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An NMR [nuclear magnetic resonance] investigation of the chemical association and molecular dynamics in asphalt ridge tar sand ore and bitumen

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AN NMR INVESTIGATION OF THE CHEMICAL ASSOCIATION AND
MOLECULAR DYNAMICS IN ASPHALT RIDGE TAR SAND ORE AND BITUMEN

by
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September 1987

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SUMMARY

Investigations of the chemical association and molecular dynamics in fossil fuel materials using nuclear magnetic resonance relaxation spectroscopy have been done extensively for coal, less so for oil shales, and almost not at all for tar sand.

Preliminary studies on tar sand bitumen given in this report have shown that the reassociation of tar sand bitumen to its original molecular configuration after thermal stressing is a first-order process requiring nearly a week to establish equilibrium. The first-order rate constant was found to be 0.0139 hr^{-1} .

Preliminary studies were also conducted on the dissolution of tar sand bitumen in solvents of varying polarity. It was observed that at a high-weight fraction of solute to solvent the apparent molecular weight of the bitumen molecules was greater than that of the original bitumen when dissolved in chloroform- d_1 and benzene- d_6 . This increase in the apparent molecular weight may be due to micellar formation or a weak solute-solvent molecular complex. Upon further dilution with any of the solvents studied, the apparent molecular weight of the tar sand bitumen decreased because of reduced van der Waals forces of interaction and/or hydrogen bonding. However, to define the exact nature of the interactions, it will be necessary to have viscosity measurements of the solutions because the viscosity affects, in part, the relaxation measurements.

INTRODUCTION

A fundamental understanding of the inter- and intramolecular interactions of organic molecules and the association of organic molecules with mineral matrices is paramount to the development of any viable commercial process for the extraction of tar sand bitumen as well as for the conversion of kerogen in oil shale to shale oil. These molecular interactions affect the mobility of molecules and, in turn, dictate the mechanical and thermal energy required for the conversion of the bitumen and kerogen to useful oil by-products.

Several types of molecular interactions are responsible for the chemical and physical properties of a complex mixture such as tar sand bitumen in its native state (tar sand ore) and tar sand bitumen in its free state (extracted bitumen). These molecular interactions include the long-range van der Waals forces (dispersion, dipole-dipole, and dipole-induced dipole) and the short-range valence or chemical forces (H-bonding and chemisorption). The strength of these interactions either between the organic constituents or organic constituents and the mineral matrix all depend, in part, upon the dipolar nature and intermolecular distances of the molecules.

One technique used in the investigation of mobility (molecular dynamics) and molecule associations (chemical association) in complex molecular systems is nuclear magnetic resonance (NMR) relaxation spectroscopy (Netzel and Miknis 1977). With this technique, the nuclear dipolar spin-lattice (T_1) and spin-spin (T_2) relaxation times are measured and used to investigate the mobility of molecules and molecular interactions.

The spin-lattice and spin-spin relaxation rates (the inverse of the relaxation times) can be derived from theoretical principles. Mathematically, the relaxation times are the product of a nuclear interaction constant, k_j and a molecular correlation time, τ_c . The nuclear interaction constant for each relaxation rate is derived from a set of nuclear constants and molecular parameters that include the internuclear distances. The nuclear interaction constants are usually independent of temperature. The molecular correlation time can either be a measure of the time for a molecule to rotate one radian if the nuclear interaction is intramolecular or the time for a molecule to traverse one molecular diameter if the nuclear interaction is intermolecular. The molecular correlation times depend on the molecular weight and symmetry of the molecule, intermolecular interactions, viscosity, density and temperature, all of which affect the observed spin-lattice and spin-spin relaxation times.

There is little reported research on the characterization of the type and strength of the intermolecular interactions in fossil fuel materials. The rates of intermolecular association of molten asphalt were studied by Ensley (1975) using a sensitive microcalorimeter. Hydrogen bonding in coal-derived materials was reported in a series of papers by Tewari et al. (1978, 1979, 1984). Hydrogen bonding was also studied by Weyrich and Larsen (1983) and Young et al. (1984).

Intermolecular forces in coal liquefaction product distillates were recently investigated by White and Schmidt (1987) using average molar volume and average molar polarizability data. Though the evidence is not conclusive, van der Waals forces appear to be the dominate interactions in coals.

Recently NMR ^1H spin-lattice relaxation spectroscopy was used to study the mobility of hydrogen in solvent-swollen coals (Kamienski 1987), to identify the rigid and mobile components in coal structure (Tekely 1986; Jurkiewicz et al. 1987), and to delineate the thermoplastic behavior of coal during heating (Webster and Lynch 1981; Tekely et al. 1987; Sakurovs et al. 1987).

