4}

[*] Mole Fraction Interval = 0→0.2 Unless Otherwise Indicated

Overall, the Langmuir approximation to solving for the mole fraction using the aqueous phase concentration is more accurate at larger mole fraction intervals. The Langmuir approach can analyze larger mole fraction intervals since the RMS errors between the UNIFAC data and the Langmuir approximation are on the order of 10^{-4} for x= 0 to 0.2. In comparison, the Freundlich errors for the same interval were on the order of 10^{-3} for the same interval as previously shown on Table V.

It must be reiterated that the values represented in figures (28) through (31) are expressed in terms of x; hence, the presence of negative numbers is not unreasonable. The conversion to the "typically" expressed parameters which are normally associated with q can be accomplished using a similar analysis to that presented for the Freundlich parameter conversion. This conversion will not be shown in this paper since Langmuir model simulations were not conducted in this investigation.

CHAPTER 6
CONCLUSIONS

This investigation yields several conclusions which deal with non-linear partitioning effects on NAPL characterization via partitioning tracer tests. UNIFAC computer simulations show that non-linear partitioning behavior does, in fact, exist between tracer/NAPL interactions at compositions likely to be experienced during tracer tests. To study the effects of these non-linearities, the Freundlich fit to the UNIFAC data provides reasonable approximations at low concentrations; these Freundlich fits include the following two relations: (1) tracer mole fraction (x) vs. aqueous phase concentration (c), and (2) tracer storage in the NAPL phase (q) vs. aqueous phase concentration (c).

Several errors may result when predicting NAPL saturation values using the currently accepted methods. First, the assumption that the non-reactive tracer is "truly" non-reactive may be inaccurate. The NAPL saturation errors using methanol as the non-reactive tracer in this investigation were as high as 39 percent. Additional investigation in this area needs to be conducted, however, since methanol is miscible in water. A second type of error results when using the assumption of linear tracer/NAPL partitioning. The NAPL saturation errors using 2-methyl-2-hexanol/TCE and 3-methyl-2-hexanol/TCE were approximately 22 percent under the model conditions in this study.

Freundlich parameter variations also lead to changes in the tracer effluent response. As the Freundlich exponent, A, increases, less retardation and less spreading occurs. To conserve mass, the peak of the effluent curve is higher as A increases. Therefore, higher exponent values yield effluent curves which tend to resemble non-reactive tracers. As the Freundlich coefficient, B, increases, increased retardation and spreading of the effluent curve occurs. Thus, the peak of the effluent curve decreases as B increases. A higher coefficient value indicates that more oil is present in the aquifer. Finally, higher injection concentrations, c_0, yield effluent curves with increased retardation and spreading. Thus, care must be exercised in field applications; a balance must be found in which c_0 is high enough so that the tracer can be detected in the effluent, but low enough to minimize the non-linear effects associated with high c_0 values.

Models other than the Freundlich may also be used to determine the non-linear partitioning effects on NAPL saturation calculations. The Langmuir model is a promising candidate for further investigations; for the tracer/TCE pairs investigated in this study, the Langmuir model displayed excellent correlations to the UNIFAC data at tracer mole fraction intervals between 0 and 0.2.

APPENDICES

A. Sample UNIFAC Input and Output Files for 2-Methyl-2-Hexanol/TCE

B. α and β Values Determined By Microsoft $^{\circledR}$ Excel Spreadsheet Solver Solution for 2-Methyl-2-Hexanol/TCE (With RMS Error Calculations)

C. A and B Values Determined By Microsoft $^{\circledR}$ Excel Spreadsheet Solver Solution for 2-Methyl-2-Hexanol/TCE (With RMS Error Calculations)

D. COMBALL Program

E. Sample COMBALL Input and Output File for 2-Methyl-2-Hexanol/TCE System Using A and B Values and A-D Fractional Breakthrough Curve

Appendix A
Sample UNIFAC Input File for 2-Methyl-2-Hexanol/TCE
For Tracer Mole Fractions From 0→1.0


```
'2-methyl-2-hexanol/trichloroethylene        ' /    ←Text Line
1  1  0          /     ←Use "VLE" internal file parameters and write to both screen  &"gamma.out"
2                /        ←# of components being compared
0                /     ←Retrieve "R" and "Q" values from internal data files
3  1  3  2  1  4  1  15 /      ←1st compound's # in subgroup, subgroup #...  (There are 4  subgroups)
1  8  3  70  /                  ←2nd compound's # in subgroup, subgroup #...  (There are 2  subgroups)
0                /
298.             /     ←Temperature (K)
0.0   1.0 /          ←Mole fraction of 1st compound followed by mole fraction of 2nd compound
298. /                           .
0.1  .90 /                       .
.2  .80 /                        .
298.  /
.3  .70 /
298. /
.4  .60  /
298.  /
.5  .50  /
298. /
.6  .40  /
298.  /
.7  .30  /
298.  /
.8  .20  /
298.  /
.9  .10/
298.  /
1.0  0.0 /
0.0              /    ←Signifies end of data file
```

1

IOUT = 1
IF IOUT = 0 : OUTPUT ONLY ON FILE
IF IOUT = 1 : OUTPUT ON BOTH FILE AND SCREEN

2-methyl-2-hexanol/trichloroethylene

MODEL USED FOR LIQUID PHASE: ORIGINAL UNIFAC   (VLE)

GROUP SPECIFICATION:

SUBGROUP		MAIN	R	Q	PRESENCE IN COMPONENT NO.	
NO.	NAME	GROUP			1	2
1	CH3.....	1	0.9011	0.8480	3	0
2	CH2.....	1	0.6744	0.5400	3	0
4	C.......	1	0.2195	0.0000	1	0
8	CHC.....	2	0.8886	0.6760	0	1
15	OH......	5	1.0000	1.2000	1	0
70	CL-(C=C)	37	0.7910	0.7240	0	3

PARAMETER COEFFICIENTS FOR INTERACTIONS

	1	2	5	37
1				
	0.0000	86.02	986.5	-4.189
2				
	-35.36	0.0000	524.1	-66.46
5				
	156.4	457.0	0.0000	225.8
37				
	47.41	124.2	738.9	0.0000

MOLECULAR PARAMETERS

COMP.   R   Q

1	5.9460	5.3640
2	3.2616	2.8480

TEMPERATURE: 298.000

MOLE PER CENT   ACTIVITY COEFFICIENT
    0.000000   5.14722

100.000000   1.00000

TEMPERATURE: 298.000

MOLE PER CENT   ACTIVITY COEFFICIENT
   10.000000   2.72672
   90.000000   1.03114

TEMPERATURE: 298.000

MOLE PER CENT   ACTIVITY COEFFICIENT
   20.000000   1.87894
   80.000000   1.09943

TEMPERATURE: 298.000

MOLE PER CENT   ACTIVITY COEFFICIENT
   30.000000   1.48710
   70.000000   1.18730

TEMPERATURE: 298.000

MOLE PER CENT   ACTIVITY COEFFICIENT
   40.000000   1.27762
   60.000000   1.28741

TEMPERATURE: 298.000

MOLE PER CENT   ACTIVITY COEFFICIENT
   50.000000   1.15647
   50.000000   1.39583

TEMPERATURE: 298.000

MOLE PER CENT   ACTIVITY COEFFICIENT
   60.000000   1.08387
   40.000000   1.51006

TEMPERATURE: 298.000

MOLE PER CENT   ACTIVITY COEFFICIENT
   70.000000   1.04043
   30.000000   1.62835

TEMPERATURE: 298.000

MOLE PER CENT   ACTIVITY COEFFICIENT
   80.000000   1.01567
   20.000000   1.74932

TEMPERATURE: 298.000

MOLE PER CENT   ACTIVITY COEFFICIENT
   90.000000   1.00346
   10.000000   1.87190

TEMPERATURE: 298.000

MOLE PER CENT   ACTIVITY COEFFICIENT
   100.000000   1.00000
    0.000000   1.99518

2-METHYL-2-HEXANOL/TCE UNIFAC GENERATED ACTIVITIES COMPARED WITH FREUNDLICH APPROXIMATIONS, "BETA" AND "ALPHA" OBTAINED BY EXCEL SOLVER ROUTINE

