# New Approach for Estimating Alcohol Partition Coefficients between Nonaqueous Phase Liquids and Water

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The partitioning interwell tracer test (PITT) has emerged during the past few years as a useful tool for characterizing aquifers contaminated by nonaqueous phase liquids (NAPLs) and in particular the location and volume of NAPLs. Accurate partition coefficients are needed for a wide variety of tracers and NAPLs to use this technology to its maximum benefit. A new approach to estimate the partition coefficients of alcohol tracers partitioning between NAPL and water is presented. This approach is based upon defining an equivalent alkane carbon number for each contaminant and for each alcohol tracer and is very useful for both minimizing the number of experiments required and for extracting the maximum information from such experiments.

#### Introduction

The contamination of aquifers with nonaqueous phase liquids (NAPLs) is a widespread and serious environmental problem. The location and quantitative characterization of dense nonaqueous phase liquids (DNAPLs) is an especially difficult problem (1). The partitioning interwell tracer test (PITT) has been developed and demonstrated in the field during the past few years to address this difficult characterization problem. About 30 field demonstrations were completed by the end of 1997. The PITT involves the simultaneous injection of partitioning and nonpartitioning tracers into the subsurface at sufficiently dilute concentrations that the tracers by definition have negligible effect on the properties of the pore fluids. The partitioning tracer molecules partition into and out of the NAPL and are retarded relative to the nonpartitioning tracer. The chromatographic separation of the tracers is directly proportional to the volume of NAPL contacted. The simplest and most robust method for calculating the NAPL volume is based upon the first temporal moment of the tracer response data. The difference between the first temporal moments of the partitioning and nonpartitioning tracers is used to estimate either the volume of the NAPL or the residual NAPL saturation in the swept volume of the subsurface (2-5). Alternately, the three-dimensional spatial distribution of the NAPL saturation can be estimated using inverse methods if sufficient tracer data are collected for this purpose, and with the compositional correlation presented in this paper, it may also be possible to compute the composition of the in-situ NAPL in some cases.

Partitioning tracers are very useful tools for quantifying NAPL volume and assessing performance of remediation projects. Partitioning tracers can be used to estimate the volume of NAPL before a remedial action, and they can also be used for estimating the volume of NAPL remaining after remedial actions and hence as a performance assessment method (2–11). A design protocol for PITTs can be found in ref 10.

The most common partitioning tracers that have been used to date in saturated zones are aliphatic alcohols such as 1-hexanol and 1-heptanol since these have been found to have sufficiently high partition coefficients for many NAPLs at the low average saturations typical of most sites. The partition coefficient  $(K_{i,j})$  is defined as the concentration of the alcohol (in mg/L) in the NAPL divided by the concentration of the alcohol (in mg/L) in the water. At sufficiently low concentrations, alcohol tracers show a linear partitioning into the NAPL as the aqueous concentration of the alcohol increases, and thus the partition coefficient is constant over the dilute range of interest in field tests. This behavior is a good approximation for the data presented here but should always be checked for the conditions of interest. In addition to the desirable range of partition coefficients, aliphatic alcohols are environmentally acceptable as groundwater tracers, have sufficient water solubility up to 1-octanol to use as partitioning tracers, have very low adsorption on typical alluvium soils, are easy to detect, have low analytical detection limits, and are relatively inexpensive, thus making them suitable for many saturated zone field applications. However, other suitable tracer candidates have also been identified and merit further research.

The accuracy of a PITT is contingent on selection of suitable tracers and the accurate measurement of their partition coefficients between NAPL and water (or air in the case of vadose PITTs). The error in NAPL volume estimates based on PITTs is directly proportional to the error in the partition coefficients. Accurate experimental measurements of partition coefficients are essential for final tracer selection and use but are time-consuming and costly. In some cases, NAPL samples may not be available, may not be representative of the in-situ NAPL, or may have been altered by the remediation process. Therefore, it is advantageous to use estimation techniques for preliminary estimates, for identifying errors in the measurements, for use in inverse models, and for estimating the values for mixtures from pure component values.

