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# Heats of Dissolution of Tar Sand Bitumen in Various Solvents

**Topical Report**

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## SUMMARY

The dissolution of tar sand bitumen from a tar sand matrix was examined using three solvents: (1) dichloromethane, a polar-polarizable solvent; (2) toluene, a nonpolar-polarizable solvent; and (3) hexane, a nonpolar-nonpolarizable solvent. The dichloromethane had the highest dissolution energy followed by toluene with hexane having the lowest dissolution energy. These data were combined with heat of dissolution of recovered bitumen and heat of wetting of spent sand to calculate the bonding energy between bitumen and the mineral matrix. The interfacial bonding energy between tar sand bitumen and the mineral matrix was found to be in the region of 0 to 0.09 cal/g of bitumen, which is very small. This conclusion may find application in recovery of energy or bitumen from bitumen-wet tar sand deposits.

## INTRODUCTION

There are various reasons for studying the enthalpies of dissolution. One fundamental reason is to better understand the bonding characteristics of bitumen to the mineral matrix. Another reason to study enthalpies of dissolution is because the selection of the best solvents will optimize commercial recovery methods of tar sand bitumen. Recovery of bitumen from mined tar sand has only been commercialized where a water layer separates the bitumen and the mineral surface. In the Athabasca region, Alberta, Canada, both Suncor and Syncrude operate commercial above-ground bitumen recovery plants (Reddy et al. 1982) utilizing water-wet tar sand material. At the present, no commercial recovery method exists for recovery of bitumen from mined bitumen-wet tar sand.

Various above ground methods for recovery of bitumen from the U.S. bitumen-wet tar sand deposits have been investigated using solvent extraction. The basic recovery scheme requires mining, crushing, extraction, removing the solvent from the sand, and distillation of the solvent from the desired products.

This discussion is primarily concerned with factors that influence solvent extraction and solvent recovery. A thermodynamic approach is used to better understand the fundamental parameters that govern dissolution of tar sand bitumen and recovery.

In this study three solvents, with differing polarity properties, were selected to study the bonding properties between bitumen and the mineral matrix. The solvents used in the thermodynamic study include dichloromethane, a polar-polarizable solvent; toluene, a nonpolar-polarizable solvent; and hexane, a nonpolar-nonpolarizable solvent.

## EXPERIMENTAL PROCEDURE

### Materials

The solvents were used as received. The dichloromethane was high pressure liquid chromatography gas chromatograph/mass spectrometer (HPLC-GC/MS) grade. The toluene and the hexane were HPLC grade. The tar sand was from the Asphalt Ridge, Utah deposit. The bitumen was extracted in a double-cone extractor using a mixture of toluene and pyridine as the extracting solvent. The solvent was removed from the bitumen in a rotary evaporator.

### Equipment

Enthalpies of dissolution of tar sand bitumen and tar sand, and enthalpy of wetting of spent sand were determined in a microcalorimeter. The calorimeter has been described in detail by Ensley and Scholz (1972). In brief, the calorimeter consists of two thermopile assemblies connected in opposition. The hot junctions are in contact with a cell holder adjacent to a cell sleeve, and the cold junctions are in contact with an aluminum heat sink.

Solvent is contained in a reaction cell and surrounds a small cylinder with a Teflon trap door. The material to be contacted with the solvent is contained in the cylinder. Tar sand is contained in a wire basket inside the cylinder. To study heat of dissolution of extracted bitumen, the basket is replaced with a metal rod that is coated with the bitumen. Spent sand is contained in the wire basket for enthalpy-of-wetting studies. The cell, containing the materials to be contacted, is placed in the calorimeter for five hours, to reach thermal equilibrium. The trap door is then opened, allowing dissolution (or wetting) to occur. The energy produced or absorbed is detected by the thermopile assembly. The signal is amplified and recorded. A calibration curve allows the energy flow to be calculated.

## RESULTS AND DISCUSSION

In an attempt to understand the bonding of tar sand bitumen to the mineral matrix, three thermodynamic measurements were made. They include the following heats or enthalpies of dissolution.