BETA=	0.41835494
ALPHA=	1.24654054

		FREUNDLICH APPROXIMATION CALC.		
UNIFAC ACTIVITY (Cw)	MOLE FRACTION TRACER	UNIFAC ACTIVITY (Cw)	FREUND. MOLE FRACTION	ERROR
0	0	0	0	0
0.005103932	0.001	0.005103932	0.00058124	1.7536E-07
0.01012258	0.002	0.01012258	0.00136477	4.03517E-07
0.015057834	0.003	0.015057834	0.002238989	5.79138E-07
0.019911536	0.004	0.019911536	0.003171831	6.85864E-07
0.024685475	0.005	0.024685475	0.004146274	7.28847E-07
0.029381406	0.006	0.029381406	0.005151518	7.19921E-07
0.034001023	0.007	0.034001023	0.006180023	6.72361E-07
0.038545984	0.008	0.038545984	0.00722621	5.98751E-07
0.043017912	0.009	0.043017912	0.00828578	5.1011E-07
0.04741838	0.01	0.04741838	0.009355323	4.15608E-07
0.051748917	0.011	0.051748917	0.010432075	3.22539E-07
0.05601102	0.012	0.05601102	0.011513757	2.36432E-07
0.060206146	0.013	0.060206146	0.012598467	1.61228E-07
0.064335726	0.014	0.064335726	0.013684605	9.94739E-08
0.068401125	0.015	0.068401125	0.0147708	5.25328E-08
0.072403728	0.016	0.072403728	0.015855892	2.07672E-08
0.076344824	0.017	0.076344824	0.016938868	3.73715E-09
0.08022573	0.018	0.08022573	0.018018867	3.55966E-10
0.084047659	0.019	0.084047659	0.019095124	9.04862E-09
0.08781186	0.02	0.08781186	0.020166991	2.7886E-08
0.091519533	0.021	0.091519533	0.021233899	5.47087E-08
0.095171824	0.022	0.095171824	0.022295345	8.72288E-08
0.098769889	0.023	0.098769889	0.023350902	1.23132E-07
0.102314832	0.024	0.102314832	0.024400191	1.60153E-07
0.105807725	0.025	0.105807725	0.02544288	1.96142E-07
0.109249634	0.026	0.109249634	0.026478686	2.29141E-07
0.112641597	0.027	0.112641597	0.027507366	2.57421E-07
0.115984624	0.028	0.115984624	0.028528707	2.79531E-07
0.119279668	0.029	0.119279668	0.029542518	2.94326E-07
0.12252774	0.03	0.12252774	0.030548659	3.01026E-07
0.125729707	0.031	0.125729707	0.031546976	2.99183E-07
0.12888656	0.032	0.12888656	0.032537385	2.88782E-07
0.131999142	0.033	0.131999142	0.033519778	2.70169E-07
0.135068366	0.034	0.135068366	0.034494096	2.44131E-07
0.138095055	0.035	0.138095055	0.035460273	2.11852E-07
0.141080076	0.036	0.141080076	0.036418277	1.74956E-07
0.144024202	0.037	0.144024202	0.037368065	1.35472E-07

Appendix B
Excel Spreadsheet Solver Solution For 2-Methyl-2-Hexanol/TCE
(With RMS Error Calculation)

0.146928292	0.038	0.146928292	0.038309639		9.5876E-08
0.149793033	0.039	0.149793033	0.039242961		5.90303E-08
0.15261928	0.04	0.15261928	0.040168066		2.82462E-08
0.155407712	0.041	0.155407712	0.041084942		7.21514E-09
0.158159064	0.042	0.158159064	0.04199361		4.08313E-11
0.160874094	0.043	0.160874094	0.042894111		1.12124E-08
0.163553456	0.044	0.163553456	0.043786464		4.55978E-08
0.166197825	0.045	0.166197825	0.044670703		1.08437E-07
0.168807902	0.046	0.168807902	0.045546884		2.05314E-07
0.171384325	0.047	0.171384325	0.04641505		3.42167E-07
0.173927664	0.048	0.173927664	0.04727523		5.25292E-07
0.176438661	0.049	0.176438661	0.048127519		7.61224E-07
0.1789178	0.05	0.1789178	0.048971934		1.05692E-06
				ERROR:	1.32774E-05
				RMS=	0.000515314

EQUATION USED FOR RMS ERROR-->

$$RMS\_ERROR = \sqrt{\frac{\left(X - \bar{X}\right)^2}{\#\_DATA\_POINTS}}$$

Excel Spreadsheet Solver Solution for 2-Methyl-2-Hexanol
(With RMS Error Calculation)

2-METHYL-2-HEXANOL/TCE UNIFAC GENERATED ACTIVITIES COMPARED WITH FREUNDLICH APPROXIMATIONS, "B" AND "A" OBTAINED BY EXCEL SOLVER ROUTINE

