Evaluation for estimating partition coefficients of alcohol tracer partitioning between benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds and water

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Abstract

The partitioning tracer method has been studied in laboratory research and field investigations as an alternative method for characterizing aquifers contaminated by nonaqueous phase liquids (NAPLs). Accurate partition coefficients of tracers partitioning between NAPL and water are needed to improve the reliability of the partitioning tracer method. In this research, partition coefficients of alcohol tracers partitioning between benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds and water are estimated using the approach of equivalent alkane carbon number (EACN). General agreement was observed between the measured and estimated partition coefficients of alcohol tracer between BTEX compounds and water. Based on these results we can verify that the EACN approach is suitable for estimating the partition coefficient of alcohol tracers between BTEX compounds and water.
Keywords: partitioning tracer method, alcohol tracers, partition coefficient, BTEX compounds.

1   Introduction

The contamination of soil and groundwater by nonaqueous phase liquids (NAPLs) has become an issue of great interest. In particular, petroleum, such as gasoline, has been used in large quantities in various industry field and its spills or leaks into aquifers cause environmental problems. The major components of petroleum are benzene, toluene, ethylbenzene, and xylenes (BTEX) and they

have known to be carcinogenic organic contaminants [1]. If petroleum leaks into the ground from a storage tank it is necessary to monitor the distribution and quantity of petroleum and also to cleanup contaminants immediately [2].

However, traditional site characterization methods, such as analysis of soil gas, core sampling, and monitor-well sampling, are often not capable of providing sufficient data required for effective remediation system design. A major weakness of these methods is that they provide data at discrete points. As a result there is a probability of under-estimation of NAPL's residual saturation without a cost-prohibitive amount of sampling [3].

The partitioning tracer method has been developed and demonstrated in the field during the past few years as an alternative method for site characterization. The major advantage of the partitioning tracer method is to provide a continuous measurement of the target area and characterize a relatively large and reliable detection volume in comparison with traditional methods [4, 5]. The partitioning tracer method consists of the simultaneous injection of several tracers, which have different partition coefficients with respect to NAPL at one or more injection wells and subsequent measurement of tracer concentrations at one or more extraction or monitoring wells. Injected tracers are retarded in proportion to its partition coefficient between NAPL and water due to their chromatographic separation in aquifers. This separation of the partitioning tracers indicates the presence of NAPL in the targeted zone and is used to determine the volume and distribution of NAPL present [4].

The accuracy of a partitioning tracer method mainly depends on the selection of suitable tracers and the accurate measurement of their partition coefficients between NAPL and water. Dwarakanath and Pope [5] suggest that the error in NAPL volume estimates based on partitioning tracer methods is directly proportional to the error in the partitioning coefficients. Therefore, the accurate experimental measurements of partition coefficients are important to minimize the errors in the partitioning tracer method. However, it requires time-consuming experiments to obtain the partition coefficient of each proposed tracer. Moreover, if samples of NAPL are not available, it is difficult to measure the partition coefficient directly.

Dwarakanath and Pope [5] proposed a new approach for estimating partition coefficients of alcohol tracers between NAPL and water using the concept of equivalent alkane carbon number (EACN), which is simply an equivalent of the alkane carbon numbers for more complex organic molecules (e.g., 6 for hexanol), and suggested that it is very effective and useful in estimating the partition coefficient of alcohol tracers between water and NAPLs. They also suggested the bilinear equation by multiple regression analysis on the basis of the results that the correlation between the logarithm of the partitioning coefficient of various alcohols and EACN of NAPLs and alcohol tracers is a linear relationship. Wu and Sabatini [6] have extended this approach and focused on more hydrophobic oils (high EACN LNAPLs) to find the hydrophobicity of NAPLs. These studies mainly focus on dense nonaqueous phase liquids (DNAPLs) and high EACN number of LNAPLs.

In order to estimate the partition coefficient of alcohol tracers between petroleum and water by using EACN approach, BTEX are selected to represent gasoline as petroleum-contaminants and the EACN approach is applied for estimating the partition coefficients of several alcohol tracers for various BTEX mixtures. To confirm the accuracy of the EACN approach for petroleum, and in particular for gasoline, the partition coefficients from experimental measurements are compared with the estimated values from the EACN approach.

