

CHEMICAL CHARACTERIZATION OF THE SURFACE SITES OF COAL

Technical Progress Report for the Period

October - December, 1989

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August 1990

PREPARED FOR THE UNITED STATES

DEPARTMENT OF ENERGY

Under Contract No. DE-FG22-87PC79925

Received by OSTI
OCT 09 1990

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CHEMICAL CHARACTERIZATION OF THE SURFACE SITES OF COAL

I. OBJECTIVES AND SCOPE OF WORK

We propose to do experimental studies in four related areas concerning the acid-base properties of coal surfaces; 1) develop high precision flow microcalorimetric methods for determining the concentrations and strengths of the acidic and basic surface sites of coal powders; 2) develop photo-acoustic FTIR and solid-state NMR spectral shift techniques for determination of the concentrations and strengths of acidic and basic surface sites of coal powders; 3) determine the concentrations and strengths of the acidic and basic surface sites of some of the well-characterized coal samples from Argonne National Labs, comparing the coal samples before and after demineralization treatments with HCl and HF; 4) study the effects of surface acidity and basicity on the coal/water interface, with emphasis on the role of interfacial acid-base interactions in the adsorption of ions, surfactants and coal/water slurry stabilizers.

A practical application of the new measurements of the reactions of surface sites will be to determine the acid-base contributions to adsorption of ions and of surfactants from aqueous media onto coal, where more than just hydrophobic bonds and electrostatic attractions are involved. An example is the adsorption of phosphates, which adsorb more strongly than sulfates.

II. TECHNICAL PROGRESS

One of the major goals of this research effort is to identify and characterize acidic and basic molecules which have NMR active nuclei such that through measurements of NMR chemical shifts one can deduce the surface acidity or basicity of solids such as coals. There are four general requirements for these probe molecules.

- The NMR active nucleus should be adjacent to but not actually the atom involved in the acid-base bonding.
- The native concentration of the NMR active nucleus must be low or the chemical composition of the NMR active nucleus native to the coal must be distinctly different from that of the probe such that the chemical shift of the probe is readily apparent.
- The probes selected must have significantly different E and C parameters such that the E and C parameters and hence the chemical identity of the surface sites of the solid under investigation can be determined.
- The chemical shift of the probe must be directly proportional to the enthalpy of acid-base interaction.

We have previously presented data for two basic ^{31}P probes, triethylphosphine oxide ($E_{\text{P}}=1.65$, $C_{\text{P}}=2.67$, $C/E=1.6$), and tricyclohexylphosphine sulfide ($E_{\text{P}}=0.61$, $C_{\text{P}}=9.67$, $C/E=16$), see reports DOE/PC/79925-5 and -6. One of the acidic probes which we have been working with is diphenyl mercury in which the ^{199}Hg chemical shifts is dependent on the strength of acid-base bonding, see report DOE/PC/79925-6. This is a soft acid with an expected C/E close to one. Another acidic probe we are studying is triphenylsilanol. This is a hard acid with an expected E/C ratio of ≈ 0.3 in which the ^{29}Si chemical shift is indicative of the strength of acid-base bonding. In this report we will show that Ph_3SiOH fulfills the four requirements given above.

- The NMR active nucleus should be adjacent to but not actually the atom involved in the acid-base bonding. This is true since the acidic site in Ph_3SiOH is the hydrogen atom of the hydroxyl group bound to the silicon atom.

- The native concentration of the NMR active nucleus must be low or the chemical composition of the NMR active nucleus native to the coal must be distinctly different from that of the probe such that the chemical shift of the probe is readily apparent. The major source of silicon in coals is in quartz and silicates which have quite different chemical shifts than the organo-silicon in Ph_3SiOH .

- The probes selected must have significantly different E and C parameters such that the E and C and hence the chemical identity of the surface sites of the solid under investigation can be determined. We have not yet determined the actual E_A and C_A parameters for Ph_3SiOH . However based on the similar structure of Ph_3SiOH with surface hydroxyl groups on SiO_2 for which the parameters are known, it is safe to say that this compound is a hard acid with an E/C ratio of ≈ 0.3 .

