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Chapter 6: Environmental Transport and Fate of Fuel Hydrocarbon Alkylates

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6.1. Introduction

Alkylates—high-octane solutions of branched alkanes—are already components in gasoline, but gasoline distributed in California after a phase-out of methyl tertiary butyl ether (MTBE) will likely include an increased amount of alkylates. MTBE is a high-octane, anti-knock additive; and to maintain octane levels in gasoline after MBTE is removed, additional amounts of alkylates will be required. For example, although ethanol also has a high-octane level, its oxygen content is about twice that of MTBE; consequently, less ethanol is required to meet a specified oxygen content (e.g., 2.5 wt% oxygen). To compensate for the resulting octane deficit that would be produced, petroleum companies could add more alkylates as the high-octane blending components. If an oxygen requirement is eliminated altogether, even greater amounts of high-octane components, such as alkylates, must be added to gasoline.

Assuming that California gasoline contains on average approximately 10 wt% MTBE and approximately 14 wt% alkylate, and that the oxygen requirement is to remain fixed at about 2 wt%, ethanol would have to be added at the 5 wt% level. The octane rating of ethanol is close to that of MTBE (approximately 110), and the octane rating of an alkylate solution is about 92. To achieve an overall gasoline octane rating of 88 in the ethanol fuel, a linear calculation indicates the need to increase the percentage of alkylate component from approximately 14 to approximately 34 wt%. This is a rough estimation because there are other requirements that gasoline formulations must meet besides octane rating, and many of the specification parameters (including octane rating and vapor pressure) are not linear functions of the mass. However, it illustrates that the percentage of alkylate in gasoline could increase significantly (approximately 20%) after a phaseout of MTBE.

The goal of this chapter of the report is to characterize the environmental transport and fate of representative alkylate components, based on available information about their physicochemical properties as well as on relevant studies conducted on their environmental chemistry in soil, air, and water. Unlike ethanol or MTBE, the physicochemical properties of alkylate components resemble those of other hydrocarbons present in gasoline, that is, very low solubility in water, high octanol-water partition coefficient, high Henry's law constant, etc. Therefore, an increase in the alkylate percentage of gasoline may not effect significantly the way gasoline behaves in environmental releases.

6.2. Background

Alkylation is an industrial synthetic process used to produce a high-octane solution of branched alkanes (called isoalkanes). This solution is called alkylate and is used as a blending component for gasoline. During World War II, alkylate production was increased to meet the demand for high-octane gasoline used by fighter planes. After the war, the demand for high-octane components for aviation fuels diminished, and the use of alkylate shifted towards the automotive market (Owen, 1995; Kinnear, 1998). The production capacity remained more or less constant during the 1950s and 1960s because of the competitive cost of other high-octane blending components for automotive fuel, such as tetraethyl lead. In 1985, the United States Environmental Protection Agency (US EPA) imposed a drastic reduction of lead in gasoline formulations lowering it, from 1.1 to 0.5 g/gal, which increased the demand for alkylates. Today, approximately 14% of the gasoline in the United States consists of alkylates (Miller, 1999). However, as noted above, this percentage may be increased significantly in the future to compensate for the loss in octane number, resulting from either the removal of MTBE and use of ethanol (EtOH) or no oxygenates in fuel.

Compared to products of other refining processes, alkylates have relatively low Reid vapor pressure[1] as well as relatively low concentrations of aromatics, olefins, and sulfur. From an environmental standpoint, these are some of the more desirable properties for a blending component for gasoline. Therefore, as environmental regulations move toward cleaner burning fuels, it is likely that the use of alkylates as blending stock for gasoline could rise. However, alkylates have not been examined critically and systematically in terms of their potential environmental, health, and safety impacts. This examination becomes particularly important before they are used in greater quantities. Here we briefly examine some of the relevant transport and fate issues related to alkylates.

6.3. Production of Alkylates

In the alkylation process, isobutane is combined with light olefins (double-bonded compounds of 3 to 5 carbon atoms: C_3 to C_5) in the presence of a strong acid catalyst. The only catalysts presently used for industrial production of alkylates are sulfuric and hydrofluoric acids (H_2SO_4 and HF, respectively), with sulfuric acid accounting for about 46% of the world's production capacity (Peterson, 1999). Currently, research on alternative, solid catalysts is taking place. In addition, there is some effort to convert alkylation units from hydrofluoric- to sulfuric-acid catalysis because of the more serious health hazards associated with using hydrofluoric acid.