2   Materials and methods

2.1   Materials

The properties of benzene, toluene, ethylbenzene, and xylenes and alcohol tracers used in this study are summarized in table 1. BTEX mixtures are made with certain mixing ratios given in table 2. Mixtures A to D are blended for representing the mixtures with a certain mole ratio and Mixture E is blended with the special mixing ratio, which represent the composition ratio of BTEX found in soils contaminated by petroleum [7].

Table 1:   Properties of BTEX and tracers used in this study.

Chemicals	Molecular formula	Molecular weight (g/mol)	Density (g/mL)	Solubility (mg/L)	Manufactured company	Purity (%)
Benzene	C_6-H_6	78.11	0.88	1780	JUNSEI	99.5
Toluene	C_6-H_5-C-H_3	92.14	0.87	500	Aldrich	99.5
Ethylbenzene	C-H_3-C-H_2-C_6-H_5	106.17	0.86	140	Aldrich	98.0
Xylene	C_6-H_4-$(C$-$H_3)_2$	106.17	0.87	170	Aldrich	83.0
Methanol	C-H_3-O-H	32.04	0.79	-	Duksan	99.8
1-Butanol	C_4-H_9-O-H	74.12	0.81	-	Aldrich	99.9
1-Pentanol	C_4-H_9-C-H_2-O-H	88.15	0.81	-	Aldrich	99+
Hexanol	C_6-H_{14}-O	102.18	0.81	-	Aldrich	99+
2-Ethyl-1-Butanol	$(C_2$-$H_5)_2$-C-H-C-H_2-O-H	102.18	0.83	-	Aldrich	98.0
4-Methyl-2-Pentanol	$(C$-$H_3)$-C-H-C-H_2-C-H-$(O$-$H)$-C-H_3	102.18	0.81	-	Aldrich	99.0

Table 2:   Mixing ratios for BTEX compounds.

BTEX compounds	Mixing ratios							
	Mole ratio				Weight ratio			
	Benzene	Toluene	Ethyl-benzene	Xylene	Benzene	Toluene	Ethyl-benzene	Xylene
Mixture A	1	1	1	1	1	1.18	1.36	1.36
Mixture B	2	1	1	1	1	0.59	0.68	0.68
Mixture C	1	2	1	1	1	2.35	1.36	1.36
Mixture D	1	1	2	1	1	1.18	2.72	1.36
Mixture E	1	13.18	3.96	17.01	1	15.55	5.39	23.12

2.2 Experimental method

The partition coefficient was measured by using six tracers and nine BTEX compounds, which were benzene, toluene, ethylbenzene, xylenes, and Mixture A to E. The alcohol aqueous concentrations were varied between 100 and 600 mg/L (100, 200, 400, 600 mg/L). Equal volumes of BTEX compounds and water (10 mL each) were placed in a 20 mL vial that was crimp-capped with a Teflon septum, leaving minimum headspace. The vial was shaken on a vortex mixer and rotary shaker for each 30 seconds and 24 hours. After shaking these samples, they were allowed to stabilize for 1 hour and than centrifuged for 5 minutes to allow a complete separation of the phases. Reacted alcohol aqueous solution was translated from aqueous phase to the 2 mL vial using a pipette and were analyzed by an Agilent 6890 GC-FID (each sample was made in duplicate). Then, the partition coefficient was calculated from using a mass balance.

3 Results and discussions

The partitioning of 4-methyl-2-pentanol between BTEX compounds and water is shown in fig. 1. Linear relationships are found between the concentration of a tracer in water and that of a tracer in BTEX compounds. The other 4 tracers, which are 1-butanol, 1-pentanol, hexanol, and 2-ethyl-1-butanol, also show linear relationships between the concentration of a tracer in water and that of a tracer in BTEX compounds.

From these linear relationships the slope of the regression curve represents the partition coefficient of used alcohol tracer. All of partition coefficients for each alcohol tracer between BTEX compounds and water are listed in table 3 and the regression coefficient of results have a value of over 0.95.