- The chemical shift of the probe must be directly proportional to the enthalpy of acid-base interaction. This has not been proven definitively as yet since this relies on knowing the actual enthalpies of interaction between Ph_3SiOH and the test bases. We have however completed the chemical shift measurements for the interaction of Ph_3SiOH with seven bases of different E_B and C_B values. The experimental procedure and method of analysis are the same as that previously described in report DOE/PC/79925-5.

The first thing which one must know in order to analyze NMR chemical shifts due to acid-base interactions is the concentration dependence of the ^{29}Si chemical shift. This data is shown in Figure 1. The chemical shift, δ_{F} , appears to be independent of concentration up to 60 millimole/liter. The

value of -13.260 ppm was used in the analysis of chemical shifts due to acid-base interactions since all Ph_3SiOH concentrations used were below this value. A summary of the experimental conditions is presented in Table 1 along with the calculated values the chemical shift due to acid-base interaction, $\Delta\delta_c$, and the equilibrium constant of these reactions, K_a , based on the fast exchange model. Although the fast exchange model appears to hold for these experiments, the proof that the chemical shift is proportional to the enthalpy

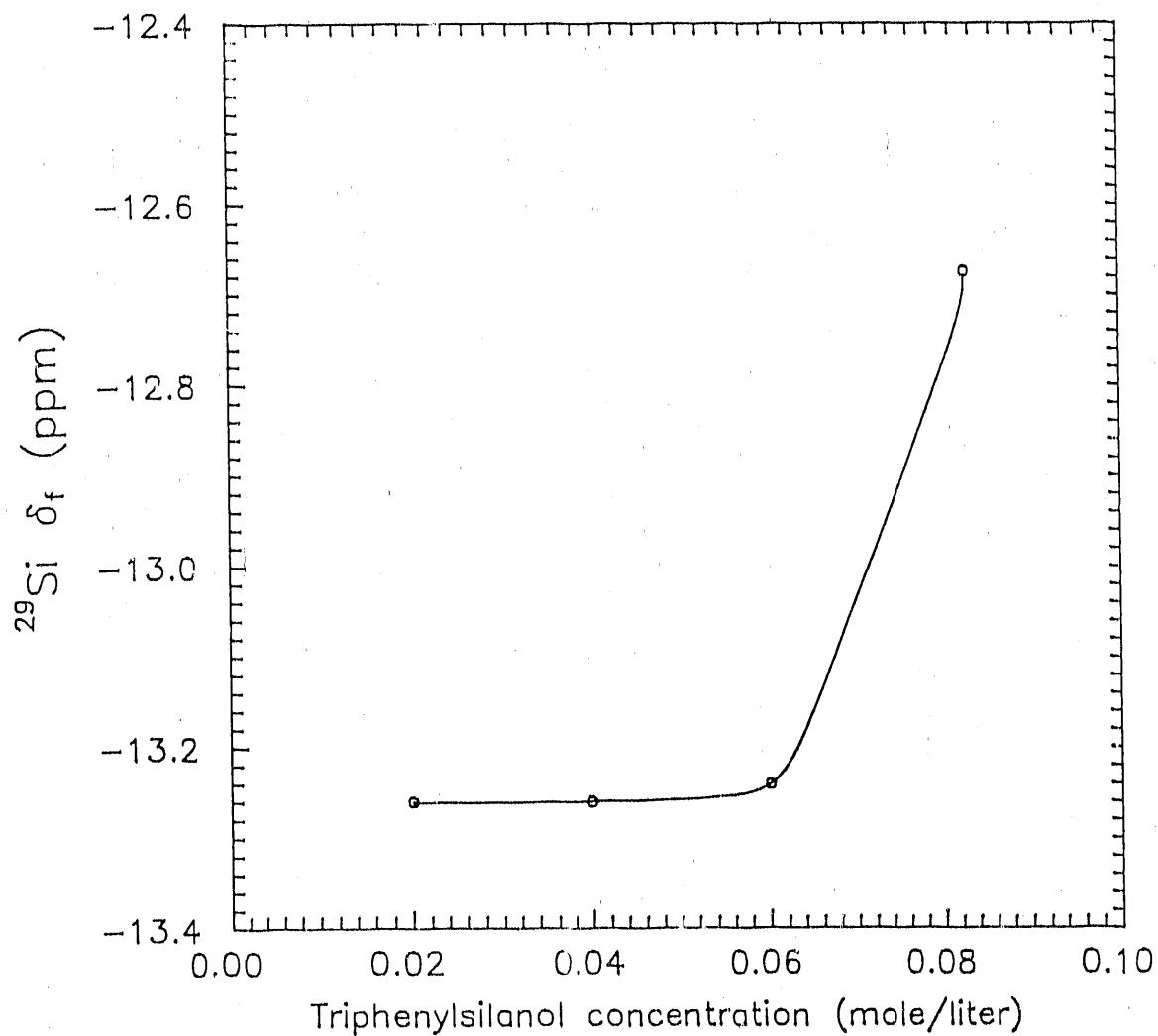


Figure 1. Concentration dependence of the ^{29}Si NMR chemical shift of triphenylsilanol in CCl_4 .

TABLE 1

Concentration dependence of the observed ^{29}Si NMR chemical shifts for triphenylsilanol - base adduct formation in CCl_4 , and the adduct chemical shifts and equilibrium constants calculated from the fast exchange model.

Base	$[\text{Ph}_3\text{SiOH}]$ (mmole/l)	$[\text{Base}]$ (mmole/l)	δ_o (ppm)	δ_f^\dagger (ppm)	$\Delta\delta_o^\ddagger$ (ppm)	$\Delta\delta_o^{\dagger\dagger}$ (ppm)