BETA=	0.418355			
ALPHA=	1.246541			

B'=	0.47007241	ZETA (g/l)=	21.2505
A =	1.28623477	B	9.989273676

FREUNDLICH APPROXIMATION

UNIFAC ACTIVITY (Cw)	MOLE FRACTION TRACER	X/(1-X)	CALC. X/(1-X)	ERROR
0	0	0	0	0
0.005103932	0.001	0.001001001	0.000529654	2.22168E-07
0.01012258	0.002	0.002004008	0.001277912	5.27215E-07
0.015057834	0.003	0.003009027	0.002129803	7.73034E-07
0.019911536	0.004	0.004016064	0.003050803	9.31729E-07
0.024685475	0.005	0.005025126	0.004022232	1.0058E-06
0.029381406	0.006	0.006036217	0.005032067	1.00832E-06
0.034001023	0.007	0.007049345	0.006071817	9.55561E-07
0.038545984	0.008	0.008064516	0.007135131	8.63757E-07
0.043017912	0.009	0.009081736	0.008217071	7.47646E-07
0.04741838	0.01	0.01010101	0.009313681	6.19886E-07
0.051748917	0.011	0.011122346	0.010421731	4.90861E-07
0.05601102	0.012	0.012145749	0.011538533	3.68712E-07
0.060206146	0.013	0.013171226	0.012661826	2.59488E-07
0.064335726	0.014	0.014198783	0.013789692	1.67356E-07
0.068401125	0.015	0.015228426	0.014920473	9.48351E-08
0.072403728	0.016	0.016260163	0.016052756	4.30173E-08
0.076344824	0.017	0.017293998	0.017185297	1.1816E-08
0.08022573	0.018	0.018329939	0.018317024	1.66796E-10
0.084047659	0.019	0.019367992	0.019446982	6.23948E-09
0.08781186	0.02	0.020408163	0.02057435	2.7618E-08
0.091519533	0.021	0.02145046	0.021698399	6.1474E-08
0.095171824	0.022	0.022494888	0.022818481	1.04713E-07
0.098769889	0.023	0.023541453	0.023934035	1.5412E-07
0.102314832	0.024	0.024590164	0.025044557	2.06473E-07
0.105807725	0.025	0.025641026	0.026149602	2.5865E-07
0.109249634	0.026	0.026694045	0.027248783	3.07734E-07
0.112641597	0.027	0.027749229	0.028341758	3.5109E-07
0.115984624	0.028	0.028806584	0.029428224	3.86435E-07
0.119279668	0.029	0.029866117	0.030507905	4.11891E-07
0.12252774	0.03	0.030927835	0.031580585	4.26083E-07
0.125729707	0.031	0.031991744	0.032646038	4.281E-07
0.12888656	0.032	0.033057851	0.033704111	4.17652E-07
0.131999142	0.033	0.034126163	0.034754636	3.94977E-07
0.135068366	0.034	0.035196687	0.035797494	3.60969E-07
0.138095055	0.035	0.03626943	0.036832565	3.17121E-07
0.141080076	0.036	0.037344398	0.037859768	2.65606E-07
0.144024202	0.037	0.038421599	0.038879011	2.09226E-07
0.146928292	0.038	0.03950104	0.039890254	1.51488E-07

Excel Spreadsheet Solver Solution for 2-Methyl-2-Hexanol
(With RMS Error Calculation)

0.149793033	0.039	0.040582726	0.040893417	9.65289E-08
0.15261928	0.04	0.041666667	0.041888498	4.92089E-08
0.155407712	0.041	0.042752868	0.042875447	1.50257E-08
0.158159064	0.042	0.043841336	0.043854254	1.66862E-10
0.160874094	0.043	0.044932079	0.044824929	1.14813E-08
0.163553456	0.044	0.046025105	0.04578746	5.64748E-08
0.166197825	0.045	0.047120419	0.046741857	1.43309E-07
0.168807902	0.046	0.048218029	0.04768815	2.80772E-07
0.171384325	0.047	0.049317943	0.048626359	4.78289E-07
0.173927664	0.048	0.050420168	0.049556488	7.45943E-07
0.176438661	0.049	0.051524711	0.050478617	1.09431E-06
0.1789178	0.05	0.052631579	0.051392739	1.53472E-06
			ERROR:	1.88453E-05
			RMS=	0.000613926

EQUATION USED FOR RMS ERROR:

$$RMS\_ERROR = \sqrt{\dfrac{\left(\dfrac{X}{1-X} - \psi\right)^2}{\#\_DATA\_POINTS}}$$