The EACN values of benzene, toluene, ethylbenzene, and toluene are respectively 0, 1, 2, and 2 and those of butanol, pentanol, and hexanol are respectively 4, 5, and 6. BTEX's EACN values are from the literature [8, 9] and the tracer's EACN values are from the assumption that the EACN value of linear alcohol can be found just by its carbon number [5].

A linear relationship was observed when the logarithm of the partition coefficient of several alcohol tracers was plotted against both of the EACN values of BTEX compounds (fig. 2) and those alcohol tracers (fig. 3). These results are similar with that of Dwarakanath and Pope [5].
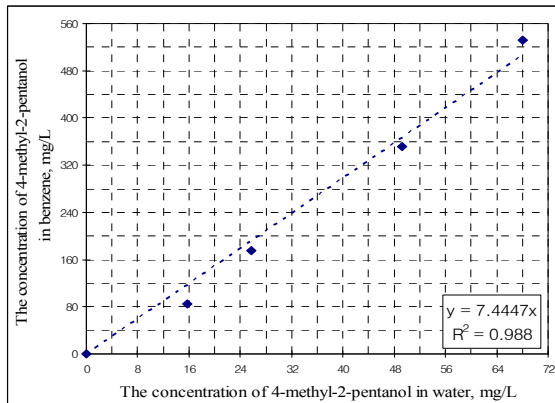
According to these results, the bilinear equation for correlating the logarithm of partition coefficient (K) as a function of the alcohol tracer's EACN (A) and the BTEX EACN (N) was obtained by multiple regression analysis, eqn (1).

$$\log K = -2.39829 + 0.584492 \cdot A - 0.07418 \cdot N \qquad (1)$$
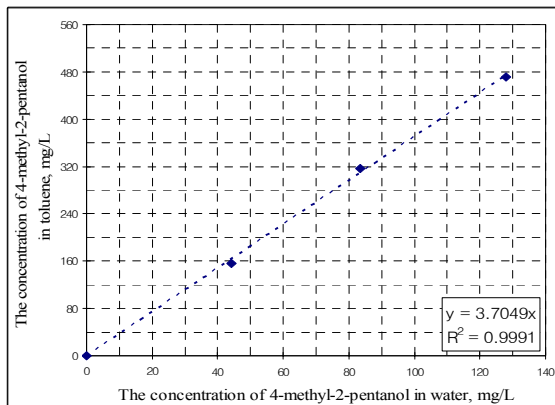
Based on the regression of the data, the standard deviation is 15.5% and the correlation coefficient of the regression is 0.935. This equation for BTEX compounds is analogous to that of Dwarakanath and Pope [5].

Using the experimental value of the partition coefficient for single BTEX and eqn. (1), the logarithm of the experimental partition coefficient of the BTEX mixture is compared with the logarithm of the estimated partition coefficient of the BTEX mixtures (table 4) and the accuracy of measurements is given in percent (estimated value over experimental value times 100). The overall difference and tendency between the experimental and estimated results is also plotted in fig. 4. On the 1:1 line, experimental values are equal to estimated value and most over-estimated or under-estimated values are on the 1:1.19 line and 1:0.58 line respectively. Though there is a tendency that estimated results are underestimated, most of the estimated results are similar to experimental results.
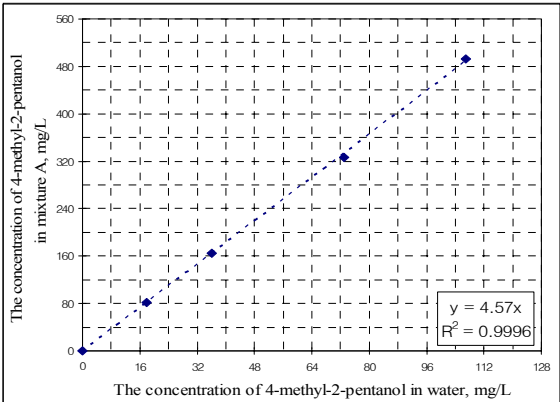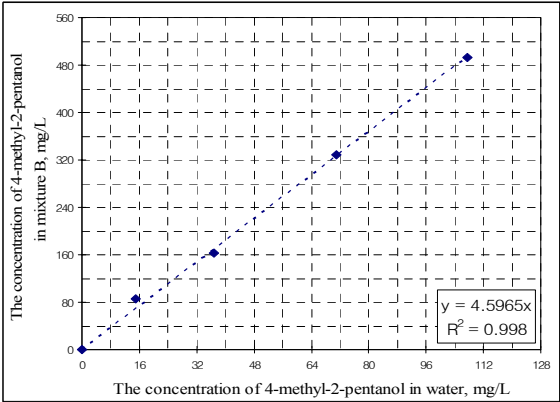