The temperature-dependent hydrogen T_1 values of oil shales were studied by Harrell and Kohno (1984) and by Miknis and Netzel (1976). Spin-spin relaxation times were reported by Lynch and Webster (1983) for Australian oil shales.

Miknis and Netzel (1976) also conducted a preliminary study on the spin-lattice relaxation time as a function of temperature for a tar sand ore and bitumen. Using both spin-lattice and spin-spin relaxation time measurements, Sobol et al. (1985) concluded that the bitumen is composed of three phases: solid-like (rigid), solid-like (mobile), and semi-liquid. They also concluded that water exists in two different environments, one in the bridges between the sand grains and the other on the clay surface.

Most of the reported research for tar sand bitumen is in the area of physicochemical characterization involving measuring the physical properties and identifying and quantifying compounds or compound types using chemical and spectroscopic techniques. Although important, the chemical characterization of tar sand bitumen provides little insight into the molecular interactions and mobility of molecules subjected to variations in temperature or solvent polarity.

An understanding of the associative properties of bitumen in its native state (tar sand ore) and in its free state (extracted bitumen) may provide the information to optimize in situ and above-ground thermal and solvent extraction processes. In addition, a knowledge of the associative properties may also provide insight for developing novel surfactant-type extraction processes or for developing environmental methods for site cleanup of residue materials.

The primary objective for the program is to investigate the chemical association and mobility of tar sand bitumen in its native state and in the free state by NMR relaxation spectroscopy. These investigations include the study of tar sand ore and bitumen when subjected to thermal stress and to solvents of different polarity.

EXPERIMENTAL

Sample Description

Tar Sand Ore

The tar sand ore was obtained from the Asphalt Ridge site at the Uinta County quarry, Vernal, Utah. The ore, a composite of drums 6A and 6B, had a bitumen content of ~13.6%.

Tar Sand Bitumen

The bitumen was obtained using a standard Soxhlet extraction technique for recovering organic materials from mineral matrices. The tar sand ore was weighed into a glass extraction thimble and extracted with 700 mL of toluene until the solvent leaving the thimble was colorless. The fine mineral matter was filtered from the extraction solvent containing the organic material. The toluene was then removed by rotary evaporation. The remaining tar sand ore was extracted with 700 mL of pyridine for 24 hours. The bulk of the pyridine was removed by rotary evaporation. Traces of pyridine were removed by two azeotropic distillations with ~50 mL of toluene. Previous experiments in which a simulated distillation technique was used showed that less than 1% by volume of solvent remained in the bitumen. All bitumen fractions were combined.

Coal

The coal sample used was a high-volatile bituminous standard coal obtained from Alpha Resources, Inc., containing on a dried basis 0.90% sulfur, 9.24% ash, 36.17% volatile matter, 54.59% fixed carbon. It had a heating value of 13,187 Btu/lb.

Oil Shales

The western reference shale is a Mahogany zone, Parachute Creek Member, Green River Formation oil shale obtained from the Exxon Colony mine located near Parachute, Colorado. The eastern reference shale is a Clegg Creek Member, New Albany shale obtained from the Knieriem Quarry, which is located approximately 16 miles south of the Ohio River at Louisville, Kentucky. Complete descriptions of the reference oil shales have been given in a report by Miknis and Robertson (1987).

The oil shale material was reduced to size by grinding to approximately 100 mesh and then riffled to obtain representative samples.

Paraffin Wax

The wax sample, obtained locally, was the type used in sealing preserves.

Solvents

Benzene assayed at 99.9% was obtained from MCB Manufacturing Chemists, Inc. Chlorobenzene assayed at 99.5% was obtained from Eastman Kodak Company. Carbon tetrachloride assayed at 99.8% was obtained from J. T. Baker Chemical Co. Chloroform-d₁ assayed at 99.8 atom % of deuterium was obtained from Cambridge Isotope Laboratories. Benzene-d₆ and Pyridine-d₅ assayed at 99.5 and 99.0 atom % of deuterium, respectively, were obtained from Norell Chemical Co., Inc.

All samples were used as received and without degassing.

Instrumentation

An IBM PC-20 spectrometer with a 4.7-kg fixed magnet and an oscillating field of 20 MHz for hydrogen was used for all NMR experiments. The temperature of the magnet and probe assembly was held constant at 40° ±0.01°C (104°F). A 7.5-mm variable temperature solid/liquid probe was used but modified by placing a 1-cm Teflon spacer in the bottom of the probe assembly. This spacer was used to ensure that the samples were within the 20-mm coil height when placed in a 7.5-mm flat bottom NMR tube. The spectrometer was operated in the phase-sensitive detector mode with the bandwidth set at high for all relaxation time experiments. The number of transients averaged to ensure good signal-to-noise ratio varied from 4 to 100 depending upon the sample. The attenuation was set at a value of 39 and the delay time between pulse sequences was set at 5 and 10 seconds for spin-lattice and spin-spin relaxation time, respectively.