COMBALL Program

```
C     **********************************************************
C     *                                                        *
C     *      THIS PROGRAM DETERMINES THE EFFLUENT CURVE FOR A MULTI-  *
C     * WELL INJECTION TEST.  TO RUN THE MODEL IT IS NECESSARY TO     *
C     * ASSUME AN ISOTHERM, AND ITS PARAMETERS, AS WELL AS THE FRAC-  *
C     * TIONAL BREAKTHROUGH CURVE.                              *
C     *      COMBALL WAS WRITTEN BY WILLIAM R. WISE AT THE UNIVERSITY  *
C     * OF TEXAS AT AUSTIN IN THE SUMMER OF 1984, BASED ON THE THEORY  *
C     * OF THE COMBINATION DIAGRAM ALSO DEVELOPED BY THE AUTHOR.      *
C     *                                                        *
C     **********************************************************
C
C
C     **********************************************************
C     *                                                        *
C     *                 DATA ENTRY INSTRUCTIONS                *
C     *                 -----------------------                *
C     *                                                        *
C     * VARIABLE        DEFINITION                      FORMAT *
C     * --------        ----------                      ------ *
C     *                                                        *
C     * ISOTHER         ISOTHERM (EITHER LANGMUIR OR     A10   *
C     *                          FREUNDLICH)                   *
C     *                                                        *
C     * K OR B          K IF ISOTHER=LANGMUIR           F15.5  *
C     *                 B IF ISOTHER=FREUNDLICH                *
C     *                                                        *
C     * Q OR A          Q IF ISOTHER=LANGMUIR           F15.5  *
C     *                 A IF ISOTHER=FREUNDLICH                *
C     *                                                        *
C     * C0              INJECTED CONCENTRATION          F15.5  *
C     *                                                        *
C     * DELT            INJECTION TIME                  F15.5  *
C     *                                                        *
C     * TMAX            MAXIMUM TIME OF EVALUATION       F15.5  *
C     *                                                        *
C     * TINCR           TIME INCREMENT OF EVALUATION     F15.5  *
C     *                                                        *
C     * NDIV            NUMBER OF DIVISIONS FOR INTEGRATING  I5 *
C     *                 ACROSS SPREADING WAVE                  *
C     *                                                        *
C     * NF              NUMBER OF COORDINATES OF FRACTIONAL I5 *
C     *                 BREAKTHROUGH CURVE                     *
C     *                                                        *
C     * TFPOINT(J),     JTH COORDINATE OF F CURVE      2F15.5 *
C     * FPOINT(J)                                               *
C     *                                                        *
C     **********************************************************
C
      PROGRAM COMBALL
      COMMON ISOTHER,B,A,K,Q,C0,DELT,TMAX,TINCR,NDIV,NF,ITMAX,
C          TFPOINT(200),FPOINT(200),
C          CE(200),PERCENT(200),CMASSIN,CMASSOU,MASSREM
      REAL K
      CHARACTER*10 ISOTHER,INPUT,OUTDAT
      WRITE (*,*) 'PLEASE ENTER INPUT DATA FILE NAME'
      READ (*,*) INPUT
      WRITE (*,*) 'PLEASE ENTER OUTPUT DATA FILE NAME'
      READ (*,*) OUTDAT
      OPEN (1,FILE=INPUT)
      OPEN (2,FILE=OUTDAT)
      CALL ASSEMBL
      ITMAX = IFIX(TMAX / TINCR)
      IF (ISOTHER.EQ.'FREUNDLICH') THEN
      IF (A.LT.1) THEN
          DO 110 J=1,ITMAX
          T = J * TINCR
```

```
                 CE(J)  = CEF01(T)
     110         CONTINUE
           ELSE IF (A.EQ.1) THEN
                 DO 120 J=1,ITMAX
                 T = J * TINCR
                 CE(J)  = CEF1(T)
     120         CONTINUE
           ELSE
                 DO 130 J=1,ITMAX
                 T = J * TINCR
                 CE(J)  = CEF1UP(T)
                 WRITE(2,125) T,CE(J)
     125         FORMAT(2F15.5)
     130         CONTINUE
           END IF
           ELSE
                 DO 140 J=1,ITMAX
                 T = J * TINCR
                 CE(J)  = CEL(T)
     140         CONTINUE
           END IF
           CALL MASSBAL(CE,TINCR,DELT,ITMAX,CMASSIN,CMASSOU,PERCENT,MASSREM,
          C              C0)
           CALL OUTPUT
           END
C
C          ****************************************************************
C          *                                                              *
C          *       THE ASSEMBL SUBROUTINE READS THE INPUT DATA.           *
C          *                                                              *
C          ****************************************************************
C
           SUBROUTINE ASSEMBL
           COMMON ISOTHER,B,A,K,Q,C0,DELT,TMAX,TINCR,NDIV,NF,ITMAX,
          C          TFPOINT(200),FPOINT(200),
          C          CE(200),PERCENT(200),CMASSIN,CMASSOU,MASSREM
           REAL K
           CHARACTER*10 ISOTHER
           READ (1,500) ISOTHER
     500 FORMAT (A10)
           IF (ISOTHER.EQ.'FREUNDLICH') THEN
           READ (1,510) B,A,C0,DELT
           ELSE IF (ISOTHER.EQ.'LANGMUIR  ') THEN
           READ (1,510) K,Q,C0,DELT
           ELSE
           WRITE (2,515) ISOTHER
     515 FORMAT ('1',///,20X,'EXECUTION WAS TERMINATED',///,
          C          20X,A10,' IS NOT AN ACCEPTABLE ISOTHERM',///,
          C          20X,'ONLY LANGMUIR OR FREUNDLICH MAY BE USED')
           STOP
           END IF
           READ (1,510) TMAX
           READ (1,510) TINCR
     510 FORMAT (F15.5)
           READ (1,520) NDIV
           READ (1,520) NF
     520 FORMAT (I5)
           DO 540 J=1,NF
                 READ (1,530) TFPOINT(J), FPOINT(J)
     530         FORMAT (2F15.5)
                 WRITE(2,535) TFPOINT(J),FPOINT(J)
     535         FORMAT(2F15.5)
     540         CONTINUE
           RETURN
           END
C
C          ****************************************************************
C          *                                                              *
C          *       THE CEL FUNCTION SUBROUTINE DETERMINES THE EFFLUENT    *
C          * CONCENTRATION AT THE PRODUCTION WELL AT A TIME T FOR THE     *
C          * LANGMUIR ISOTHERM.                                           *
C          *                                                              *
```

```
C
C      ************************************************************
C
       FUNCTION CEL(T)
       COMMON ISOTHER,B,A,K,Q,C0,DELT,TMAX,TINCR,NDIV,NF,ITMAX,
      C        TFPOINT(200),FPOINT(200),
      C          CE(200),PERCENT(200),CMASSIN,CMASSOU,MASSREM
       REAL K
       CHARACTER*10 ISOTHER
       T0 = TF(0.)
       T1 = TF(1.)