Studies on alkylation catalyzed by sulfuric acid have shown that there are at least four basic reaction mechanisms. The first mechanism results in the direct alkylation of isobutane with C_3 to C_5 olefins to produce C_7 to C_9 isoalkanes, including isooctane (2, 2, 4-trimethylpentane). The following equation shows a typical alkylation reaction by this process (that is, isobutene and isobutane are combined in the presence of HF or H_2SO_4 at a temperature greater than 10°C):

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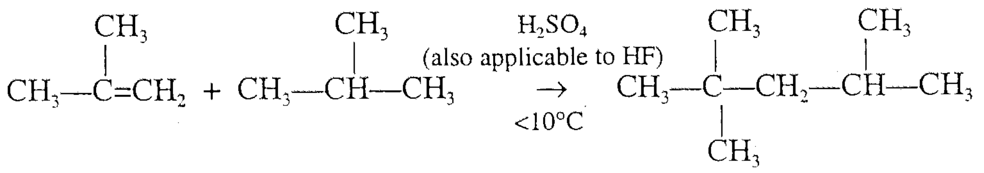
[1] Vapor pressure of a liquid measured by the American Society for Testing and Materials (ASTM) D323 procedure and generally applied to gasoline and gasoline components (Owen and Coley, 1995).



$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 + CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3 \xrightarrow[<10^\circ C]{H_2SO_4 \text{ (also applicable to HF)}} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3 \qquad (6\text{-}1)$$

Isobutene Isobutane Isooctane

(2-Methyl propene) (2-Methyl propane) (2,2,4-Trimethylpentane)

The second mechanism consists of polymerization-fragmentation reactions that produce less branched paraffins, typically C_5 to C_{10}. The third mechanism is a polymerization reaction that results in C_{10} and heavier isoalkanes. Finally, the fourth mechanism is a hydride transfer that accounts for the production of isopentane and trimethylpentane (Kinnear, 1998; Peterson, 1999).

Kinnear (1998) indicates that a typical alkylate product can be composed of 100 to 200 paraffins ranging from C_5 to C_{16}. Calculations based on the analysis of an alkylate indicate that more than 86 moles per 100 moles of alkylate correspond to the C_8 family of isoalkanes (see Table II in Albright *et al.*, 1993). In addition, the average number of carbon atoms in an alkylate molecule is shown to be between 7 and 8 under various alkylation conditions (Albright *et al.*, 1993). It is important to keep in mind that any current gasoline blend already does contain alkylate hydrocarbons. Therefore, the concentration of any given hydrocarbon in gasoline will be the result of its weighted contribution to the entire blended mixture. Only the alkylate component is discussed in this chapter.

6.4. Chemical Composition and Properties of Alkylates

In 1963, Durrett *et al.* (1963) presented a detailed component analysis of alkylates, including five commercial ones produced by either sulfuric- or hydrofluoric-acid catalysis. Based on the yields (see Table V in Durrett *et al.*, 1963), 13 compounds were chosen to represent, in principle, more than 90% by mass of a typical alkylate; and these are listed in Table 6-1. (Note that Table 6-1 is intended as a generic list; it is not a complete list and component yields of alkylates vary depending on process parameters.) In the same reference, 2,2,4-trimethylpenatane (isooctane) accounts for approximately 30–49% of the yield, and the isomers 2,3,4 and 2,3,3 account for approximately 18–32%. Miller (1999) indicated that a typical alkylate produced in a refinery contains approximately 26% isooctane and approximately 25% of other alkylated octanes, which agrees favorably with Durrett *et al.* (1963).

Table 6-1 summarizes some physical properties along with the Chemical Abstracts registry numbers. Other physicochemical properties are presented in Table 6-2.

6.5. Environmental Behavior and Fate of Alkylates

Alkylates are produced in refineries and used as a high-octane blending stock for gasoline. Therefore, typical scenarios for gasoline releases in the environment apply to alkylates as well. Refueling, evaporative emissions, and incomplete combustion introduce alkylate compounds to the atmosphere. In addition, accidental spills on land or water, or leaking underground fuel tanks (LUFTs) discharge alkylate compounds to the environment. Unlike MTBE or ethanol, however, alkylate components behave very much like other gasoline hydrocarbons. The average molar mass of an alkylate solution is close to that of gasoline (approximately 100 g/mol), and these compounds have high Henry's law constants, very low solubilities in water, and high octanol-water partition coefficients. If they are spilled into surface waters, they will float because of the density contrast and form surface pools or films from which the hydrocarbons will evaporate into the atmosphere. A small fraction will also dissolve in the water. These compounds will be retained in the organic fraction of soils and sediments after release from LUFTs because of their high octanol-water partition coefficients.

6.5.1. Air

The principal release mechanisms to the atmosphere include incomplete combustion, and evaporative emissions from automotive-fuel systems and from direct spills on land and/or water. For hydrocarbon solutions, such as light-crude oils and refined products, evaporation can account for up to 75% of volume loss a few days after a spill occurs (Fingas, 1995). A similar behavior should be expected for alkylates. The evaporation process of an alkylate (or any other hydrocarbon solution) is difficult to describe because the vapor pressure is a function of the changing composition of the solution. Qualitatively, as the solution evaporates, the vapor composition becomes richer in the more volatile components, and the liquid composition becomes richer in the less volatile components. As a result, the vapor pressure of the remaining solution decreases as the evaporation progresses.