The inversion-recovery (π - τ - $\pi/2$) technique and an iterative, non-linear, three-parameter curve fit were used to obtain the spin-lattice relaxation times, T_1 . Equation 1 was used for the calculation:

$$M_\tau = M_\infty(1 - \theta e^{-\tau/T_1}) \quad (1)$$

where, M = the intensity at a pulse delay time of τ
 τ = pulse delay time between π and $\pi/2$ pulses
 θ = flip angle
 M_∞ = the intensity at infinite τ (single 90° pulse)

The Carr-Purcell-Meiboom-Gill technique (CPMG) and a nonlinear, two-parameter curve fitted to equation 2 were used to obtain the spin-spin relaxation times, T_2 .

$$M_\tau = M_\infty e^{-\tau/T_2} \quad (2)$$

RESULTS AND DISCUSSION

Hydrogen T_1 Values of Related Materials

To validate the instrumental and operational conditions used to obtain T_1 and T_2 values, several different types of materials were studied. In Table 1 the ^1H spin-lattice relaxation times are listed for pure compounds (benzene, chlorobenzene, and water), a paraffin wax, and several fossil fuels (coal, western and eastern reference oil shales, and the Asphalt Ridge tar sand ore and bitumen). Reported values for the hydrogen spin-lattice relaxation times for benzene and chlorobenzene at 40°C (104°F) are not readily available. However, the T_1 value of water (deionized) at 40°C has recently been reported by Schmidt et al. (1986) using a PC-20 spectrometer. The value reported was 3.84 ± 0.02 sec, which compares favorably with the value of 3.98 ± 0.01 sec listed in the table.

Woessner (1964) reported the hydrogen spin-lattice relaxation times for several liquid n-alkanes. He obtained a value of 1.0 sec for n-hexadecane. The trend in the ^1H T_1 values reported for n-alkanes shows a decrease in T_1 with increasing molecular weight. Thus a value of 0.19 sec listed in Table 1 for the spin-lattice relaxation time of solid paraffin ($C > 20$) is not unreasonable.

The ^1H spin-lattice relaxation times for coals were measured by Sullivan et al. (1983). The T_1 values ranged from 8 to 103 msec depending upon the rank of the coal. The T_1 value listed in Table 1 for the coal sample falls well within the range reported in the literature.

The spin-lattice relaxation time for a western oil shale was reported by Harrell and Kohno (1984) and by Miknis and Netzel (1976). The T_1 values in the literature for western oil shale differ from the measured value listed in Table 1, but this may be due to the different sources of the western oil shale. Essentially no difference was noted for the eastern oil shale between the T_1 values reported in this work and the value reported in the literature.

The value in the literature for T_1 of a tar sand ore and bitumen was estimated from the plot of T_1 versus temperature given in the paper by Miknis and Netzel (1976). The T_1 values of the Asphalt Ridge tar sand ore and bitumen reported in Table 1 are in close agreement with the estimated values in the literature.

Aside from the reported T_1 value for water, all other reported T_1 values were measured using either a different type of instrument or technique. From the close agreement of the T_1 values reported here for the widely different materials with those reported in the literature, it was concluded that both the instrumental and operational techniques could be used in subsequent T_1 and T_2 studies of the kinetics and solvent effects on the chemical association in tar sands even though T_2 values were not readily available in the literature.

Table 1. ¹H Spin-Lattice and Spin-Spin Relaxation Times for Various Materials

Material	Spin-Lattice Relaxation Time, T ₁ , sec ^a		Spin-Spin Relaxation Time, T ₂ , sec ^a
	This Work	Literature	This Work
Benzene	4.452±0.018	N.F. ^b	0.646±0.009
Chlorobenzene	3.867±0.026	N.F.	
Water (deionized)	3.983±0.006	3.84±0.02 ^c	0.564±0.005
Wax	0.191±0.005	1.0 ^d	
Coal	0.038±0.004	0.008-0.103 ^e	
Western Reference Oil Shale	0.058±0.004	0.014 ^f , 0.025 ^g 0.100 ^h	
Eastern Reference Oil Shale	0.003 ⁱ	0.004 ^f	
Asphalt Ridge Tar Sand Ore	0.052±0.002	0.056 ^g	
Asphalt Ridge Tar Sand Bitumen	0.062±0.000	0.056 ^g	