Tricyclohexylphosphine Sulfide	54.7	49.4	-13.672	-13.260	-0.412	-0.412
	46.9	84.7	-13.878	-13.260	-0.618	-0.618
	$\Delta\delta_c = -1.3 \pm 0.7$ (ppm)		$K_a = 14 \pm 7$ (l/mole)		chi-squared=0.000	
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Acetonitrile	56.2	261.5	-14.098	-13.260	-0.838	-0.838
	52.9	492.2	-14.519	-13.260	-1.259	-1.257
	50.0	697.3	-14.760	-13.260	-1.499	-1.505
	47.3	880.8	-14.931	-13.260	-1.671	-1.668
$\Delta\delta_c = -2.77 \pm 0.06$ (ppm)		$K_a = 1.77 \pm 0.07$ (l/mole)		chi-squared=0.002		
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Ethyl Acetate	51.1	157.5	-14.168	-13.260	-0.907	-0.909
	47.4	292.6	-14.607	-13.260	-1.346	-1.346
	44.3	409.6	-14.860	-13.260	-1.600	-1.596
	41.5	512.0	-15.014	-13.260	-1.754	-1.757
$\Delta\delta_c = -2.84 \pm 0.04$ (ppm)		$K_a = 3.3 \pm 0.1$ (l/mole)		chi-squared=0.002		
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Tetrahydrofuran	55.4	189.0	-14.914	-13.260	-1.653	-1.648
	51.4	351.0	-15.422	-13.260	-2.162	-1.173
	48.0	491.4	-15.679	-13.260	-2.419	-2.415
	45.0	614.3	-15.816	-13.260	-2.556	-2.553
$\Delta\delta_c = -3.24 \pm 0.05$ (ppm)		$K_a = 6.4 \pm 0.3$ (l/mole)		chi-squared=0.004		
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N,N-dimethylformamide	51.1	198.8	-16.444	-13.260	-3.183	-3.079
	47.4	369.1	-16.459	-13.260	-3.198	-3.483
	44.3	516.8	-16.969	-13.260	-3.708	-3.624
	41.5	646.0	-17.054	-13.260	-3.794	-3.695
$\Delta\delta_c = -4.0 \pm 0.7$ (ppm)		$K_a \approx 22$ (l/mole)		chi-squared=0.11		
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Pyridine	55.4	190.2	-16.537	-13.260	-3.277	-3.270
	51.4	353.3	-16.987	-13.260	-3.726	-3.734
	48.0	494.6	-17.134	-13.260	-3.874	-3.895
	45.0	618.3	-17.259	-13.260	-3.999	-3.976
$\Delta\delta_c = -4.30 \pm 0.07$ (ppm)		$K_a = 2 \pm 2$ (l/mole)		chi-squared=0.011		