       IF (T.GT.(1 + Q / (K + C0)) * T0) GO TO 200
       CEL = 0.
       RETURN
  200  IF (T.GT.DELT + (1 + K * Q / (K + C0)**2) * T0) GO TO 210
       TFSTEP = T / (1 + Q / (K + C0))
       CEL = C0 * F(TFSTEP)
       RETURN
  210  TPLAT = DELT * (K + C0 + Q) * (K + C0) / (Q * C0)
       TF0 = (T - DELT) / (1 + Q / K)
       IF (TF0.GT.T1) RETURN
       IF (TF0.LT.T0) TF0 = T0
       IF (T. LE.TPLAT) THEN
       TFSTOP = (T - DELT) / (1 + K * Q / (K + C0)**2)
       IF (TFSTOP.GT.T1) TFSTOP = T1
       ELSE
       ALPHA = (1 + Q / K)**2
       BETA = 4 * DELT * C0 / K
      C        - 2 * (1 + Q / K) * (T - DELT * (1 - C0 / K))
       GAMMA = (T - DELT * (1 - C0 / K))**2
      C          - 4 * DELT * C0 * (T - DELT) / K
       TFSTOP = (-BETA + SQRT(BETA**2 - 4 * ALPHA * GAMMA)) / (2 * ALPHA)
       IF (TFSTOP.GT.T1) TFSTOP = T1
       END IF
       IF (TFSTOP.GT.T0) GO TO 220
       CEL = 0.
       RETURN
  220  TF1 = TF0
       F1 = F(TF1)
       DELF = F(TFSTOP) - F1
       C = (SQRT(K * Q * TF1 / (T - DELT - TF1)) - K) / 2
       C = C + (SQRT(K * Q * TFSTOP / (T - DELT - TFSTOP)) - K) / 2
           DO 230 J=2,NDIV
           F2 = F1 + DELF / NDIV
           TF2 = TF(F2)
           C = C + SQRT(K * Q * TF2 / (T - DELT - TF2)) - K
           F1 = F2
  230      CONTINUE
       CEL = C * DELF / NDIV
       IF (T.GE.TPLAT) RETURN
       TFSTEP = T / (1 + Q / (K + C0))
       IF (TFSTEP.GT.T1) TFSTEP = T1
       CEL = CEL + C0 * (F(TFSTEP) - F(TFSTOP))
       RETURN
       END
C
C      ****************************************************************
C      *                                                              *
C      *      THE CEF01 FUNCTION DETERMINE THE EFFLUENT CONCENTRATION  *
C      * FOR THE FREUNDLICH ISOTHERM WHEN THE EXPONENT IS LESS THAN 1. *
C      *                                                              *
C      ****************************************************************
C
       FUNCTION CEF01(T)
       COMMON ISOTHER,B,A,K,Q,C0,DELT,TMAX,TINCR,NDIV,NF,ITMAX,
      C        TFPOINT(200),FPOINT(200),
      C          CE(200),PERCENT(200),CMASSIN,CMASSOU,MASSREM
       REAL IOTA
       CHARACTER*10 ISOTHER
       T0 = TF(0.)
       T1 = TF(1.)
       ZETA = A - 1
       ETA = B * C0**ZETA
```

```fortran
      IF (T.LE.(1 + ETA) * T0) THEN
      CEF01 = 0.
      ELSE IF (T.LE.DELT + (1 + A * ETA) * T0) THEN
      TFSTEP = T / (1 + ETA)
      IF (TFSTEP.GT.T1) TFSTEP = T1
      CEF01 = C0 * F(TFSTEP)
      ELSE
      TPLAT = (1 + ETA) * DELT / (ETA * (-ZETA))
      IF (T.LE.TPLAT) THEN
      TFSTOP = (T-DELT) / (1 + A * ETA)
      IF (TFSTOP.GT.T1) TFSTOP = T1
      ELSE
      R = T / (1 + ETA)
      IOTA = DELT * C0 * (A**(A/ZETA)) * (B**(1/ZETA)) / (-ZETA)
           DO 310 J=1,1000
           G = R**(ZETA/A) - (T - DELT) / R**(1/A) + IOTA**(ZETA/A)
           IF (ABS(G).LE.10E-8) GO TO 320
           DGDR = (ZETA / A) / R**(1/A) + (1 / A) * (T - DELT) /
    C            R**((A+1)/A)
           R = R - G / DGDR
310        CONTINUE
           STOP
320   TFSTOP = R
      IF (TFSTOP.GT.T1) TFSTOP = T1
      END IF
      IF (TFSTOP.LE.T0) THEN
      CEF01 = 0.
      ELSE
      TF1 = T0
      F1 = F(TF1)
      DELF = F(TFSTOP) - F1
      C = (((T - DELT - TF1) / (A * B * TF1))**(1/ZETA)) / 2
      C = C + (((T - DELT - TFSTOP) / (A * B * TFSTOP))**(1/ZETA)) / 2
           DO 330 J = 2,NDIV
           F2 = F1 + DELF / NDIV
           TF2 = TF(F2)
           C = C + ((T - DELT - TF2) / (A * B * TF2))**(1/ZETA)
           F1 = F2
330        CONTINUE
      CEF01 = C * DELF / NDIV
      IF (T.GE.TPLAT) RETURN
      TFSTEP = T / (1 + ETA)
      IF (TFSTEP.GT.T1) TFSTEP = T1
      CEF01 = CEF01 + C0 * (F(TFSTEP) - F(TFSTOP))
      END IF
      END IF
      RETURN
      END
C
C
C     ****************************************************************
C     *                                                            *
C     *     THE CEF1 FUNCTION DETERMINES THE EFFLUENT CONCENTRATION *
C     * FOR THE FREUNDLICH ISOTHERM WHEN THE EXPONENT EQUALS 1.     *
C     *                                                            *
C     ****************************************************************
C
      FUNCTION CEF1(T)
      COMMON ISOTHER,B,A,K,Q,C0,DELT,TMAX,TINCR,NDIV,NF,ITMAX,
    C        TFPOINT(200),FPOINT(200),
    C        CE(200),PERCENT(200),CMASSIN,CMASSOU,MASSREM
      CHARACTER*10 ISOTHER
      T0 = TF(0.)
      T1 = TF(1.)
      TFSTEP = T / (1 + B)
      IF (TFSTEP.GT.T1) TFSTEP = T1
      IF (T.LE.(1 + B) * T0) THEN
      CEF1 = 0.
      ELSE IF (T.LE.DELT + (1 + B) * T0) THEN
      CEF1 = C0 * F(TFSTEP)
      ELSE
      TFC0 = (T - DELT) / (1 + B)
      IF (TFC0.GT.T1) TFC0 = T1
```

```fortran
      CEF1 = C0 * (F(TFSTEP) - F(TFC0))
      END IF
      RETURN
      END
C
C
C     ********************************************************************
C     *                                                                  *
C     *      THE CEF1UP FUNCTION DETERMINES THE EFFLUENT CONCENTRATION    *
C     * FOR THE FREUNDLICH ISOTHERM WHEN THE EXPONENT EXCEEDS 1.          *
C     *                                                                  *
C     ********************************************************************
C
      FUNCTION CEF1UP(T)
      COMMON ISOTHER,B,A,K,Q,C0,DELT,TMAX,TINCR,NDIV,NF,ITMAX,
      C          TFPOINT(200),FPOINT(200),
      C          CE(200),PERCENT(200),CMASSIN,CMASSOU,MASSREM
      REAL IOTA
      CHARACTER*10 ISOTHER
      T0 = TF(0.)
      T1 = TF(1.)
      ZETA = A - 1
      ETA = B * C0**ZETA
      IF (T.LE.T0) THEN
      CEF1UP = 0.
      ELSE
      TFPLAT = DELT / (ETA * ZETA)
      TPLAT = (1 + A * ETA) * TFPLAT
      IF (T.LT.TPLAT) THEN
      IF (T0.LT.TFPLAT) THEN
      IF (T.LT.(1 + A * ETA) * T0) THEN
      TF1 = T0
      ELSE
      TF1 = T / (1 + A * ETA)
      END IF
      ELSE
      TF1 = T0
      END IF
      ELSE
      R = (T - DELT) / (1 + ETA)
      IOTA = DELT * C0 * (A**(A/ZETA)) * (B**(1/ZETA)) / ZETA
          DO 410 J=1,100000
          G = (R**(ZETA/A)) - (T / (R**(1/A))) + (IOTA**(ZETA/A))
          IF (ABS(G).LE.10E-6) GO TO 420
          DGDR = ((ZETA/A) / (R**(1/A))) + (1/A) * T / (R**((A+1)/A))
          R = R - G / DGDR
 410      CONTINUE
          STOP
 420  TF1 = R
      IF (TF1.GT.T1) THEN
      CEF1UP = 0.
      RETURN
      ELSE
      CONTINUE
      END IF
      IF (TF1.LT.T0) TF1 = T0
      END IF
      TFSTOP = T
      IF (TFSTOP.GT.T1) TFSTOP = T1
      F1 = F(TF1)
      DELF = F(TFSTOP) - F1
      C = (((T - TF1) / (A * B * TF1))**(1/ZETA)) / 2
      C = C + (((T - TFSTOP) / (A * B * TFSTOP))**(1/ZETA)) / 2
          DO 430 J=2,NDIV
          F2 = F1 + DELF / NDIV
          TF2 = TF(F2)
          C = C + ((T - TF2) / (A * B * TF2))**(1/ZETA)
          F1 = F2
 430      CONTINUE