Several predictive techniques to estimate partition coefficients are discussed in the literature. For example, the partition coefficients for many organic components between octanol and water have been estimated using empirically derived group fragment constants (12-14) or linear free energy relationships (14). Octanol-water partition coefficients have also been estimated using UNIFAC (15). This approach was recently applied to estimating the partition coefficients of aliphatic alcohols between water and various NAPLs (16). Although the UNIFAC estimates of the partition coefficients were sufficiently accurate to be useful, the partition coefficients for alcohols between pure NAPL and water were not in general within the experimental error of the measurements. Furthermore, the binary interaction parameters of all groups of typical NAPL mixtures are often not known, and this was another limitation of the UNIFAC solubility approach. More recently, we have discovered that an approach based upon the concept of equivalent alkane carbon number (EACN) is both simpler and more accurate, and this is the approach presented in this paper.

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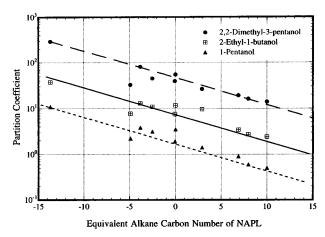


FIGURE 1. Partition coefficient as a function of NAPL EACN.

## Equivalent Alkane Carbon Number Correlation from Surfactant Data

The Equivalent Alkane Carbon Number (EACN) concept was introduced by Wade and Schechter and co-workers in the 1970s for understanding and correlating the behavior of surfactants for enhanced oil recovery (17, 18) and more recently was found to be of great value in understanding and evaluating surfactant-enhanced remediation of chlorocarbons (19). The EACN of a pure alkane is just its carbon number. For example, alkane carbon numbers (ACN) of 8-10 were assigned for linear alkanes such as n-octane and n-decane. Phase behavior experiments were carried out with various anionic surfactants and the linear alkanes, and the optimum salinity for each of these surfactants and hydrocarbons was measured. Optimal salinity is defined as the electrolyte concentration (sodium chloride in this context) at which equal volumes of water and oil (or NAPL) are solubilized by the microemulsion (18). The logarithm of the optimal salinity was observed to be a linear function of the ACN. The optimum salinity of the same surfactant was then measured for various other hydrocarbons and mixtures of hydrocarbons including even very complex mixtures of unknown composition such as crude oils. The EACN of each of these other hydrocarbons and mixtures was then estimated by interpolation on the straight line established by the normal alkane data. More recently, the same approach was found to work for a wide variety of chlorocarbons and mixtures of chlorocarbons and hydrocarbons (19, 20). A very useful and significant aspect of the EACN approach is that the EACN of a multicomponent oil or NAPL is the mole fraction average of the pure component values:

$$N_{\text{mixture}} = \sum_{i=1}^{n} x_i N_i \tag{1}$$

# Equivalent Alkane Carbon Number Correlation from Alcohol Partitioning Data

When the logarithm of the partition coefficient of various alcohols was plotted versus the EACN of the NAPL (NAPL EACNs from refs 19 and 20), a linear relationship was observed that was analogous to that of optimum salinity for surfactants. An example is shown in Figure 1. It can also be seen that the slope of these curves is the same for all the alcohol tracers plotted. By analogy with the EACN of normal alkanes, the EACN of the linear aliphatic alcohols such as 1-pentanol is defined as the number of carbon atoms in the alcohol. The logarithm of the partition coefficient for several alcohols and two representative NAPLs were plotted against the alcohol

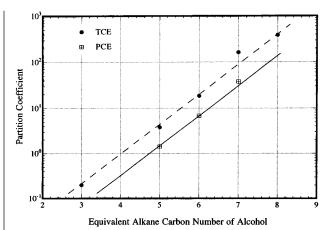


FIGURE 2. Partition coefficient as a function of alcohol EACN.