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Table 1 Continued

Base	[Ph ₃ SiOH] (mmole/l)	[Base] (mmole/l)	δ_o (ppm)	δ_f^\dagger (ppm)	$\Delta\delta_o^\ddagger$ (ppm)	$\Delta\delta_o^{\dagger\dagger}$ (ppm)
Dimethyl Sulfoxide	51.1	216.6	-17.119	-13.260	-3.858	-3.854
	47.4	402.3	-17.358	-13.260	-4.097	-4.109
	44.3	563.2	-17.447	-13.260	-4.187	-4.189
	41.5	704.0	-17.497	-13.260	-4.237	-4.227
	$\Delta\delta_c = -4.38 \pm 0.03$ (ppm)		$K_a = 43 \pm 4$ (l/mole)		chi-squared=0.005	
Triethylphosphine Oxide	51.1	57.9	-17.893	-13.260	-4.632	-4.628
	47.4	107.6	-18.496	-13.260	-5.236	-5.247
	44.3	150.7	-18.594	-13.260	-5.334	-5.341
	41.5	188.3	-18.652	-13.260	-5.392	-5.377
	$\Delta\delta_c = -5.48 \pm 0.03$ (ppm)		$K_a = 370 \pm 30$ (l/mole)		chi-squared=0.007	
Triethylamine	51.1	110.4	-18.140	-13.260	-4.880	-4.880
	47.4	205.0	-18.994	-13.260	-5.733	-5.733
	$\Delta\delta_c = -7 \pm 3$ (ppm)		$K_a = 40 \pm 20$ (l/mole)		chi-squared=0.000	

† For Ph₃SiOH concentrations less than or equal to 60 millimole/l the free shift, δ_f , is concentration independent.

‡ Calculated from the measured shift $\Delta\delta_o = \delta_o - \delta_f$.

†† Predicted by the fast exchange model using least-squares $\Delta\delta_c$ and K_a values.

of acid-base interaction requires that these enthalpies be known or that they can be calculated. We are in the process of determining the E_A and C_A parameters for Ph₃SiOH through calorimetric and infrared spectral shifts measurements. However since the parameters are known for surface silanols on silica, and the silanols are thought to be structurally similar to Ph₃SiOH, we have used these parameters in order to estimate the enthalpies using the Drago E and C equation. This data is shown in Figure 2. Although the actual slope of this line is probably incorrect, the linear trend is indicative that the chemical shifts due to acid-base interactions are linear with the enthalpy of interaction. The point for Ph₃SiOH interacting with tricyclohexylphosphine sulfide labeled "TCHPS" was excluded from the linear best fit solid line.