^a Measured at 40°C

^b Not found

^c Schmidt et al. (1986)

^d Woessner (1964)

^e Sullivan et al. (1983)

^f Harrell et al. (1983)

^g Miknis and Netzel (1976)

^h Sydansk (1978)

ⁱ Estimated from the null method

Chemical Association Kinetics for Tar Sand Ore and Bitumen After Thermal Stressing

The Asphalt Ridge tar sand ore and the extracted bitumen samples were placed in an NMR tube and heated to 180°C (356°F) in a fluidized sand bath (Conn et al. 1984) for 1 hour. The samples were removed and quenched in water at ~ 21°C (70°F). The samples were then placed in the NMR spectrometer and allowed to equilibrate at 40°C (104°F) before the relaxation time was measured. The samples were removed and stored at ambient temperature until the next measurement in which the sample was again heated to 40°C (104°F) before the relaxation measurement was taken.

The ¹H spin-lattice relaxation times for the tar sand ore and bitumen at various times after quenching are listed in Table 2. The T₁ values for the tar sand ore are highly scattered with no obvious trend in the data. However, the T₁ values for the tar sand bitumen show a definite decrease with time, approaching the initial value after nearly a week.

For a nonviscous molecular system consisting of small spherical molecules tumbling isotropically, the molecular rotational correlation time, τ_c, is related to the intramolecular dipolar spin-lattice relaxation time, T₁, as given by equation 3 (Farrar and Becker 1971):

$$R_1 = \frac{1}{T_1} = \frac{\hbar^2 \gamma_H^4 \tau_c}{r_{HH}^6} \quad (3)$$

where, R₁ = the intramolecular dipolar spin-lattice relaxation rate
ħ = Planck's constant divided by 2π
γ_H = the magnetogyric ratio for the ¹H nucleus
r_{HH} = the H-H intranuclear distance.

A physical description of the motions of a molecule is contained in the molecular correlation time. The correlation time depends on the molecular weight and symmetry of the molecule, the viscosity, density and the temperature which, in turn, affects the spin-lattice relaxation rate. A measure of the relaxation rate gives only the "mean" or "effective" correlation time and, thus, a description of the molecular dynamics of molecules in solution requires that the correlation time be related to some physical model describing molecular motion. One such model consists of calculating the rotational diffusion constant for the reorientation of a molecule in random steps of small angular displacement using the Stokes-Einstein equation (Lyerla 1971).

The derivation of the relationship of the relaxation rate, R₁, as a function of molecular parameters (equation 4) is given in the thesis by Netzel (1975) and references cited therein.

$$R_1 = k_p [Mn/T\rho] \quad (4)$$

Table 2. ^1H Spin-Lattice Relaxation Times After Quenching of Asphalt Ridge Tar Sand Ore and Bitumen Heated to 180°C for 1 Hour

Time After Quenching, hours	Tar Sand Ore Spin-lattice Relaxation Time, sec ^a	Tar Sand Bitumen Spin-lattice Relaxation Time, sec ^a
0.00	0.0519 ^b	0.0615 ^b
0.18		0.0646
0.75	0.0528	
1.50		0.0647
5.83	0.0499	
17.75	0.0532	
18.50		0.0641
26.00		0.0632
29.33	0.0482	
41.91	0.0504	
42.70		0.0630
50.60		0.0624
53.91	0.0470	
66.24	0.0521	
66.85		0.0615
78.27		0.0623
90.24	0.0527	
90.85		0.0623
102.85		0.0614
115.18		0.0613
116.24	0.0506	
139.39	0.0502	
187.18		0.0608

^a Measured at 40°C
^b Before heating to 180°C

where M = the molecular weight
 η = viscosity
 ρ = density
 T = temperature
 k_p = the proportionality constant

To a first approximation, equation 4 may be used to explain the data for tar sand bitumen given in Table 2. The relaxation rate as a function of time for the tar sand bitumen is shown in Figure 1. The increase in the relaxation rate suggests that the molecular weight and/or viscosity is increasing with time after quenching (see equation 4). It can be assumed that at 180°C (356°F), the tar sand bitumen is partially dissociated relative to ambient temperature, that is, a reduction of the van der Waals forces and/or hydrogen bonding occurs. The dissociated state of the tar sand bitumen is "frozen" by quenching the system to room temperature. Reassociation of the tar sand bitumen molecules begins after quenching and continues for nearly a week before equilibrium is reestablished.