Fingas (1995) reviewed models used to predict evaporation from oil spills. One of the most frequently used models is that of Stiver and MacKay (1984). In this model, it is assumed that a liquid evaporates at a rate given by

$$N = k\,A\,P\,/\,(RT), \qquad (6\text{-}2)$$

where N (mol s^{-1}) is the evaporative molar flux, A (m^2) is the area, k (m s^{-1})is the mass-transfer coefficient under the prevailing wind, P (Pa) is the vapor pressure of the bulk liquid, R (8.314 Pa m^3 mol^{-1} K^{-1}) is the gas constant, and $T(K)$ is the ambient temperature. Stiver and MacKay (1984) rearranged this equation to give

$$dF_v = H\,d\theta \qquad (6\text{-}3)$$

where F_v is the volume fraction evaporated, H is a dimensionless Henry's law constant, and θ is defined as a dimensionless "evaporative exposure." If the liquid is not pure, H is a function of F_v, and Equation (6-3) can only be integrated if the vapor pressure is expressed as a function of composition. In those cases, the evaporation rate slows, as expected, as the evaporation proceeds.

In a recent study (Kirchstetter *et al.*, 1999), vehicle emissions were measured in a heavily used roadway tunnel (Caldecott tunnel) located in the San Francisco Bay Area. The researchers also measured the composition of liquid gasoline in samples from local service stations. In 1996, the average local gasoline formulation contained, in weight percent, 3.64% isooctane (2,2,4-trimethylpentane), 0.58% benzene, and 10.91% MTBE. (For purpose of comparison, only the results for isooctane, benzene, and MTBE are discussed here.) From these values, Kirchstetter *et al.* (1999) calculated a headspace-vapor composition of 1.21% isooctane, 0.36% benzene, and 16.83% MTBE. Their measurements of the non-methane, organic-carbon emissions in the tunnel during the summer of 1996 were 2.67±0.20% isooctane, 3.34±0.29% benzene, and 5.47±0.74% MTBE. From this study, it is clear that isooctane, a typical alkylate component, is already measurable in automotive emissions; and its concentration should be expected to rise if the percentage of alkylate in gasoline increases. In addition, it is important to note that the relative fractions measured in the tunnel show more isooctane and benzene, and less MTBE than the values corresponding to the equilibrium vapor composition. One possible explanation is that MTBE burns more efficiently than isooctane or benzene.

Once in the atmosphere, the isoalkanes representing the alkylate mixture can be destroyed by chemical degradation and, to a lesser degree, removed by precipitation. The oxidation reactions normally used to estimate the residence time of a chemical in the atmosphere are those involving hydroxyl radicals (OH) and ozone. Alkanes react primarily with hydroxyl radicals to form alkyl radicals:

$$R{-}H + OH \rightarrow R^{\cdot} + H_2O. \qquad (6\text{-}4)$$

The alkyl radicals ($R^{\cdot}$) formed react subsequently with oxygen to form peroxyls. The reaction of alkanes with ozone is relatively slow; thus, the reaction with OH is considered the main initiation path for the oxidation of hydrocarbons in the atmosphere. The oxidized species eventually undergo deposition and biodegradation. The rate of reaction ($-d[RH]/dt$) (see Equation 6-4) is given by the product of a temperature-dependant rate constant ($k(T)$) and the reactant concentrations:

$$\frac{-d[RH]}{dt} = k(T)\,[OH]\,[RH]. \qquad (6\text{-}5)$$

For alkanes having between 2 to 8 carbons, the rate constant range is about $(0.3–9) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Finlayson-Pitts and Pitts, 1986). Note that methane has a very low hydroxyl-rate constant (0.0084×10^{-12} cm^3 molecule^{-1} s^{-1}) compared to other alkanes and is, by far, the most abundant alkane in the atmosphere. For a typical akylate component, such as isooctane, the rate constant is 3.66×10^{-12} cm^3 molecule^{-1} s^{-1}. For a mean global concentration of OH of 1×10^6 molecules cm^{-3} (Prinn *et al.*, 1995), the half-life ($t_{1/2}^{OH} = \ln(2)/k(T)[OH]$) for 2,2,4-trimethylpentane would be 2.2 days. Similar estimations of half-life for benzene, ethanol, and MTBE are 5.8, 2.7, and 2.7 days, respectively, based on may be 10^7 molecules cm^{-3} or higher in polluted atmospheres (Lyman, 1990a). Therefore, under such conditions, the half lives may be reduced by an order of magnitude or more.