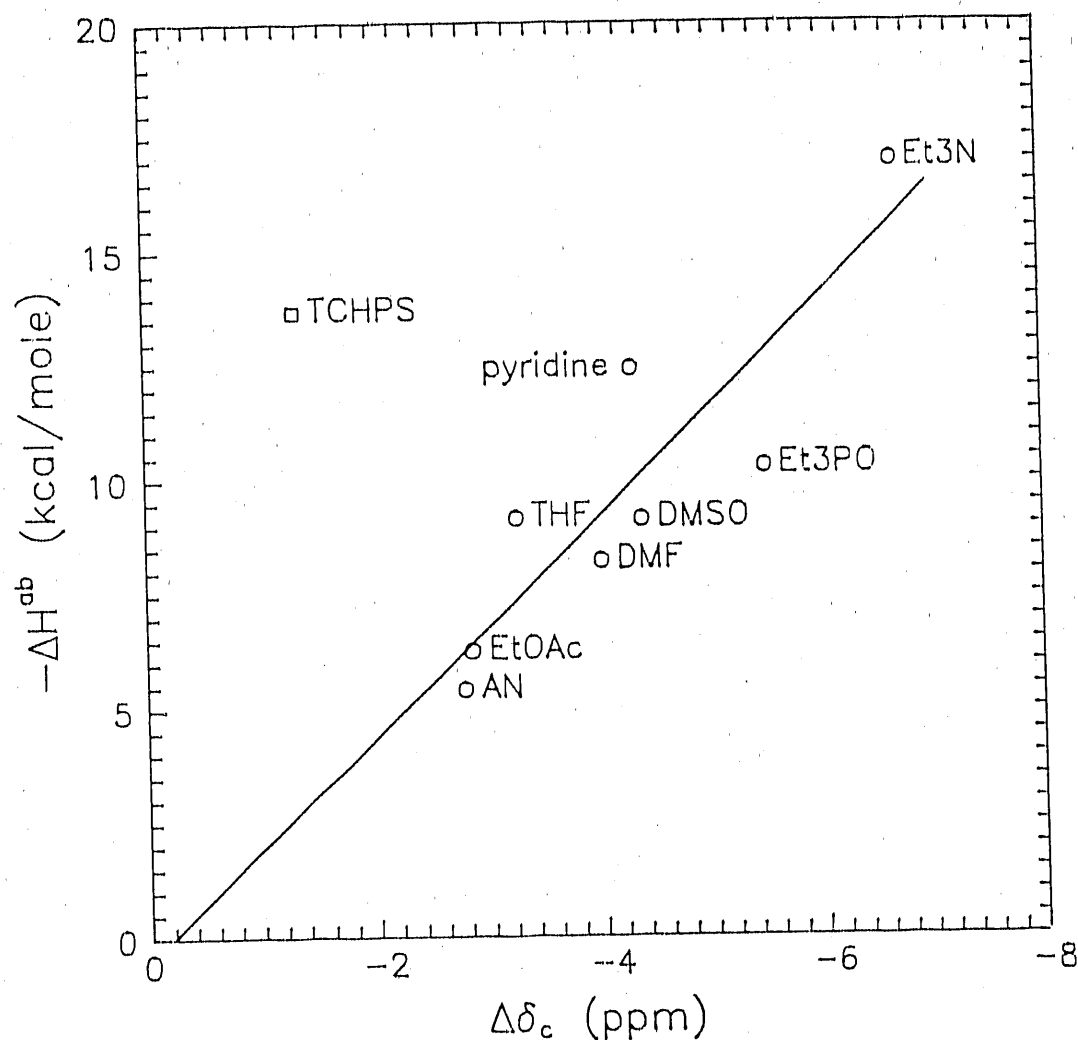


Figure 2. Estimated enthalpy of acid-base interaction versus the ^{29}Si NMR chemical shift of triphenylsilanol adducts with nine bases. $\Delta\delta_c$ is the best fit values from the fast exchange model and $-\Delta H^{ab}$ was calculated from E and C parameters. Trial E and C parameters for Ph_3SiOH were estimated from that of SiOH groups on silica, $E_A=4.39$, $C_A=1.14$ ($\text{kcal/mole}^{1/2}$). Legend: TCHPS is tricyclohexylphosphine sulfide, AN is acetonitrile, EtOAc is ethyl acetate, THF is tetrahydrofuran, DMF is N,N-dimethylformamide, DMSO is dimethyl sulfoxide, Et3PO is triethylphosphine oxide, and Et3N is triethylamine.

III. CONCLUSIONS

The NMR chemical shifts due to acid-base interactions between triphenylsilanol and seven bases have been obtained. Based on an estimation that the E_A and C_A parameters of this compound are close to those for surface silanol on silica, a linear dependence of the shift verses the enthalpy of interaction was shown. It is believed that this dependence will be proven to be true after we calculate the true enthalpies using the E and C parameters which we are now determining. The anomalous point for tricyclohexylphosphine sulfide suggests that further work is needed to verify the E_B and C_B values for this molecule.

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