The solid line in Figure 1 represents the best statistical fit of the data for a first-order rate equation of the form

$$R_1^t = R_1^0 + (R_1^\infty - R_1^0) (1 - e^{-kt}) \quad (5)$$

where R_1^t , R_1^0 and R_1^∞ are the spin-lattice relaxation rates at time t , zero time, and infinite time (initial value before heating), respectively. t is the time in hours and k is the first-order rate constant.

The correlation coefficient, r^2 , for the data was found to be 0.965. The calculated values for R_1^0 and R_1^∞ were determined to be 15.45 sec⁻¹ and 16.50 sec⁻¹, respectively, and the first-order rate constant for the reassociation was found to be 0.0139 hr⁻¹.

Solvent-Solute (Tar Sand Bitumen) Interaction

The spin-lattice and spin-spin relaxation times were measured for various weight fractions of tar sand bitumen dissolved in solvents of different polarity. These values are listed in Table 3 for the bitumen in chloroform-d₁, carbon tetrachloride, benzene-d₆ and pyridine-d₅.

It is known that tar sand bitumen solubility depends on the polarity of the solvent. The solvation depends upon the disruption of the van der Waal intermolecular forces and hydrogen bonding. The relative extent to which the molecular interactions of a solute are increased or reduced by different solvents can be determined from NMR relaxation studies in which nonhydrogen-containing or deuterated solvents are used to avoid interference with the ¹H relaxation rate measurements of the solute. Changes in the relaxation rate of the tar sand bitumen as a function of its weight fraction in solution can be