(a)

(b)

Figure 1:   Partitioning   of   4-methyl-2-pentanol   between   water   and:
             (a) benzene, (b) toluene, (c) Mixture A and (d) Mixture B.
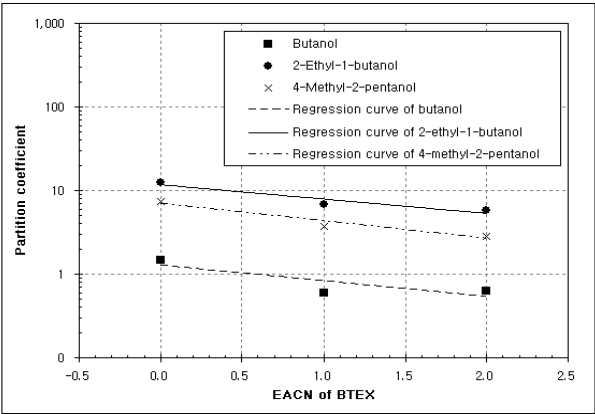
(c)

(d)

Figure 1: Continued

Figure 2:   Partitioning coefficient as a function of BTEX EACN.

Table 3:   Measured partition coefficients of tracers between BTEX compounds and water.

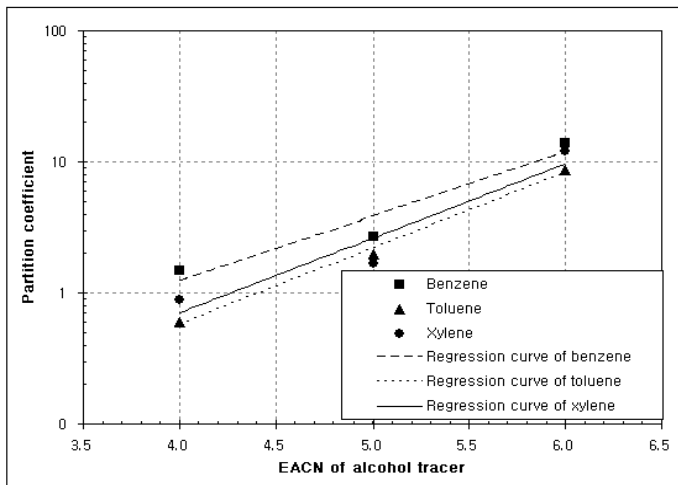| Tracers	Contaminants	K [a]	R² [b]	Contaminants	K	R²
Methanol	Benzene	0.05	-	Mixture A	-	-
	Toluene	0.22	-	Mixture B	-	-
	Ethylbenzene	0.28	-	Mixture C	-	-
	Xylene	0.19	-	Mixture D	-	-
				Mixture E	-	-
Butanol	Benzene	1.47	0.9999	Mixture A	1.99	0.9745
	Toluene	0.60	0.9784	Mixture B	1.10	0.9955
	Ethylbenzene	0.62	0.9992	Mixture C	0.76	0.9984
	Xylene	0.88	0.9429	Mixture D	0.96	0.9719
				Mixture E	0.42	0.9983
Pentanol	Benzene	2.68	0.9793	Mixture A	2.36	0.9922
	Toluene	1.98	0.9918	Mixture B	2.49	0.9994
	Ethylbenzene	2.20	0.9915	Mixture C	2.31	0.9988
	Xylene	1.68	0.9990	Mixture D	2.37	0.9905
				Mixture E	2.88	0.9480
Hexanol	Benzene	14.00	0.9954	Mixture A	14.48	0.9679
	Toluene	8.65	0.9900	Mixture B	10.67	0.9979
	Ethylbenzene	14.51	0.9931	Mixture C	7.62	0.9952
	Xylene	12.06	0.9963	Mixture D	18.23	0.9579
				Mixture E	19.29	0.9643
2-Ethyl-1-butanol	Benzene	12.59	0.9885	Mixture A	6.97	0.9996
	Toluene	6.86	0.9903	Mixture B	6.74	0.9879
	Ethylbenzene	5.71	1.0000	Mixture C	8.07	0.9851
	Xylene	5.95	0.9995	Mixture D	6.56	0.9918
				Mixture E	5.74	0.9992
4-Methyl-2-pentanol	Benzene	7.44	0.9880	Mixture A	4.57	0.9996
	Toluene	3.70	0.9991	Mixture B	4.60	0.9980
	Ethylbenzene	2.83	0.9899	Mixture C	6.15	0.9752
	Xylene	3.48	0.9951	Mixture D	4.55	0.9883
				Mixture E	9.18	0.9488