      CEF1UP = C * DELF / NDIV
      IF (T.GE.TPLAT) RETURN
      IF (T0.GE.TFPLAT) RETURN
      IF (T.LE.(1 + A * ETA) * T0) RETURN
```

```
      TFSTEP = (T- DELT) / (1 + ETA)
      IF (TFSTEP.LT.T0) TFSTEP = T0
      IF (TFSTEP.GT.T1) TFSTEP = T1
      TFC0 = T / (1 + A * ETA)
      IF (TFC0.GT.T1) TFC0 = T1
      CEF1UP = CEF1UP + C0 * (F(TFC0)- F(TFSTEP))
      END IF
      RETURN
      END
C
C
C     ****************************************************************
C     *                                                            *
C     *       THE F FUNCTION SUBROUTINE DETERMINES THE F VALUE FOR A *
C     * GIVEN TF (THE ARGUMENT TH) THROUGH LINEAR INTERPOLATION.    *
C     *                                                            *
C     ****************************************************************
C
      FUNCTION F(TH)
      COMMON ISOTHER,B,A,K,Q,C0,DELT,TMAX,TINCR,NDIV,NF,ITMAX,
     C         TFPOINT(200),FPOINT(200),
     C          CE(200),PERCENT(200),CMASSIN,CMASSOU,MASSREM
      REAL K
      CHARACTER*10 ISOTHER
      IF (TH.GT.TF(0.)) GO TO 700
      F = 0.
      RETURN
  700 J = 2
  710 IF (TH - TFPOINT(J)) 740,730,720
  720 J = J + 1
      IF (J.LT.NF) GO TO 710
      WRITE (2,777)
  777 FORMAT ('1',///,20X,'EXECUTION WAS TERMINATED',///,20X,
     C         'FRACTIONAL BREAKTHROUGH CURVE IS INSUFFICIENT',///,
     C          20X,'FOR GENERATED TF ARGUMENT FOR FUNCTION F')
      STOP
  730 F = FPOINT(J)
      RETURN
  740 F = FPOINT(J-1) + ((FPOINT(J) - FPOINT(J-1)) / (TFPOINT(J) -
     C    TFPOINT(J-1))) * (TH - TFPOINT(J-1))
      RETURN
      END
C
C
C     ****************************************************************
C     *                                                            *
C     *       THE TF FUNCTION SUBROUTINE DETERMINES THE VALUE OF TF FOR *
C     * A CORRESPONDING VALUE OF F (THE ARGUMENT FH) THROUGH LINEAR  *
C     * INTERPOLATION.                                             *
C     *                                                            *
C     ****************************************************************
C
      FUNCTION TF(FH)
      COMMON ISOTHER,B,A,K,Q,C0,DELT,TMAX,TINCR,NDIV,NF,ITMAX,
     C         TFPOINT(200),FPOINT(200),
     C          CE(200),PERCENT(200),CMASSIN,CMASSOU,MASSREM
      REAL K
      CHARACTER*10 ISOTHER
      IF (FH.NE.0) GO TO 800
      TF = TFPOINT(1)
      RETURN
  800 J = 2
      IF (FH.EQ.1..AND.FPOINT(NF).LT.1.) THEN
      TF = 10 * TFPOINT(NF)
      RETURN
      ELSE
      END IF
  810 IF (FH - FPOINT(J)) 840,830,820
  820 J = J + 1
      IF (J.LT.NF) GO TO 810
      WRITE (2,888)
  888 FORMAT ('1',///,20X,'EXECUTION WAS TERMINATED',///,20X,
     C         'FRACTIONAL BREAKTHROUGH CURVE IS INSUFFICIENT',///,
     C          20X,'FOR GENERATED F ARGUMENT FOR FUNCTION TF')
```

```fortran
      STOP
  830 TF = TFPOINT(J)
      RETURN
  840 TF = TFPOINT(J-1) + ((TFPOINT(J) - TFPOINT(J-1)) / (FPOINT(J)
     C      - FPOINT(J-1))) * (FH - FPOINT(J-1))
      RETURN
      END
C
C     *****************************************************************
C     *                                                               *
C     *        THE MASSBAL SUBROUTINE PERFORMS A MASS BALANCE ON THE  *
C     * INJECTED AND PRODUCED MASS.                                   *
C     *                                                               *
C     *****************************************************************
C
      SUBROUTINE MASSBAL(CE,TINCR,DELT,ITMAX,CMASSIN,CMASSOU,
     C                   PERCENT,MASSREM,C0)
      DIMENSION CE(200),PERCENT(200)
      CMASSIN = C0 * DELT
      CMASSOU = 0.
      M = 1
          DO 900 L=1,ITMAX
          IF (L.GT.1.AND.M.EQ.1) THEN
          IF (CE(L-1).EQ.0..AND.CE(L).GT.0) THEN
          PERCENT(1) = L * TINCR
          M = 2
          ELSE
          END IF
          ELSE
          END IF
          CMASSOU = CMASSOU + CE(L)
          IF (CMASSOU.GE.(CMASSIN * (M - 1))/10..AND.M.GT.1) THEN
          PERCENT(M) = (L - 1) * TINCR
          M = M + 1
          ELSE
          END IF
  900     CONTINUE
      MASSREM = M - 1
      RETURN
      END
C
C     *****************************************************************
C     *                                                               *
C     *        THE OUTPUT SUBROUTINE PRINTS THE INPUT AND OUTPUT RESULTS.*
C     *                                                               *
C     *****************************************************************
C
      SUBROUTINE OUTPUT
      COMMON ISOTHER,B,A,K,Q,C0,DELT,TMAX,TINCR,NDIV,NF,ITMAX,
     C        TFPOINT(200),FPOINT(200),
     C         CE(200),PERCENT(200),CMASSIN,CMASSOU,MASSREM
      REAL K
      CHARACTER*10 ISOTHER
      IF (ISOTHER.EQ.'LANGMUIR  ') THEN
      WRITE (2,610)
  610 FORMAT ('1',/////,25X,'LANGMUIR MULTIWELL INJECTION SIMULATION')
      WRITE (2,620) K,Q,C0,DELT
  620 FORMAT (////,40X,'INPUT DATA',////,35X,'LANGMUIR PARAMETERS',//,
     C        24X,'EQUILIBRIUM CONSTANT (K)   = ',F12.3,//,
     C        24X,'ADSORPTION CAPACITY (Q)    = ',F12.3,//,
     C        24X,'INJECTED CONCENTRATION (C0) = ',F12.3,//,
     C        24X,'INJECTION TIME (DELT)      = ',F12.3,////,
     C        41X,'ISOTHERM',//,32X,'C        = (Q)(C) / (K + C)',
     C        /,33X'SORBED')
      ELSE
      WRITE (2,615)
  615 FORMAT ('1',/////,24X,'FREUNDLICH MULTIWELL INJECTION SIMULATION')
      WRITE (2,625) B,A,C0,DELT
  625 FORMAT (////,40X,'INPUT DATA',////,34X,'FREUNDLICH PARAMETERS',//,
     C        24X,'FREUNDLICH COEFFICIENT (B) = ',F12.3,//,
     C        24X,'FREUNDLICH EXPONENT (A)    = ',F12.3,//,
     C        24X,'INJECTED CONCENTRATION (C0) = ',F12.3,//,
```

```fortran
      C          24X,'INJECTION TIME (DELT)        = ',F12.3,////,
      C          41X,'ISOTHERM',//,52X,'A',/,36X,'C        = (B)(C)',
      C          /,37X,'SORBED')
      END IF
      WRITE (2,630)
  630 FORMAT (///,35X,'MASS BALANCE RESULTS',//,31X,'PERCENT',15X,
      C          'TIME',/,31X,'REMOVAL',/)
           DO 632 I = 1,MASSREM
           M = 10 * (I - 1)
           WRITE (2,631) M,PERCENT(I)
  631      FORMAT (33X,I3,9X,F13.3)
  632      CONTINUE
      WRITE (2,633) CMASSIN,CMASSOU
  633 FORMAT (//,31X,'MASS INJECTED = 'F11.3,//,
      C          31X,'MASS REMOVED  = 'F11.3)
      WRITE (2,635)
  635 FORMAT ('1',///,30X,'FRACTIONAL BREAKTHROUGH CURVE',///,
      C          34X,'F',19X,'TF',/)
      DO 650 J=1,NF
      WRITE (2,640) FPOINT(J),TFPOINT(J)
                        ',10X,F15.5)
  650 CONTINUE
      WRITE (2,660)
  660 FORMAT ('1',///,39X,'OUTPUT DATA',///,33X,'TIME',9X,
      C          'CONCENTRATION (CE)',/)
      DO 680 J=1,ITMAX
      T = J * TINCR
      WRITE (2,670) T,CE(J)
  670 FORMAT (25X,F15.5,'  ',10X,F15.5)
  680 CONTINUE
      RETURN
      END
```