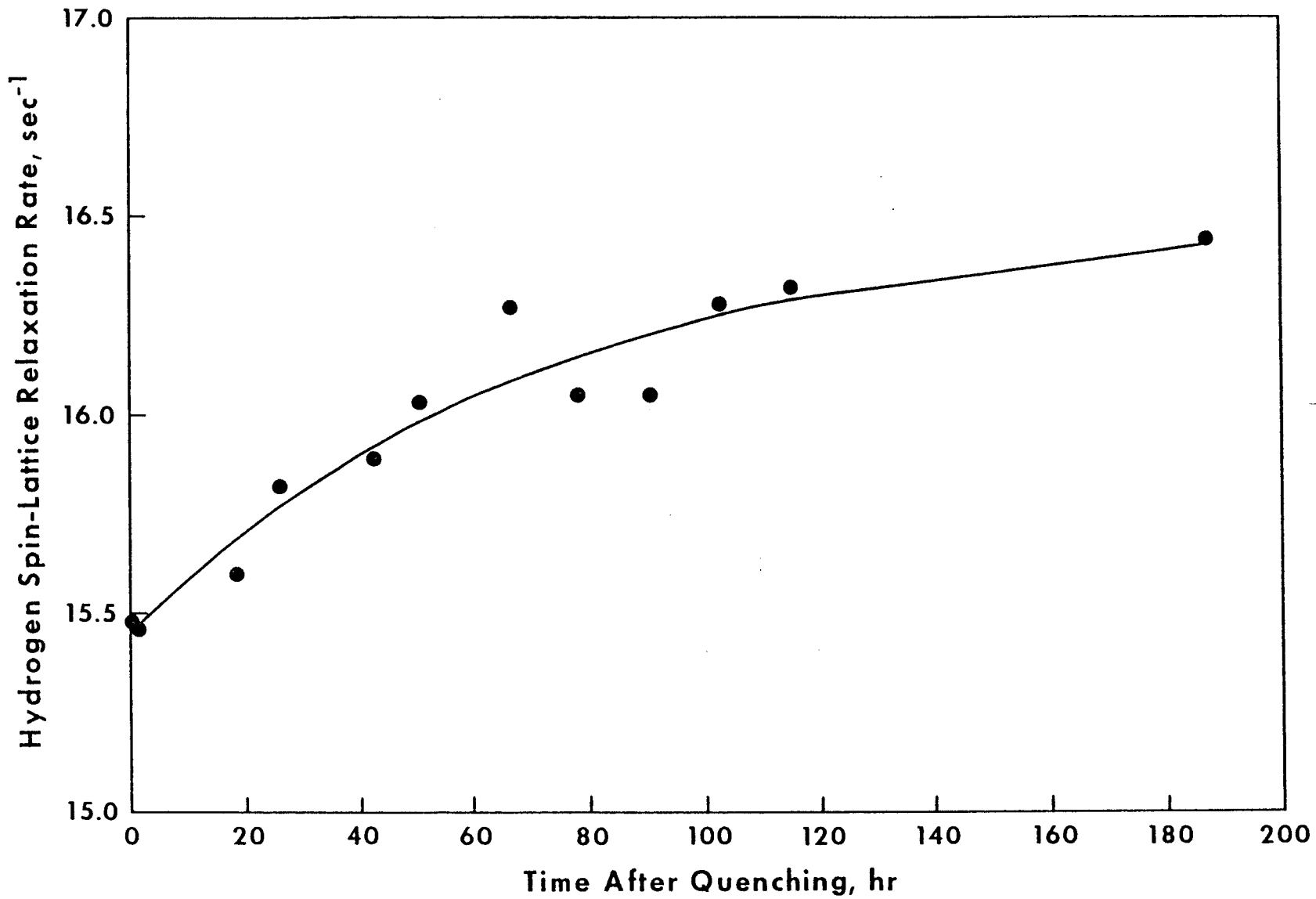


Figure 1. ¹H Spin-Lattice Relaxation Rate of Asphalt Ridge Tar Sand Bitumen as a Function of Time After Quenching

Table 3. ¹H Spin-lattice and Spin-Spin Relaxation Times for Asphalt Ridge Tar Sand Bitumen in Various Solvents

	Chloroform-d ₁				
	Weight Fraction of Bitumen				
	<u>0.2009</u>	<u>0.4279</u>	<u>0.6023</u>	<u>0.8009</u>	<u>1.000^d</u>
Spin-lattice Relaxation Time ^b , sec	0.1453	0.0820	0.0479	0.0408	0.0615
Spin-Spin Relaxation Time ^b , sec	0.1281	0.0638	0.0062	0.0049	0.0003
	Carbon Tetrachloride				
	Weight Fraction of Bitumen				
	<u>0.1881</u>	<u>0.3966</u>	<u>0.6013</u>	<u>0.8008</u>	1.0000
Spin-lattice Relaxation time, sec	0.1165	0.0708	0.0455	-- ^c	0.0615
Spin-Spin Relaxation time, sec	0.1163	0.0381	0.0069	--	0.0003
	Benzene-d ₆				
	Weight Fraction of Bitumen				
	<u>0.2123</u>	0.4041	0.6135	<u>0.8024</u>	<u>1.000</u>
Spin-lattice Relaxation time, sec	0.1524	0.1141	0.0711	0.0420	0.0615
Spin-Spin Relaxation time, sec	0.1657	0.0745	0.0080	0.0022	0.0003
	Pyridine-d ₅				
	Weight Fraction of Bitumen				
	<u>0.2120</u>	<u>0.4091</u>	<u>0.6040</u>	-- ^d	1.000
Spin-lattice Relaxation time, sec	0.1318	0.0856	0.0605	--	0.0615
Spin-Spin Relaxation time, sec	0.1641	0.0596	0.0143	--	0.0003

^aFor spin-lattice relaxation time, the value listed is before quenching experiment.

For spin-spin relaxation time, the value listed is after the quenching experiment.

^bMeasured at 40°C

^cSolution too viscous to get into NMR tube without change in weight fraction

^dSolution not prepared

attributed to changes in the molecular structure caused by solute-solute and/or solute-solvent interactions. These interactions can result in the formation of micelles, complexation, and/or solvation of the solute by the solvent.

As previously mentioned, the relaxation rate is directly related to the molecular weight of the molecular moiety. If this argument is pursued further, the data in Table 3 and Figure 2 can be explained on the basis that the molecular weight of molecular moiety changes upon dilution with a solvent and that the relative change depends on the polarity of the solvent.

It appears from the data presented in Figure 2 that there is an initial increase in the relaxation rate followed by an almost uniform decrease upon dilution with each of the solvents. The initial increase in the relaxation rate for the tar sand bitumen in chloroform- d_1 and benzene- d_6 (only solvents for which data are available) may be due to an increase in the apparent molecular weight and/or viscosity of the solution. If it is due to an increase in the apparent molecular weight through association, the molecular moiety may be the result of the formation of "micelles" or weak solute-solvent complexes. Upon further dilution, the van der Waals intermolecular forces and hydrogen bonding decrease, resulting in smaller molecular fragments. The decrease in the relaxation rate with increasing dilution may also be due to a decrease in the viscosity of the solution (see equation 4).

For a weight fraction of bitumen in any solvent less than 0.6, the molecular weight of the molecular species present is less than in the original starting material providing viscosity is not a factor. The chemical association in the solutions cannot be ascertained until viscosity measurements are made. Also from Figure 2, it appears that benzene is a better solvent for the dissolution of tar sand bitumen than any of the other solvents studied as seen by the smaller relaxation rate (smaller molecules) for a given weight fraction.