[a] K - Partitioning coefficient
[b] R² - Regression coefficient

Figure 3:   Partitioning coefficient as a function of alcohol EACN.

Table 4:   Measured and estimated partition coefficients of alcohol tracers.

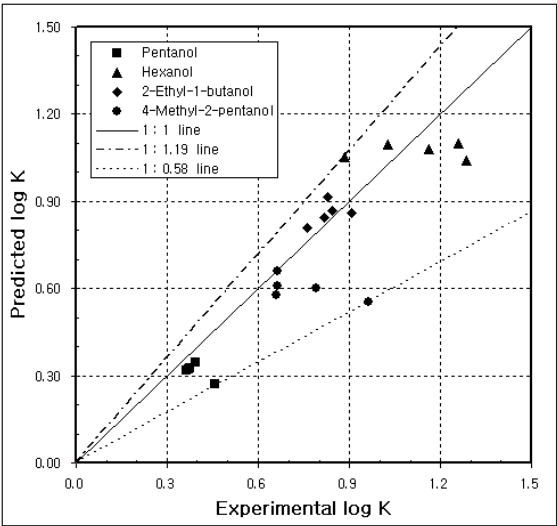| Tracers	Mixtures	Exp. logK	Est. logK	Accuracy(%)
Pentanol	Mixture A	0.3729	0.3231	86.65
	Mixture B	0.3962	0.3441	86.86
	Mixture C	0.3636	0.3178	87.41
	Mixture D	0.3747	0.3270	87.26
	Mixture E	0.4594	0.2727	59.36
Hexanol	Mixture A	1.1608	1.0815	93.17
	Mixture B	1.0282	1.0945	106.45
	Mixture C	0.8820	1.0526	119.35
	Mixture D	1.2608	1.0976	87.05
	Mixture E	1.2852	1.0394	80.87
2-Ethyl-1-butanol	Mixture A	0.8432	0.8669	102.80
	Mixture B	0.8287	0.9135	110.24
	Mixture C	0.9069	0.8608	94.92
	Mixture D	0.8169	0.8448	103.42
	Mixture E	0.7589	0.8084	106.53
4-Methyl-2-pentanol	Mixture A	0.6599	0.6083	92.18
	Mixture B	0.6628	0.6609	99.73
	Mixture C	0.7889	0.6003	76.09
	Mixture D	0.6580	0.5770	87.69
	Mixture E	0.9628	0.5548	57.62

Figure 4:   Comparison of measured and estimated partition coefficients of tracers.

4   Summary and conclusion

The linear relation between the concentration of the tracer in water and that of the tracer in BTEX compounds was confirmed with high accuracy (regression

coefficients are over 0.95) and partition coefficients of alcohol tracers were obtained under this linear relation.

The bilinear relation was found for correlating the logarithm of the partition coefficient for alcohol tracer partitioning between BTEX compounds and water as a function of the alcohol tracer's EACN and the BTEX EACN. As a result of comparison between experimental and estimated partition coefficients, a general agreement was observed although there is a tendency that the estimated results are underestimated.

Therefore, we can conclude that the EACN approach can be extended to estimate the partition coefficient for alcohol tracer partitioning between BTEX compounds and water.

Acknowledgements

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