- Heat of dissolution of tar sand bitumen on the mineral matrix, $\Delta H_1$.
- Heat of dissolution of recovered bitumen, $\Delta H_2$.
- Heat of wetting of spent tar sand, $\Delta H_3$.

From these data, and using Hess's law (Castellan 1964), it is possible to calculate the bonding energy of the bitumen to the mineral matrix using the following equations.

$$Q{:}B + S \rightarrow Q + B \cdot S \qquad \Delta H_1 \qquad (1)$$

$$B + S \rightarrow B \cdot S \qquad \Delta H_2 \qquad (2)$$

$$Q + S \rightarrow Q \cdot S \qquad \Delta H_3 \qquad (3)$$

$$Q{:}B \rightarrow Q + B \qquad \Delta H_4 \qquad (4)$$

Equation 1 represents the energy of dissolution of tar sand bitumen (B), on a mineral matrix into a solvent (S). The energy value, $\Delta H_1$, for the interactions is the algebraic sum of breaking of the bitumen-mineral matrix bond (Q:B), the energy required to form the tar sand bitumen-solvent bond (B•S), and the energy of wetting of spent sand (Q•S). Equation 2 represents the energy of dissolution of recovered tar sand bitumen into a solvent. The energy term, $\Delta H_2$, is the sum of contributions from breaking bitumen-bitumen bonds and forming bitumen-solvent bonds (B•S). The energy term, $\Delta H_3$, represents the heat of wetting of spent tar sand (Q) with a solvent. The interfacial bond energy, $\Delta H_4$, is calculated by the following thermodynamic equation.

$$\Delta H_4 = \Delta H_1 - \Delta H_2 - \Delta H_3 \qquad (5)$$

Therefore, $\Delta H_4$ represents the energy required to break the bond between the organic material and the mineral matrix. The values for the various enthalpies are listed in Table 1.

**Table 1. Enthalpies of Dissolution and Wetting of Asphalt Ridge Material Using Three Solvents**

| | cal/g | | | |
|---|---|---|---|---|
| | $\Delta H_1$ QB | $\Delta H_2$ Bitumen | $\Delta H_3$ Q | $\Delta H_4$ Bond |
| Dichloromethane | +0.96 | +1.26(6.33)[a] | -0.25 | -0.05 |
| Toluene | +0.42 | +0.55(2.76) | -0.04 | -0.09 |
| Hexane | +0.07 | +0.07(0.35) | ~0 | ~0 |

[a]values in parentheses based on weight percent bitumen in tar sand sample.

The $\Delta H$ values in Table 1 are in units of cal/g and based on 1 gram of tar sand. $\Delta H_2$ and $\Delta H_3$ were determined from microcalorimetric data and corrected for weight percent bitumen in the tar sand sample. The weight percent bitumen used was 19.9 based on dissolution with dichloromethane.

The values for $\Delta H_2$ in Table 1 divided by the bitumen fraction, (0.199), gives the heat of dissolution for neat bitumen. The heats of dissolution of neat bitumen in dichloromethane, toluene, and hexane are 6.33, 2.76 and 0.35 cal/g units respectively. The reported heats of dissolution of an Athabasca bitumen in dichloromethane and toluene are 4.35 and 4.40 cal/g, respectively (Zhang and Hepler 1986). The data discrepancies could be due to differences in bitumen composition, although the same trend should be seen.

After hexane treatment, the tar sand was washed with toluene. Only a slight discoloration of the toluene was noted. It is quite possible that the hexane dissolved the maltene fraction of the bitumen and left the asphaltene fraction suspended in solution. The asphaltene fraction could have been removed when the hexane solution was decanted, even though it was not dissolved.

The low heat of dissolution for bitumen in hexane indicates it is a poor solvent in contrast to dichloromethane that has a much larger heat of dissolution. The characteristics of good solvents or poor solvents are often determined by solubility parameters. According to the Hildebrand-Scratchard equation (Barton 1983), if the solvent and solute have similar solubility parameters they are compatible. This equation, shown below, expresses heat of dissolution in terms of solubility parameters.

$$\Delta H_m = (X_i V_i + X_j V_j)\ (\delta_i - \delta_j)^2 \phi_i \phi_j \qquad (6)$$

where:

$\Delta H_m$ = heat of mixing
$X_i, X_j$ = mole fractions of components i and j
$V_i, V_j$ = molar volumes of components i and j
$\delta_i$, $\delta_j$ = solubility parameters of components i and j
$\phi_i, \phi_j$ = volume fractions of components i and j

The solubility parameter is equal to the square root of the cohesive energy density. The cohesive energy density is approximately equal to the heat of vaporization divided by the molar volume. The solubility parameters for the three solvents are given in Table 2.