The changes in the spin-spin relaxation rates of tar sand bitumen at various weight fractions in various solvents are shown in Figure 3. Information on the spin-spin relaxation rate of tar sand bitumen without any solvents could not be obtained with the instrumental configuration used in these experiments. The arguments presented in the previous section on spin-lattice relaxation rate of tar sand bitumen in solution also apply to the spin-spin relaxation data.

CONCLUSIONS

Nuclear magnetic resonance spectroscopy can be a useful technique in the investigation of intermolecular interactions and molecular mobility. It was found that tar sand bitumen when subjected to thermal stress followed by quenching requires almost a week at 40°C (104°F) for the molecular species to reassociate to an equilibrium molecular configuration. The reassociation was found to be first-order with a rate constant of 0.0139 hr⁻¹.

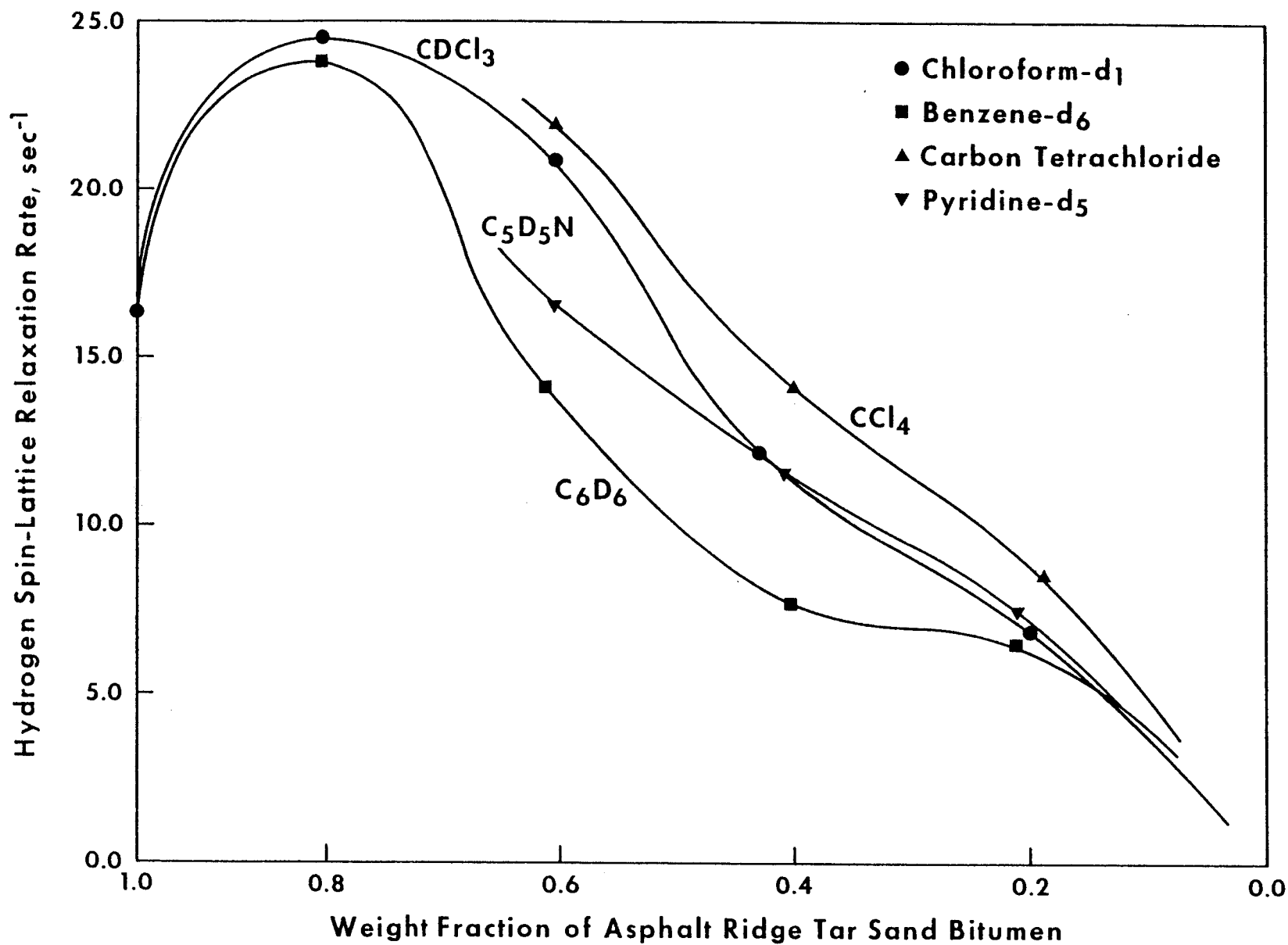


Figure 2. ¹H Spin-Lattice Relaxation Rate of Asphalt Ridge Tar Sand Bitumen as a Function of the Weight Fraction in Various Solvents