The formation of ground-level ozone is a serious pollution concern. Photochemical interactions of volatile organic compounds in combination with oxides of nitrogen generate ozone at ground level. The rate of reaction and mechanism will depend, among other parameters, on the organic compound in question. Carter (1994) discusses the various ways of quantifying the reactivity (the potential to form ozone) of a volatile organic compound. One of them is the Maximum Incremental Reactivity or MIR scenario. Isooctane, benzene, and MTBE have reactivities in the MIR scale of 0.93, 0.42, and 0.62 g of ozone per gram of organic compound (gO_3/g_{OC}), respectively (Carter, 1994). Other isoalkanes present in alkylates have reactivities in the range 0.3–1.5 gO_3/g_{OC}. Even though the ozone-forming capacity of some alkylate components is higher than MTBE or benzene, it is much lower than those corresponding to olefins that are already present in gasoline at a level between 2 and 3%, and they have reactivities reaching as much as 10 gO_3/g_{OC}.

6.5.2. Water

The solubility data in Table 6-2 consists of only three measured values, but it can be inferred from the general solubility trends of hydrocarbons that these isoalkanes are sparingly soluble in water, that is, in the range 10^{-4}–10^{-5} M. The vapor pressures are in the range 10^3–10^4 Pa at 25°C (water-vapor pressure is 3.17×10^3 Pa at 25°C). In addition, the contrast in density will cause the insoluble fraction of these compounds to float on water. Because of their low solubility in water, they have relatively large Henry's law constants (approximately 10^5 Pa m^3 mol^{-1}). This translates into a tendency for the compound to evaporate easily from aqueous solutions. As a rule, compounds in aqueous solution with Henry's law constants larger than approximately 10^2 Pa m^3 mol^{-1} are considered highly volatile (Thomas, 1990). In this case, as long as the concentration in the gas phase remains negligible, the evaporation is controlled by the liquid-phase transfer rate.

The concentration of alkylate in water from a precipitation event is expected to be negligible. For example, a calculation based on an initial concentration in the atmosphere of 1 part per billion (ppb[v])) predicted rainwater to contain 3.6×10^{-5} µg/L for isooctane, 0.17 µg/L for MTBE, and 7.33 µg/L for ethanol (see Chapter 5, Equation [5-1] in this report). The other isoalkanes will also have very low concentrations in rainwater.

6.5.3. Soil and Groundwater

As seen in Table 6-2, the components of an akylate have very high K_{ow}; therefore, they will tend to be retained by organic matter in the environment. Using a soil-partitioning model (Jury *et al.*, 1983), predictions can be made on the distribution of an organic compound in soil phases. The model considers soil to have three phases (solid, water, and air), and the properties of the soil are considered uniform. Some of these properties are water content θ_w, bulk density ρ_b, porosity ϕ, air content θ_A, and organic carbon fraction f_{oc}. The total concentration of a given compound in the soil is given by the sum of the contributions from each phase, as shown in the following equation:

compound in the soil is given by the sum of the contributions from each phase, as shown in the following equation:

$$C_T = \rho_b C_S + \theta_w C_L + \theta_A C_G, \qquad (6\text{-}6)$$

where C_T, C_S, C_L, and C_G, are the total, solid, water, and air concentrations, respectively. Using linear-equilibrium approximations, Equation (6-6) may be written as

$$C_T = R_S C_S = R_L C_L = R_G C_G \qquad (6\text{-}7)$$

where

$$R_S = \rho_b + \theta_w / K_D + \theta_A H / K_D \qquad (6\text{-}8)$$

$$R_L = \rho_b K_D + \theta_w + \theta_A H \qquad (6\text{-}9)$$

$$R_G = \rho_b K_D / H + \theta_w / H + \theta_A \qquad (6\text{-}10)$$

H is Henry's law constant, and K_D is the solid-liquid partition coefficient. The K_D of isooctane was calculated from

$$K_D = f_{oc} K_{oc} \qquad (6\text{-}11)$$

where K_{oc} was calculated using the regression equation from Kenaga and Goring (1980), as cited by Lyman (1990b).

$$\log(K_{oc}) = 0.544 \log(K_{ow}) + 1.377. \qquad (6\text{-}12)$$

Using this model and assuming an initial total concentration of 1 mg/L of the organic compound in soil (isooctane, ethanol, MTBE, and benzene), we performed calculations for two types of soil as defined by Jury *et al.* (1990):

a) Sandy soil ($\rho_b = 1590$ kg/m^3, $f_{oc} = 0.0075$, $\phi = 0.4$, and $\theta_w = 0.18$) and

b) Clayey soil ($\rho_b = 1320$ kg/m^3, $f_{oc} = 0.025$; $\phi = 0.5$, and $\theta_w = 0.375$).