Appendix E

Sample COMBALL Input File
For Freundlich Parameters Determined by Excel
and A-D Fractional Breakthrough Curve

FREUNDLICH
            9.98927
            1.28623
            0.10581
            0.50000
           10.00000
            0.02500
     100
     100
            0.02500   0.00000
            0.05000   0.00000
            0.07500   0.00000
            0.10000   0.00000
            0.12500   0.00000
            0.15000   0.00000
            0.17500   0.00000
            0.20000   0.00000
            0.22500   0.00000
            0.25000   0.00000
            0.27500   0.00000
            0.30000   0.00000
            0.32500   0.00000
            0.35000   0.00000
            0.37500   0.00000
            0.40000   0.00000
            0.42500   0.00000
            0.45000   0.00000
            0.47500   0.00000
            0.50000   0.00000
            0.52500   0.00000
            0.55000   0.00001
            0.57500   0.00004
            0.60000   0.00013
            0.62500   0.00040
            0.65000   0.00107
            0.67500   0.00258
            0.70000   0.00561
            0.72500   0.01119
            0.75000   0.02061
            0.77500   0.03536
            0.80000   0.05692
            0.82500   0.08654
            0.85000   0.12498
            0.87500   0.17235
            0.90000   0.22803
            0.92500   0.29068
            0.95000   0.35840
            0.97500   0.42896
            1.00000   0.50000
            1.02500   0.56931
            1.05000   0.63497
            1.07500   0.69550
            1.10000   0.74991
            1.12500   0.79767
            1.15000   0.83869
            1.17500   0.87318
            1.20000   0.90165
            1.22500   0.92471
            1.25000   0.94308
            1.27500   0.95748
            1.30000   0.96859
            1.32500   0.97706
            1.35000   0.98342
            1.37500   0.98813

1.40000	0.99159
1.42500	0.99409
1.45000	0.99589
1.47500	0.99716
1.50000	0.99805
1.52500	0.99868
1.55000	0.99911
1.57500	0.99940
1.60000	0.99960
1.62500	0.99974
1.65000	0.99983
1.67500	0.99989
1.70000	0.99993
1.72500	0.99995
1.75000	0.99997
1.77500	0.99998
1.80000	0.99999
1.82500	0.99999
1.85000	1.00000
1.87500	1.00000
1.90000	1.00000
1.92500	1.00000
1.95000	1.00000
1.97500	1.00000
2.00000	1.00000
2.02500	1.00000
2.05000	1.00000
2.07500	1.00000
2.10000	1.00000
2.12500	1.00000
2.15000	1.00000
2.17500	1.00000
2.20000	1.00000
2.22500	1.00000
2.25000	1.00000
2.27500	1.00000
2.30000	1.00000
2.32500	1.00000
2.35000	1.00000
2.37500	1.00000
2.40000	1.00000
2.42500	1.00000
2.45000	1.00000
2.47500	1.00000
10.00000	1.00000

FREUNDLICH MULTIWELL INJECTION SIMULATION

INPUT DATA

FREUNDLICH PARAMETERS

FREUNDLICH COEFFICIENT (B)   =   9.989

FREUNDLICH EXPONENT (A)   =   1.286

INJECTED CONCENTRATION (C0) =   .106

INJECTION TIME (DELT)   =   .500

ISOTHERM

$$C_{SORBED} = (B)(C)^A$$

FRACTIONAL BREAKTHROUGH CURVE

F	TF
.00000	.02500
.00000	.05000
.00000	.07500
.00000	.10000
.00000	.12500
.00000	.15000
.00000	.17500
.00000	.20000
.00000	.22500
.00000	.25000
.00000	.27500
.00000	.30000
.00000	.32500
.00000	.35000
.00000	.37500
.00000	.40000
.00000	.42500
.00000	.45000
.00000	.47500
.00000	.50000
.00000	.52500
.00001	.55000
.00004	.57500
.00013	.60000
.00040	.62500
.00107	.65000
.00258	.67500
.00561	.70000
.01119	.72500
.02061	.75000
.03536	.77500
.05692	.80000

.08654	.82500
.12498	.85000
.17235	.87500
.22803	.90000
.29068	.92500
.35840	.95000
.42896	.97500
.50000	1.00000
.56931	1.02500
.63497	1.05000
.69550	1.07500
.74991	1.10000
.79767	1.12500
.83869	1.15000
.87318	1.17500
.90165	1.20000
.92471	1.22500
.94308	1.25000
.95748	1.27500
.96859	1.30000
.97706	1.32500
.98342	1.35000
.98813	1.37500
.99159	1.40000
.99409	1.42500
.99589	1.45000
.99716	1.47500
.99805	1.50000
.99868	1.52500
.99911	1.55000
.99940	1.57500
.99960	1.60000
.99974	1.62500
.99983	1.65000
.99989	1.67500
.99993	1.70000
.99995	1.72500
.99997	1.75000
.99998	1.77500
.99999	1.80000
.99999	1.82500
1.00000	1.85000
1.00000	1.87500
1.00000	1.90000
1.00000	1.92500
1.00000	1.95000
1.00000	1.97500
1.00000	2.00000
1.00000	2.02500
1.00000	2.05000
1.00000	2.07500
1.00000	2.10000
1.00000	2.12500
1.00000	2.15000
1.00000	2.17500
1.00000	2.20000
1.00000	2.22500
1.00000	2.25000
1.00000	2.27500
1.00000	2.30000
1.00000	2.32500
1.00000	2.35000
1.00000	2.37500
1.00000	2.40000
1.00000	2.42500
1.00000	2.45000
1.00000	2.47500
1.00000	10.00000

1

OUTPUT DATA

TIME	CONCENTRATION (CE)
.02500	.00000
.05000	.00000
.07500	.00000
.10000	.00000
.12500	.00000
.15000	.00000
.17500	.00000
.20000	.00000
.22500	.00000
.25000	.00000
.27500	.00000
.30000	.00000
.32500	.00000
.35000	.00000
.37500	.00000
.40000	.00000
.42500	.00000
.45000	.00000
.47500	.00000
.50000	.00000
.52500	.00000
.55000	.00000
.57500	.00000
.60000	.00000
.62500	.00000
.65000	.00000
.67500	.00000
.70000	.00000
.72500	.00001
.75000	.00001
.77500	.00002
.80000	.00003
.82500	.00005
.85000	.00007
.87500	.00009
.90000	.00012
.92500	.00015
.95000	.00019
.97500	.00023
1.00000	.00026
1.02500	.00030
1.05000	.00034
1.07500	.00037
1.10000	.00040
1.12500	.00042
1.15000	.00045
1.17500	.00046
1.20000	.00048
1.22500	.00049
1.25000	.00050
1.27500	.00051
1.30000	.00052
1.32500	.00052
1.35000	.00053
1.37500	.00053
1.40000	.00054
1.42500	.00054
1.45000	.00054
1.47500	.00055
1.50000	.00055
1.52500	.00055
1.55000	.00056
1.57500	.00056
1.60000	.00057
1.62500	.00057
1.65000	.00058
1.67500	.00058
1.70000	.00059