**Table 2. Solubility Parameters at 25°C for Three Solvents**

| Solvent | $\delta$ $(MPa)^{1/2}$ | $\delta$ $(cal/cm^3)^{1/2}$ |
|---|---|---|
| Dichloromethane | 20.0 | 9.80 |
| Toluene | 18.3 | 8.97 |
| Hexane | 14.8 | 7.25 |

Note: The conversion multiplication factor from calories per cubic centimeter to megapascals is 1.0 $(cal/cm^3)^{1/2}$ = 2.04$(MPa)^{1/2}$ (Barton 1983).

The direct determination of the solubility parameter of tar sand bitumen is impossible due to the difficulty in determining the heat of vaporization of the bitumen. However, with certain approximations a solubility parameter can be calculated for a bituminous material if both the compressibility factor $(\partial V/\partial P)_T$ and compression energy $(\partial E/\partial P)_T$ can be determined for the material. A microcalorimeter was used to measure $(\partial E/\partial P)_T$. A value of 1.93 x $10^{-4}$ cal/g-psi for a paving asphalt was found. A value of 3.44 x $10^{-5}$ atm/cm³ was calculated for $(\partial P/\partial V)_T$ using a compressibility factor for a bituminous paving material that had been reported by Hoiberg (1964). Using $(\partial E/\partial V)_T = (\partial E/\partial P)_T(\partial P/\partial V)_T$, a value for $(\partial E/\partial V)_T$ was calculated and found to be 66.5 cal/cm³ or $\delta$ = 8.2 $(cal/cm^3)^{1/2}$. It should be noted that $(\partial E/\partial V)_T$ is assumed to be approximately equal to the cohesive energy density (Barton 1983).

Similarity of solubility parameters of solvent and solute indicate that of the solvents studied, toluene would be the best solvent, followed by hexane and toluene.

A second method that can be used to examine the thermodynamics of dissolution is the basic Gibbs free energy equation (Castellan 1964).

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

where:

$\Delta G$ = Gibbs free energy
$\Delta H$ = enthalpy of interaction or heat of dissolution
$T\Delta S$ = entropy contribution at constant temperature

By definition free energy change is always negative for a spontaneous process change. This implies that if $\Delta H$ is endothermic, as we have seen for heat of dissolution of tar sand bitumen, the contribution from $T\Delta S$ must be greater than $\Delta H$ for dissolution to occur. $T\Delta S$ is naturally positive because dissolution produces a much more random system than the two systems prior to dissolution. An increase in temperature also favors dissolution since it is multiplied by the entropy in the Gibbs equation.

Heats of dissolution can be either endothermic or exothermic. Dissolution requires that certain bonds be broken and others formed. For example, the primary contributors to enthalpy of dissolution of bitumen are the breaking of the bitumen-bitumen bond (energy required) and the formation of the bitumen-solvent bond (probably energy releasing).

In the interpretation of enthalpies of mixing, or enthalpies of dissolution, all bond changes must be considered. As discussed by Gardon (1977), the heat of mixing or dissolution results from breaking two "reactant" bonds and forming a "product" bond. This is depicted below for bitumen dissolution in a solvent:

$$S \cdot S + B \cdot B \rightarrow 2S \cdot B \quad (8)$$

$$\Delta H_M \sim E_S + E_B - 2E_{SB} \quad (9)$$

where: the E's represent intermolecular energy between molecules and

$E_S$ = the energy of interaction between solvent molecules, S•S
$E_B$ = the energy of interaction between bitumen molecules, B•B
$E_{SB}$ = the energy of interaction between solvent and bitumen molecules, S•B

Differences in heats of dissolution of bitumen in different solvents are, in part, due to the differences in intermolecular solvent bond energies ($E_S$) as reflected in the solubility parameters. Solvent-bitumen interactions ($E_{SB}$) and differences in amount of material dissolved, also contributes to differences in heats of dissolution.