The purpose was to see how isooctane, a typical alkylate component, compares to other gasoline components. The results of the calculations are plotted in Figure 6-1 for the sandy soil and in Figure 6-2 for the clayey soil. A distinctive feature of isooctane is its relatively high preference for the air phase in both soils, even when compared to benzene. One-year evaporation losses calculated for benzene in 1-m-deep soil are 34.3% for sandy soil and 0.01% for clayey soil (Jury *et al.*, 1990). The rate of volatilization is somewhat proportional to the concentration in the air phase; hence, isooctane would volatilize more rapidly than benzene. Therefore, volatilization into the atmosphere could be the main mechanism determining the half-life of an alkylate component in soil for surface contamination.

The limited distribution of the alkylate compounds in soil water and their high retention in soils (see Figures 6-1 and 6-2) indicates that their mobility in infiltrating water will be quite limited—particularly when compared to ethanol or MTBE. Alkylate compounds that are not volatilized to air will probably undergo slow biodegradation based on the study by Solano-Serena *et al.* (1998), discussed in the next section.

6.5.4. Biodegradation

The biodegradability of a compound can be affected by many variables (pH, temperature, substrate composition, oxygen availability, microorganisms present and their interaction, etc.). Consequently, it is quite difficult to predict the actual biodegradation rates for individual isoalkanes. A simple approach would be to consider the solution as a single compound; for example, gasoline has been considered as a single compound that is moderately biodegradable (Scow, 1990). However, an alkylate (and gasoline) is a complex solution, and the rate of biodegradation of each component may be significantly different. Unfortunately, there have not been many specific studies on the biodegradation of alkylate components. In general, n-alkanes are degraded rapidly in the environment, but highly branched alkanes tend to be more resistant to biodegradation because of their molecular structure. Under aerobic conditions, the oxidation of alkanes normally proceeds by the oxidation of a terminal methyl group to form a carboxylic acid, followed by β-oxidation of the acid. The presence of a quaternary carbon near the end of the chain interferes with the β-oxidation step and the degradation stops. It is possible that later these compounds are degraded by other, slower mechanisms (Alexander, 1994; Chapelle, 1993).

A recent laboratory study using unpolluted spruce-forest soil as substrate (Solano-Serena, 1998) has shown that all components of a model-gasoline solution were biodegraded below detection limit after 28 days with the exception of 2,2,4-trimethylpentane (isooctane), 2,3,4-trimethylpentane, and cyclohexane. From Table 2 of Solano-Serena *et al.* (1998), the percentages of degradation after 28 days of incubation at 30°C are 18% for 2,2,4-trimethylpentane, 9% for 2,3,4-trimethylpentane, and 100% for benzene. In addition, mineralization yields (fraction of compound converted to CO_2) for 23 individual components of this gasoline solution were determined (see Table 1 in Solano-Serena, 1998) by measuring the CO_2 produced after 34 days of incubation at 30°C. The mineralization yield was 2% for 2,2,4-trimethylpentane and 0% for 2,3,4-trimethylpentane. On the other hand, the mineralization yield for benzene was 56%. Note, it appears that the resistance to degradation is not due to the inhibitory capacity of isoalkanes or cycloalkanes but rather to a population deficiency of the naturally occurring microorganisms degrading these hydrocarbons.

Based on the previous values for 2,2,4-trimethylpentane, we can estimate a first-order degradation constant of approximately 0.007 day^{-1} and a half-life of about 98 days. In the case of 2,3,4-trimethylpentane, the first-order degradation constant is approximately 0.003 day^{-1} and the half-life is approximately 206 days. Because benzene degraded completely, the same constant cannot be determined for benzene from this data. In another experiment, the first-order degradation constant of benzene in an aerobic aquifer was measured to be between 0.07 and 0.5 day^{-1} (Nielsen *et al.*, 1996). These values would predict over 85% degradation of benzene in 28 days, which generally agrees with the results of Solano-Serena *et al.*, (1998) for this compound. The half-life for mineralization of 2,2,4-trimethylpentane would be around three years (compared to 25 days for the case of benzene).

A detailed laboratory study was conducted on gasoline biodegradation using microflora from an urban-waste activated sludge (Solano-Serena, 1999). Based on the kinetics of oxygen consumption, the authors concluded that there are two main degradation phases: a fast phase and a slow phase. The rate of oxygen consumption is about 40 times lower during the slow phase. Aromatic hydrocarbons were degraded mostly during the fast phase while linear, branched, and cyclic alkanes were degraded mostly during the slow phase. After 25 days of incubation, the undegraded compounds (6% of gasoline) were essentially branched alkanes with a quaternary carbon and/or alkyl chains in consecutive carbons. For example, the undegraded fractions of 2,2,4-trimethylpentane, 2,3,3-trimethylpentane, and 2,3,4-trimethylpentane were 49.7%, 72.1%, and 30.5%, respectively, after 25 days of incubation. One reason given for the relatively slow biodegradation rate of some linear alkanes and isoalkanes is their low solubilities in water and high Henry's constants. The alkane in the gas phase of the culture flask is not readily available to the microflora, and the rate-limiting step could be the transfer of the alkane from the gas to aqueous phase. However, the incomplete biodegradation of some branched alkanes seems to indicate that there is also a metabolic limit in this case.