ACNs as shown in Figure 2, and a linear relationship was again observed. On the basis of these results, we propose the following bilinear equation for correlating partition coefficients as a function of the alcohol EACN  $(A_j)$  and the NAPL EACN  $(N_j)$ :

$$\ln K_{i,j} = g + MA_i + mN_i \tag{2}$$

where g, M, and m are correlation constants obtained by regression on experimentally measured data.

A total of 198 measurements of partition coefficient was made using 22 alcohols and nine NAPLs (9). A 10-mL aliquot of a 1000 mg/L alcohol in water was placed in a separatory funnel with 10 mL of the NAPL. These samples were prepared in triplicate. The samples were thoroughly shaken for 1 h, allowed to separate for 1 h, and reshaken. These samples were allowed to separate for at least 12 h and then centrifuged for 1 h to allow a complete separation of the phases to occur. Six aqueous samples were then analyzed for alcohol using a gas chromatograph with a flame ionization detector (FID). Six more samples were measured after another 36 h of equilibration time. If the results were the same as those at 12 h within experimental error, they were considered equilibrium results. This was always the case for the data reported here. For tracers with partition coefficients greater than 15, 3 mL of NAPL was mixed with 18 mL of aqueous solution in a 24-mL vial. Otherwise, the aqueous alcohol concentration of the equilibrated samples is too low for accurate GC measurements. The partition coefficient was then calculated using a mass balance on the alcohol. The estimated error of the partition coefficient measured this way is 12% (9). Additional measurements such as column tests have been used to reduce this error to about 7% (9), but this has been done for only a few selected cases of special interest to date.

The initial estimates of alcohol and NAPL EACNs were made graphically by plotting all of the data using the defined values of EACN for the linear alcohols and normal alkanes plus the literature values of EACN for chlorocarbons and jet fuel (19, 20). The three constants g, M, and m in eq 2 were then estimated by linear regression. Then some of the values of  $A_j$  were adjusted for the branched alcohols, and the values of  $N_i$  were adjusted for the chlorocarbons to give a better linear fit of the data. A comparison of the EACNs for the NAPLs estimated this way with those from the literature (19, 20) is given in Table 1. The EACN values are in generally good agreement considering the completely different types of data from which they were derived and the difficulty of making some of the surfactant measurements accurately.

TABLE 1. Comparison of Estimated and Literature Values of EACNs for Several NAPLs

NAPL	EACN estimated	EACN from 19 and 20
trichloroethylene	-5.41	-3.81
tetrachloroethylene	2.27	2.9
1,1,1-trichloroethane	-3.05	-2.5
1,2-dichloroethane	-8.1	-12.10
carbon tetrachloride	-0.40	-0.06
trichloromethane (chloroform)	-15.13	-13.67
jet fuel (JP4)	6.31	6.9

TABLE 2. Estimated EACNs of Alcohol Tracers

alcohol	EACN	alcohol	EACN
1-pentanol	5.00	2,3-dimethyl-2-butanol	5.30
1-hexanol	6.00	3,3-dimethyl-2-butanol	5.70
1-heptanol	7.00	3,3-dimethyl-1-butanol	5.49
1-octanol	8.00	3-methyl-3-hexanol	6.31
2-methyl-2-butanol	4.29	2-methyl-3-hexanol	6.52
2-methyl-1-pentanol	5.85	3-methyl-2-hexanol	6.76
3-methyl-1-pentanol	5.75	2-methyl-2-hexanol	6.33
2-methyl-2-pentanol	5.33	5-methyl-2-hexanol	6.77
3-methyl-2-pentanol	5.70	3-ethyl-3-pentanol	6.39
4-methyl-1-pentanol	5.93	4,4-dimethyl-2-pentanol	6.67
2-methyl-3-pentanol	5.25	2,3-dimethyl-3-pentanol	6.38
4-methyl-2-pentanol	5.63	2,2-dimethyl-3-pentanol	6.95
3-methyl-3-pentanol	5.28	- '	

The estimated EACNs of the alcohols are given in Table 2. The final regression equation is as follows:

$$\log_{10} K_{i,j} = -2.9562 + 0.6548A_i - 0.0505N_i$$
 (3)

A comparison between the experimental and computed partition coefficients is given in Table 3. Based on the regression of the data, the standard deviation in  $\log_{10} K_{i,j}$  is 8.3%. The correlation coefficient  $r^2$  of the regression is 0.984. The standard deviation of the partition coefficients ( $K_{i,j}$ ) for this correlation is 18%.