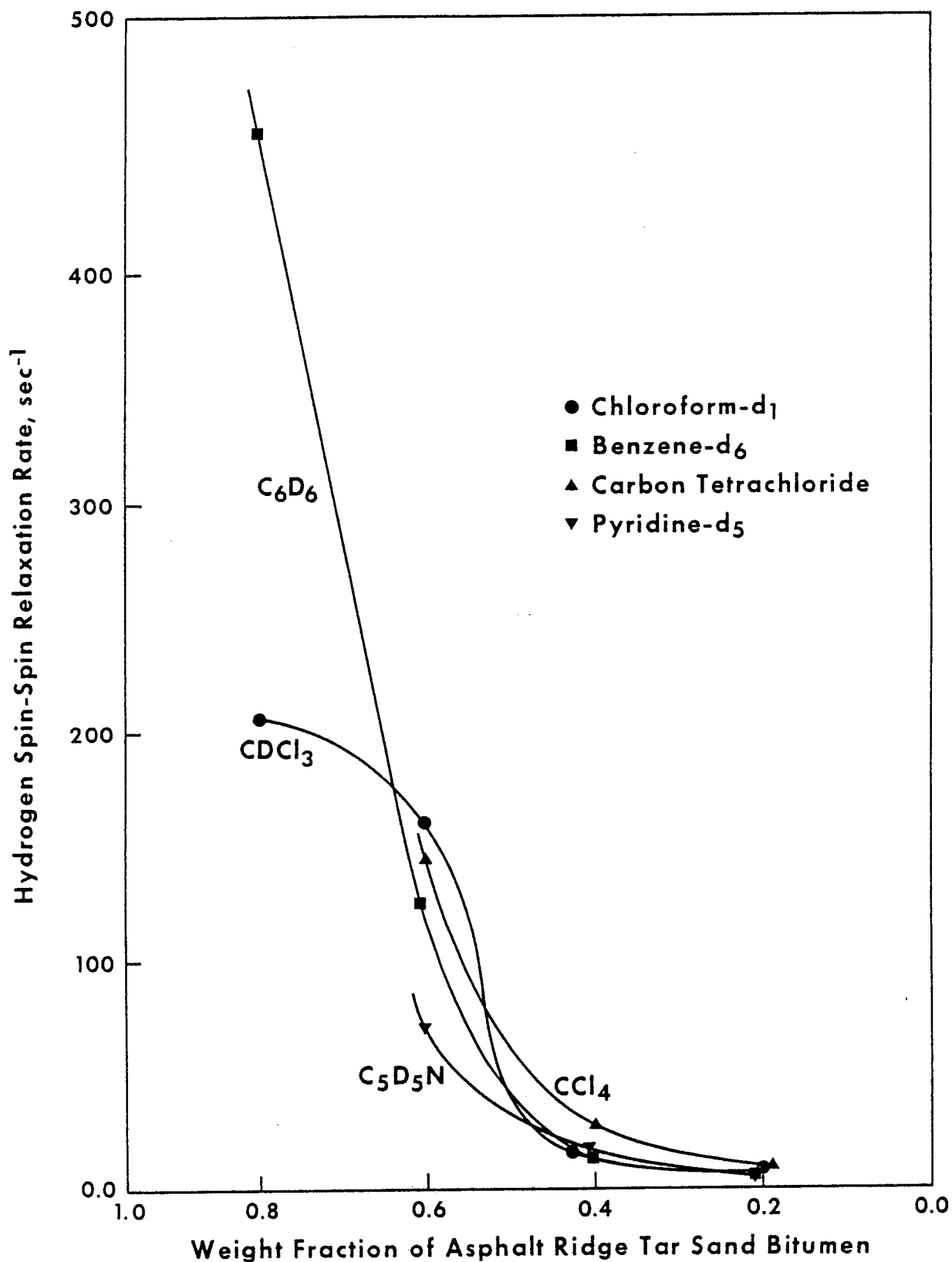


Figure 3. ¹H Spin-Spin Relaxation Rate of Asphalt Ridge Tar Sand Bitumen as a Function of the Weight Fraction in Various Solvents

It was also found that spin-lattice and spin-spin relaxation time measurements can be used to investigate the different degrees of association of tar sand bitumen dissolved in solvents of different polarity. Additional experiments are needed to ascertain if the preliminary results are caused by changes in intermolecular association of the molecular species or by changes in the viscosity of the solutions.

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DISCLAIMER

Mention of specific brand names or models of equipment is for information only and does not imply endorsement.

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