6.6. Summary

Alkylates are solutions of highly branched alkanes produced in refineries by the reaction of isobutane with light olefins, using either sulfuric or hydrofluoric acid as a catalyst. For many years, alkylates have been used as gasoline-blend stock because of their high-octane number. In the near future, the percentage of alkylate in gasoline may increase significantly to compensate for the phase out of high-octane MTBE. The purpose of this chapter was to characterize the transport and fate of alkylates in the environment. For simplicity, we concentrated on the properties of isooctane as a typical alkylate component. Clearly, alkylates are complex solutions of isoalkanes, and some properties like biodegradability may not be easily extrapolated to all components. The low water solubility and high volatility of alkylate components indicate that they would not exacerbate problems of ground or surface water contamination by gasoline in the manner MTBE has done. Overall, it appears that alkylates would not effect dramatic changes in the way gasoline behaves in the environment and, thus, in the treatment of accidental releases.

Unfortunately, there is no toxicity data on the chronic effects of isooctane in humans; however, liver and kidney effects have been observed in rats that have been exposed chronically (US EPA, 1991). Additionally, cancer risk and reproductive and developmental effects have not been addressed. It should be noted that toxicity related to alkylate addition to gasoline is a complex problem because any percentage increase of alkylate in gasoline composition must be accompanied by a percentage decrease of other blending components (e.g., BTEX) in the final formulation. Therefore, the toxicity of the final product should be evaluated in an integral manner.

The physicochemical properties of alkylate components are typical of many hydrocarbons and determine their behavior in the environment. They have very low solubility in water and very high octanol-water partition coefficient. They are less dense than water and have relatively high Henry's law constants. Surface releases of alkylate either on water or land will probably result in the evaporation of most of the alkylate into the atmosphere. In the atmosphere, their oxidation will be initiated mostly by the presence of atmospheric OH, with half-lives of about 2–3 days. Their potential to form ground-level ozone is about double that of MTBE in the MIR scale. Alkylates will be strongly absorbed by the organic fraction of soils and sediments. Their biodegradation rate is relatively slow compared to other organic compounds, and some components may not biodegrade in reasonable time frames.