Dichloromethane and toluene probably dissolve all of the bitumen on the tar sand. Hexane dissolves the maltene fraction and the insoluble material sluffs off but does not dissolve. Nuclear magnetic resonance showed that less than 0.3% carbon was retained on the aggregate with the three solvents. (Netzel and Coover 1988). The heats of dissolution for dichloromethane and toluene should reflect the making and breaking of about the same number of bonds. The internal bonding in solvents is

reflected in the solubility parameters ($\delta$). The solubility parameters of toluene and dichlomethane differ slightly but not enough to account for dissolution energy differences of 2.76 and 6.33 cal/g respectively. Therefore, it is probable that the heats of dissolution differ because the exothermic interaction between toluene and bitumen is greater than the exothermic interaction between dichloromethane and bitumen. Dichloromethane probably interacts with the large maltene and asphaltene molecules in the bitumen at localized areas. However, toluene probably interacts with the large conjugated aromatic ring structures of asphaltenes in dissolved bitumen, through $\pi$-$\pi$ bond interactions. Interaction of this type could be much stronger than those between the smaller dichloromethane molecules and the dissolved bitumen molecules.

In summary, toluene appears to be the best solvent of the three investigated based on its solubility parameter being closest to a bituminous material and the fact it has a relative low energy of vaporization. The latter value is between dichloromethane and hexane. It was necessary to assume in these calculations that tar sand bitumen and paving bitumen have similar solubility parameters.

## Application of Thermodynamic Analysis of Bitumen Dissolution to Tar Sand Bitumen Recovery

One of the most costly barriers to the economical recovery of bitumen from tar sand is the distillation step to separate the bitumen from solvent. This is because good solvents for tar sand bitumen have solubility parameters close to the relatively high solubility parameter of the bitumen. One unique approach that avoids this problem is the Beaver-Herter process (Daniel and Babcock 1986).

In the Beaver-Herter process, the bitumen is dissolved with a long-chained fatty acid. The long-chained hydrocarbon portion of the molecule has dissolution characteristics similar to hexane but has one noticeable advantage. The carboxylic end of the molecule can be made water soluble with sodium hydroxide, as is done in the Beaver-Herter process. This allows a low energy separation of bitumen and solvent. Therefore, if a solvent can be found that has a solubility parameter that is near the solubility parameter of bitumen, and can be modified to contain a water soluble functional group, the solvent may be of value in solvent-type bitumen recovery. The fatty acids have solubility parameters in the range of 9 to 14 $(cal/cm^3)^{1/2}$, and is, perhaps, one reason the process has been considered for bitumen recovery. The solubility parameter of bitumen is slightly lower than this range but close enough for the bitumen to be solubilized by a fatty acid, which is important according to the Hildebrand-Scratchard theory (6).

## CONCLUSIONS

Of the three solvents tested for dissolving tar sand bitumen, dichloromethane has the greatest dissolution energy, followed in order by toluene and hexane. Of this same set, toluene has a solubility parameter closest to a bituminous material. Its recovery or heat of vaporization is intermediate in the set. When the amount of bituminous material dissolved is considered along with solubilizing power and solvent recovery costs, toluene appears to be the best solvent of the three materials evaluated. However it should be noted that hexane may have sufficient solubilizing powers for tar sand bitumens with low asphaltene content but may not be adequate for materials with a high asphaltene content. Hexane would require the least amount of energy to recover if it had proper solubilizing power.

## FUTURE WORK

Future work on dissolution of bitumen in solvents should include the type of compounds that are capable of dissolving the bitumen on tar sand and have functionality that could be changed to render the solvent insoluble with the bitumen. A long-chain fatty acid amine is an example of a compound that would have some of the dual characteristics of the fatty acids. That is, it will dissolve the bitumen but be recoverable by chemically changing the solvent to be water soluble. The hydrochloric acid salt of the amine is an example of a water soluble form.

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