For a multicomponent NAPL, eq 2 can be generalized to

$$\log K_{\text{mixture},j} = g + MA_j + mN_{\text{mixture}}$$
 (4)

and using eq 1

$$\log K_{\text{mixture},j} = g + MA_j + m \sum_{i=1}^{n} x_i N_i$$
 (5)

It follows that

$$\ln K_{\text{mixture},j} = \sum_{i=1}^{n} x_i \ln K_{i,j}$$
 (6)

If the composition of a multicomponent NAPL is known and the partition coefficient for each pure component in the NAPL is known or can be estimated, then eq 6 can be used to estimate the partition coefficient of each alcohol *j* for the NAPL mixture. Conversely, if a sufficiently large number of tracers are used in a PITT, both the volume and composition of a field NAPL could in principle be estimated using eq 6 and the first temporal moments of the tracers (4) and/or inverse modeling.

A comparison of predicted and measured partition coefficients for several alcohols with TCE and PCE are shown in Figure 3. Similar results for 1,1,1-trichloroethane and jet fuel (JP4) are shown in Figure 4 and for octane and decane NAPLs in Figure 5. Excellent agreement between the

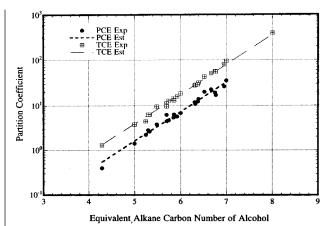
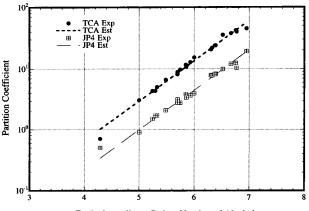


FIGURE 3. Comparison of predicted and measured partition coefficients of various alcohol tracers with PCE and TCE NAPLs.



Equivalent Alkane Carbon Number of Alcohol

FIGURE 4. Comparison of predicted and measured partition coefficients of various alcohol tracers with TCA and JP4 NAPLs.

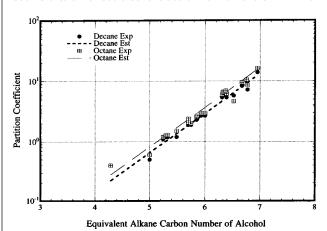


FIGURE 5. Comparison of predicted and measured partition coefficients of various alcohol tracers with decane and octane NAPLs.

measured and estimated partition coefficients is observed in all these cases.

As a further test of the mixture correlation, the partition coefficients of a mixture of 1,2-dichloroethane (DCA) and PCE were estimated and compared with our mixture data. From Figure 6 it is evident that the predicted and measured partition coefficients are in good agreement and in fact are within the experimental error of our measurements. To further extend the applicability of the EACN approach, the EACN of a DNAPL from Hill AFB OU2 was estimated based