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Figures

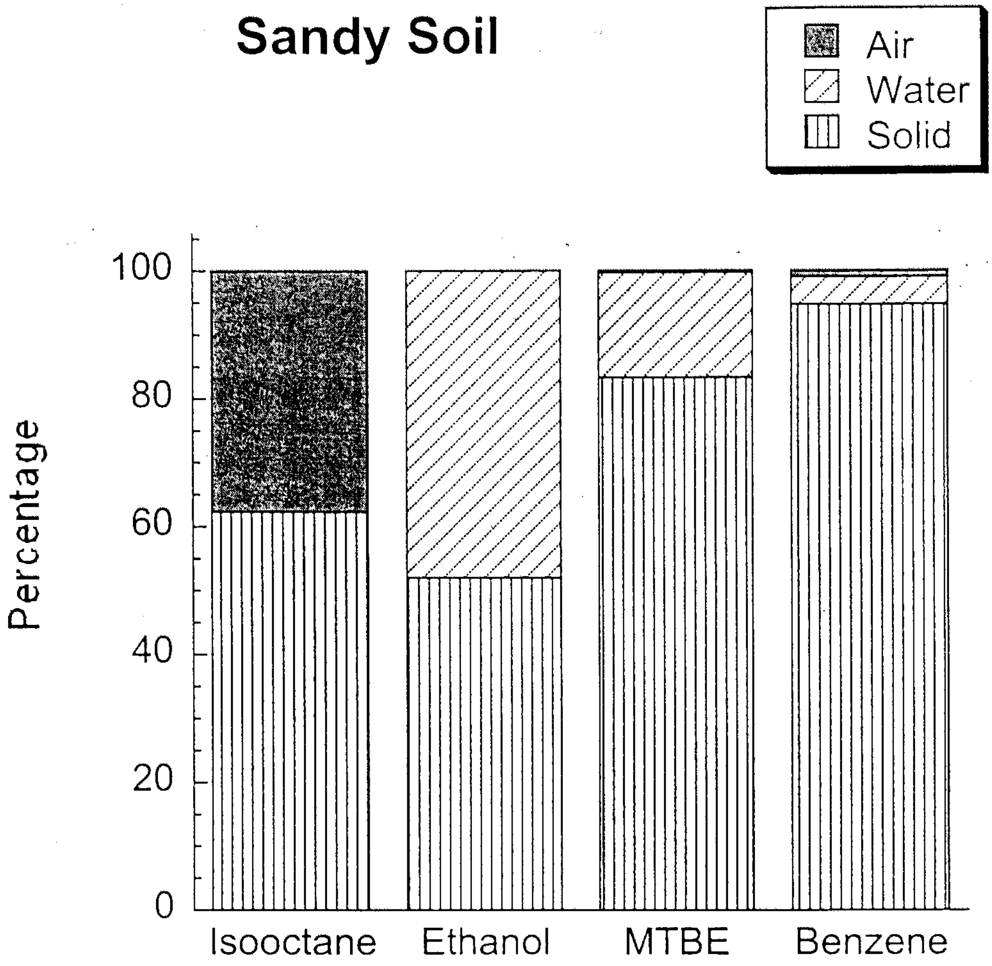

Figure 6-1. Model of equilibrium distribution for isooctane between the phases of a sandy soil (air, water, solid). This partitioning model was developed by Jury *et al.* (1983); soil characteristics were taken from Jury *et al.* (1990).

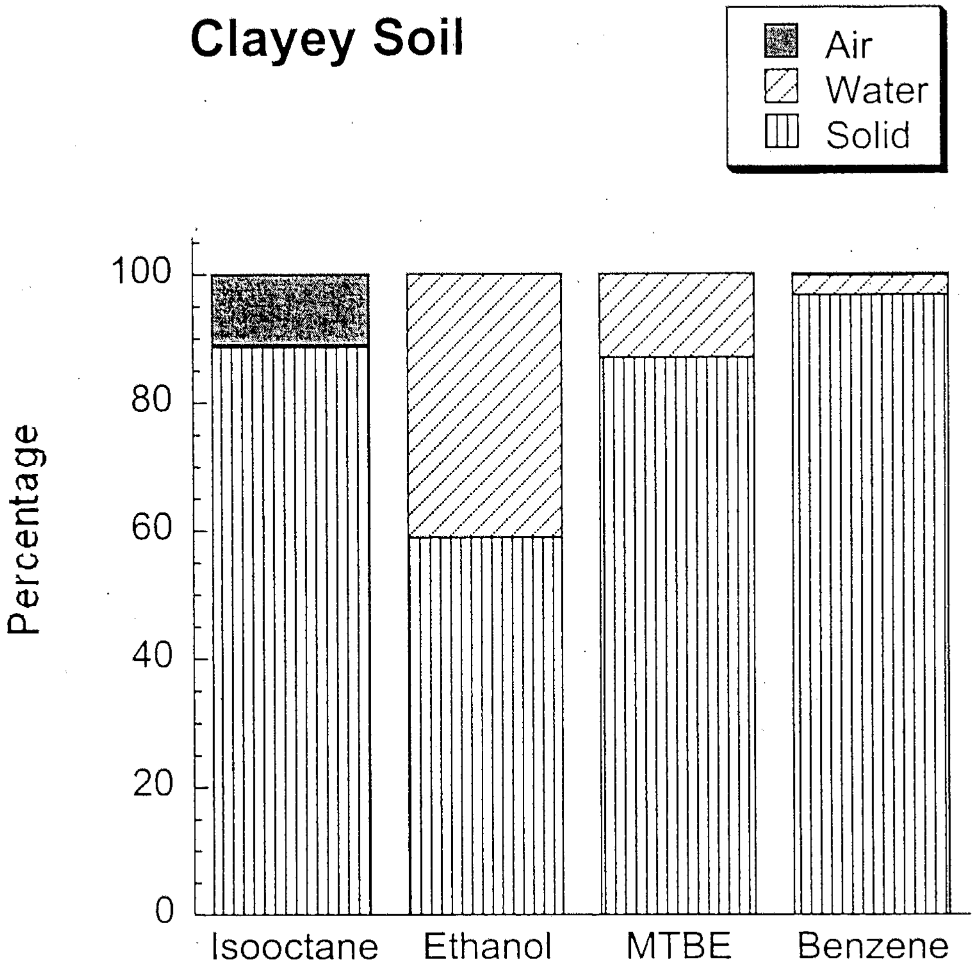

Figure 6-2. Model of equilibrium distribution for isooctane between the phases of a clayey soil (air, water, solid). This partitioning model was developed by Jury *et al.* (1983); soil characteristics were taken from Jury *et al.* (1990).

Tables

Table 6-1. Representative components of a typical alkylate[a].