1.72500	.00060
1.75000	.00061
1.77500	.00061
1.80000	.00062
1.82500	.00063
1.85000	.00064
1.87500	.00065
1.90000	.00066
1.92500	.00068
1.95000	.00069
1.97500	.00070
2.00000	.00072
2.02500	.00073
2.05000	.00075
2.07500	.00077
2.10000	.00079
2.12500	.00080
2.15000	.00083
2.17500	.00085
2.20000	.00087
2.22500	.00089
2.25000	.00092
2.27500	.00094
2.30000	.00097
2.32500	.00100
2.35000	.00103
2.37500	.00106
2.40000	.00109
2.42500	.00113
2.45000	.00116
2.47500	.00120
2.50000	.00124
2.52500	.00128
2.55000	.00132
2.57500	.00136
2.60000	.00140
2.62500	.00145
2.65000	.00149
2.67500	.00154
2.70000	.00158
2.72500	.00163
2.75000	.00168
2.77500	.00174
2.80000	.00179
2.82500	.00185
2.85000	.00191
2.87500	.00197
2.90000	.00204
2.92500	.00210
2.95000	.00217
2.97500	.00224
3.00000	.00232
3.02500	.00239
3.05000	.00247
3.07500	.00255
3.10000	.00263
3.12500	.00272
3.15000	.00281
3.17500	.00290
3.20000	.00299
3.22500	.00309
3.25000	.00319
3.27500	.00329
3.30000	.00340
3.32500	.00351
3.35000	.00362
3.37500	.00373
3.40000	.00385
3.42500	.00397
3.45000	.00409
3.47500	.00422
3.50000	.00435

3.52500	.00448
3.55000	.00462
3.57500	.00476
3.60000	.00491
3.62500	.00505
3.65000	.00520
3.67500	.00536
3.70000	.00552
3.72500	.00568
3.75000	.00584
3.77500	.00601
3.80000	.00619
3.82500	.00636
3.85000	.00654
3.87500	.00673
3.90000	.00692
3.92500	.00711
3.95000	.00731
3.97500	.00751
4.00000	.00771
4.02500	.00792
4.05000	.00814
4.07500	.00835
4.10000	.00858
4.12500	.00880
4.15000	.00904
4.17500	.00927
4.20000	.00951
4.22500	.00975
4.25000	.01000
4.27500	.01026
4.30000	.01051
4.32500	.01077
4.35000	.01104
4.37500	.01131
4.40000	.01158
4.42500	.01186
4.45000	.01214
4.47500	.01242
4.50000	.01271
4.52500	.01300
4.55000	.01330
4.57500	.01360
4.60000	.01389
4.62500	.01419
4.65000	.01450
4.67500	.01480
4.70000	.01511
4.72500	.01541
4.75000	.01571
4.77500	.01601
4.80000	.01631
4.82500	.01662
4.85000	.01693
4.87500	.01721
4.90000	.01749
4.92500	.01778
4.95000	.01807
4.97500	.01837
5.00000	.01862
5.02500	.01887
5.05000	.01912
5.07500	.01938
5.10000	.01964
5.12500	.01986
5.15000	.02006
5.17500	.02026
5.20000	.02046
5.22500	.02067
5.25000	.02086
5.27500	.02099
5.30000	.02112

5.32500	.02125
5.35000	.02138
5.37500	.02152
5.40000	.02158
5.42500	.02163
5.45000	.02167
5.47500	.02172
5.50000	.02177
5.52500	.02177
5.55000	.02173
5.57500	.02169
5.60000	.02164
5.62500	.02160
5.65000	.02153
5.67500	.02140
5.70000	.02127
5.72500	.02114
5.75000	.02101
5.77500	.02086
5.80000	.02066
5.82500	.02045
5.85000	.02024
5.87500	.02002
5.90000	.01980
5.92500	.01953
5.95000	.01926
5.97500	.01898
6.00000	.01869
6.02500	.01841
6.05000	.01809
6.07500	.01777
6.10000	.01744
6.12500	.01710
6.15000	.01677
6.17500	.01642
6.20000	.01606
6.22500	.01570
6.25000	.01534
6.27500	.01497
6.30000	.01460
6.32500	.01423
6.35000	.01386
6.37500	.01349
6.40000	.01310
6.42500	.01273
6.45000	.01237
6.47500	.01200
6.50000	.01163
6.52500	.01125
6.55000	.01088
6.57500	.01054
6.60000	.01019
6.62500	.00984
6.65000	.00948
6.67500	.00913
6.70000	.00882
6.72500	.00850
6.75000	.00817
6.77500	.00785
6.80000	.00753
6.82500	.00725
6.85000	.00696
6.87500	.00667
6.90000	.00638
6.92500	.00610
6.95000	.00585
6.97500	.00560
7.00000	.00535
7.02500	.00510
7.05000	.00485
7.07500	.00465
7.10000	.00444

7.12500	.00422
7.15000	.00401
7.17500	.00380
7.20000	.00363
7.22500	.00346
7.25000	.00328
7.27500	.00310
7.30000	.00293
7.32500	.00279
7.35000	.00265
7.37500	.00251
7.40000	.00236
7.42500	.00223
7.45000	.00212
7.47500	.00200
7.50000	.00189
7.52500	.00177
7.55000	.00167
7.57500	.00158
7.60000	.00149
7.62500	.00140
7.65000	.00131
7.67500	.00123
7.70000	.00116
7.72500	.00110
7.75000	.00103
7.77500	.00096
7.80000	.00090
7.82500	.00085
7.85000	.00079
7.87500	.00074
7.90000	.00069
7.92500	.00065
7.95000	.00061
7.97500	.00057
8.00000	.00053
8.02500	.00049
8.05000	.00046
8.07500	.00043
8.10000	.00040
8.12500	.00037
8.15000	.00034
8.17500	.00032
8.20000	.00030
8.22500	.00028
8.25000	.00026
8.27500	.00024
8.30000	.00022
8.32500	.00021
8.35000	.00019
8.37500	.00018
8.40000	.00016
8.42500	.00015
8.45000	.00014
8.47500	.00013
8.50000	.00012
8.52500	.00011
8.55000	.00010
8.57500	.00010
8.60000	.00009
8.62500	.00008
8.65000	.00008
8.67500	.00007
8.70000	.00006
8.72500	.00006
8.75000	.00005
8.77500	.52500
8.80000	1.22500
8.82500	1.47500
8.85000	1.70000
8.87500	1.92500
8.90000	2.10000

8.92500	2.25000
8.95000	2.37500
8.97500	2.50000
9.00000	2.60000
9.02500	2.67500
9.05000	2.75000
9.07500	2.82500
9.10000	2.90000
9.12500	2.95000
9.15000	3.00000
9.17500	3.07500
9.20000	3.12500
9.22500	3.15000
9.25000	3.20000
9.27500	3.25000
9.30000	3.27500
9.32500	3.32500
9.35000	3.35000
9.37500	3.40000
9.40000	3.42500
9.42500	3.45000
9.45000	3.50000
9.47500	3.52500
9.50000	3.55000
9.52500	3.57500
9.55000	3.60000
9.57500	3.62500
9.60000	3.65000
9.62500	3.67500
9.65000	3.70000
9.67500	3.72500
9.70000	3.75000
9.72500	3.77500
9.75000	3.80000
9.77500	3.82500
9.80000	3.85000
9.82500	3.87500
9.85000	3.90000
9.87500	3.92500
9.90000	3.95000
9.92500	3.97500
9.95000	4.00000
9.97500	4.02500
10.00000	4.05000

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