TABLE 3. Comparison of Measured and Estimated Partition Coefficients

alcohol	PCE Exp	PCE Est	TCE Exp	TCE Est	TCA Exp	TCA Est	JP4 Exp	JP4 Est	Dec Exp	Dec Est	Oct Exp	Oct Est	DCB Exp	DCB Est	CTET Exp	CTET Est	TCM Exp	TCM Est
	•						•						•		•		•	
1-pentanol							0.90								1.90		10.8	. —
1-hexanol	0.00	7.21	18.6		15.2	13.4	4.00	4.50	2.70	2.93	3.00	3.70	13.2	9.54	11.0	9.83	57.5	54.6
1-heptanol	35.4	32.5																
1-octanol	0.40	0 - 4	389		0.70	1 01	0.50	0 24	0.40	0 22	0.40	0.00	0.50	0.70	0.00	074	2 10	111
2-methyl-2-butanol							0.50									0.74		
2-methyl-1-pentanol							3.90						,	,		7.82	36.7	
3-methyl-1-pentanol							2.80								6.50		41.2	
2-methyl-2-pentanol							1.70								3.40		19.7	
3-methyl-2-pentanol							2.80								5.90		32.5	· · · ·
4-methyl-1-pentanol							3.70						9.20		8.50		58.9	
2-methyl-3-pentanol		2.31					1.50								3.30		18.3	
4-methyl-2-pentanol							3.40									7.96		
2,3-dimethyl-2-butanol							1.70								3.30		16.4	
3-methyl-2-pentanol	4.50			—			3.20									6.28	31.5	0
3,3-dimethyl-1-butanol	3.80						2.10						4.40		4.10		25.9	
3-methyl-3-hexanol							7.90									15.7		00
2-methyl-3-hexanol							9.90								29.8	21.6	· · · -	119.9
3-methyl-2-hexanol							12.4						29.3		30.0		216	171
2-methyl-2-hexanol							7.80						14.9		16.1	16.1	70.1	89.1
5-methyl-2-hexanol	17.1						10.3						33.7		30.4		554	175
3-ethyl-3-pentanol							8.30							17.2		17.7	99.2	,
4,4-dimethyl-2-pentanol												10.15	22.1		24.7	27.0	152	150
2,3-dimethyl-3-pentanol													15.8				81.6	
2,2-dimethyl-3-pentanol	26.4	30.2	80.2	73.9	45.1	56.1	19.2	18.9	13.9	12.3	16.1	15.5	32.4	40.0	39.1	41.2	293	229

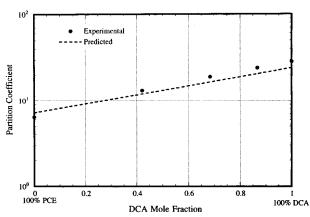


FIGURE 6. Comparison of predicted and measured partition coefficients of 1-hexanol with a mixture of PCE and DCA.

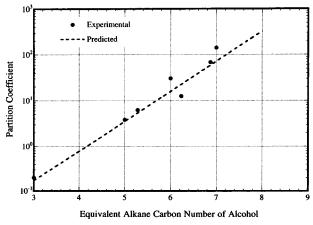


FIGURE 7. Comparison of predicted and measured partition coefficients of various alcohol tracers with Hill DNAPL.

on the composition of its principal components of TCE (approximately 73 wt %), TCA (approximately 14 wt %), and PCE (approximately 8 wt %). Small amounts of other volatile organic carbon components and grease were neglected since they made up less than 5% of the mass of the DNAPL. The

measured and estimated partition coefficients are in good agreement as shown in Figure 7. Some of the variations between the measured and estimated partition coefficients are likely due to the uncertainty in the DNAPL composition.

On the basis of the results presented in this paper, we conclude that a modified EACN approach is very effective and useful in estimating the partition coefficients of alcohol tracers between water and typical NAPLs found in contaminated aquifers. Excellent agreement was obtained between measured and estimated partition coefficients for various NAPLs.

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## **Nomenclature**

$A_j$	EACN of alcohol <i>j</i>
CTET	carbon tetrachloride
DCB	o-dichlorobenzene
Dec	decane
Est	estimated value
Exp	experimentally measured value
JP4	jet fuel
$K_{i,j}$	partition coefficient of alcohol $j$ with NAPL $i$
$K_{\text{mixture},j}$	partition coefficient of alcohol $j$ with multicomponent NAPL

n number of components in the NAPL mixture

NAPL nonaqueous phase liquid

 $N_i$  EACN of NAPL i

N<sub>mixture</sub> EACN of multicomponent NAPL

PCE tetrachloroethylene TCA 1,1,1-trichloroethane

TCE trichloroethylene TCM chloroform

 $x_i$  mole fraction of NAPL component i in the mixture

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