Alkylate compound	Formula	CAS number[b]	Molar mass (g/mol)[b]	Melting point (°C)[b]	Boiling point (°C)[b]	Density (g/cm^3)[b]
2,2,4-Trimethylpentane	C_8H_{18}	540-84-1	114.23	-107	99.2	0.692
2,3,3-Trimethylpentane	C_8H_{18}	560-21-4	114.23	-101	115	0.726
2,3,4-Trimethylpentane	C_8H_{18}	565-75-3	114.23	-109	113	0.719
2,2,3-Trimethylpentane	C_8H_{18}	564-02-3	114.23	-112	110	0.716
2,2,5-Trimethylhexane	C_9H_{20}	3522-94-9	128.25	-106	124	0.707
2,3-Dimethylbutane	C_6H_{14}	79-29-8	86.17	-128	58	0.661
2,3-Dimethylpentane	C_7H_{16}	565-59-3	100.2	N/A	90	0.695
2,4-Dimethylpentane	C_7H_{16}	108-08-7	100.2	-119	81	0.673
2,5-Dimethylhexane	C_8H_{18}	592-13-2	114.23	-91	109	0.694
2,3-Dimethylhexane	C_8H_{18}	584-94-1	114.23	N/A	116	0.712
2,4-Dimethylhexane	C_8H_{18}	589-43-5	114.23	N/A	109	0.700
2,3,5-Trimethylhexane	C_9H_{20}	1069-53-0	128.25	-128	131	0.722
2-Methylpentane	C_6H_{14}	107-83-5	86.17	-154	62	0.653

[a] From Durett *et al.* (1963).

[b] Values estimated using ChemFinder® Software (CambridgeSoft Corporation, 1998a).

Table 6-2. Physical-chemical properties of representative alkylate components.

Alkylate compound[a]	Vapor pressure[b] (Pa at 298K)	Solubility[c] (mg/L)	Henry's law constant[d] (Pa m^3 mol^{-1})	K_{ow}[e]	LeBas molar volume[f] (cm^3 mol^{-1})	D_{air}[f] (m^2 d^{-1}; at 298 K)	D_{water}[f] (m^2 d^{-1}; at 298 K)
2,2,4-Trimethylpentane	6.49×10^{3}	2.44	3.23×10^{5}	1.22×10^{4}	185	0.575	7.03×10^{-5}
2,3,3-Trimethylpentane	NA	NA	4.17×10^{5}	1.22×10^{4}	185	0.575	7.03×10^{-5}
2,3,4-Trimethylpentane	3.57×10^{3}	NA	1.83×10^{5}	1.12×10^{4}	185	0.575	7.03×10^{-5}
2,2,3-Trimethylpentane	NA	NA	3.85×10^{5}	1.22×10^{4}	185	0.575	7.03×10^{-5}
2,2,5-Trimethylhexane	2.22×10^{3}	NA	5.26×10^{5} 3.44×10^{5}	3.77×10^{4}	207.2	0.541	6.57×10^{-5}
2,3-Dimethylbutane	3.13×10^{4}	NA	1.30×10^{5}	1.38×10^{3}	140.6	0.670	8.29×10^{-5}
2,3-Dimethylpentane	9.18×10^{3}	NA	1.74×10^{5}	4.29×10^{3}	162.8	0.618	7.59×10^{-5}
2,4-Dimethylpentane	1.31×10^{4}	4.06	3.00×10^{5}	4.29×10^{3}	162.8	0.618	7.59×10^{-5}
2,5-Dimethylhexane	4.05×10^{3}	NA	3.33×10^{5}	1.33×10^{4}	185	0.575	7.03×10^{-5}
2,3-Dimethylhexane	3.12×10^{3}	NA	3.85×10^{5}	1.33×10^{4}	185	0.575	7.03×10^{-5}
2,4-Dimethylhexane	3.64×10^{3}	NA	3.57×10^{5}	1.33×10^{4}	185	0.575	7.03×10^{-5}
2,3,5-Trimethylhexane	NA	NA	5.00×10^{5}	3.47×10^{4}	207.2	0.541	6.57×10^{-5}
2-Methylpentane	2.82×10^{4}	13.8	1.71×10^{5}	1.64×10^{3}	140.6	0.670	8.29×10^{-5}

[a] Representative components of a typical alkylate (Durett *et al.*, 1963).

[b] Vapor pressure calculated using Antoine equation from National Institute of Standards and Technology (NIST) (1999).

[c] Values were obtained using Chem3D® Software (CambridgeSoft Corporation, 1998b).

[d] Henry's law constant obtained from NIST (1999). Note: 2,2,5-trimethylhexane has two values.

[e] Octanol-water partition coefficients obtained using LogKow (KowWin) Demo software (SRC, 1999).

[f] Calculated according to methods described by Tucker and Nelken (1990).