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AN INVESTIGATION OF THE EFFECT OF ANTISTRIPPING AGENTS ON THE SILICA ADSORPTION OF ASPHALT MODEL FUNCTIONALITIES

By

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ABSTRACT

The effect of anti-stripping (AS) agents on the adsorption behavior of model asphalt functionalities was examined using silica as a model aggregate at 25°C. Two commercially available AS agents, which were designated as polyamine mixtures, were used to precoat the silica. When they were adsorbed onto the silica from dichloromethane solution, they both showed a strong interaction with the silica. One of the AS agents followed the Langmuir adsorption model. After a weakly adsorbed fraction was removed from the precoated silica by the serial washings with pure dichloromethane, seven asphalt model functionalities in cyclohexane solution were subsequently adsorbed onto the precoated silica. The model functionalities used represented those present in asphalt and were benzoic acid (carboxylic acid), phenol (phenolic), quinoline (N-base), phenylsulfoxide (sulfoxide), benzophenone (ketone), benzylbenzoate (ester), and pyrene (polynuclear aromatic). The adsorption of benzoic acid and phenol was increased with the precoating of the AS agents, whereas the other functionalities showed large decreases in their adsorption due to the precoated AS agents. The cooperatively enhanced adsorption shown by benzoic acid and phenol is thought to be due to an acid-base interaction between the basic AS agents and the acidic model compounds. Silica precoated with the AS agents was serially washed with distilled water to produce precoated silica which should be more impervious to water. Benzoic acid and phenol were then adsorbed onto the precoated silica from water solution as well as from cyclohexane solution. Their adsorption from aqueous solution was significantly reduced as compared to that from organic solution. However, the precoated silica adsorbed more organic molecules than did uncoated silica in an aqueous phase. A large amount of stripping was observed for benzoic acid and phenol preadsorbed on the precoated silica when they were introduced into bulk water.

TABLE OF CONTENTS

LIST OF TABLES	iv
LIST OF FIGURES	v
I. INTRODUCTION	1
II. EXPERIMENTAL	2
Materials Used in Adsorption Studies	2
Equipment	2
Procedure	2
(1) Preparation of Precoated Silica	2
(2) Adsorption of Model Compounds onto Precoated Silica	2
(3) Adsorption onto Precoated Silica from Aqueous Solution	3
(4) Desorption of Acidic Compounds from Precoated Silica by the Introduction of Bulk Water	3
Analysis	3
(1) AS Agent Loading on Silica from Organic Solution	4
(2) Model Compounds Adsorption from Organic Solution	5
(3) AS Agent Loading on Silica after Washing with Distilled Water	5
(4) Desorption of Acidic Model Compounds from Precoated Silica by Introduction of Bulk Water	5
III. RESULTS AND DISCUSSION	5
Selection of Model Functionalities	5
Adsorption Isotherms of AS Agents	8
Adsorption of Model Compounds on Precoated Silica in Organic Phase	8
(1) Enhanced Adsorption of Acidic Compounds	9
(2) Inhibited Adsorption of Nonacidic Compounds	14
(3) Interaction between AS agents and Model Compounds	17
Adsorption and Desorption of Acidic Model Compounds in an Aqueous Environment	19
(1) Adsorption onto Uncoated Silica from Cyclohexane and Water Solutions ..	19
(2) Adsorption onto Precoated Silica from Cyclohexane and Water Solutions ..	21
(3) Desorption of Acidic Compounds from Precoated Silica by Introduction of Bulk Water	24
IV. CONCLUSIONS	26
V. ACKNOWLEDGEMENT	27
BIBLIOGRAPHY	27
APPENDICES	28
A. UV Calibration Curves	29
B. Estimation of AS Agent Loadings on Silica	32

LIST OF TABLES

- Table 1. Wavelengths of UV Maxima Used for Test Compounds
- Table 2. Amounts and Concentrations of Chemical Components in Original Asphalts and Their Fractions¹
- Table 3. Effect of Precoated AS Agents on Silica on the Adsorption of Asphalt Model Functionalities
- Table 4. Monolayer Amounts Derived from the Langmuir Plots of Adsorption Isotherms of Acidic Functionalities

LIST OF FIGURES

- Figure 1. Model Compounds Selected
- Figure 2. Adsorption Isotherms for Two Commercial AntiStripping Agents/Dichloromethane/Silica Systems at 25°C
- Figure 3. Langmuir Plot of Two Commercial Anti-Stripping Agents at 25°C
- Figure 4. Adsorption Isotherms for the Systems of Benzoic Acid/Cyclohexane/Silica with Different ASI Coating Levels at 25°C
- Figure 5. Langmuir Plot from Adsorption Isotherms for the Systems of Benzoic Acid/Cyclohexane/Silica with Different ASI Coating Levels at 25°C
- Figure 6. Adsorption Isotherms for the Systems of Phenol/Cyclohexane/Silica with Different ASI Coating Levels at 25°C
- Figure 7. Langmuir Plot from Adsorption Isotherms for the Systems of Phenol/Cyclohexane/Silica with Different ASI Coating Levels at 25°C
- Figure 8. Adsorption Isotherms for the Systems of Benzoic Acid/Cyclohexane/Silica with Different AS2 Coating Levels at 25°C
- Figure 9. Langmuir Plot from Adsorption Isotherms for the Systems of Benzoic Acid/Cyclohexane/ Silica with Different AS2 Coating Levels at 25°C
- Figure 10. Adsorption Isotherms for the Systems of Phenol/Cyclohexane/Silica with Different AS2 Coating Levels at 25°C
- Figure 11. Langmuir Plot from Adsorption Isotherms for the Systems of Phenol/Cyclohexane/Silica with Different AS2 Coating Levels at 25°C
- Figure 12. Adsorption Isotherms for the Systems of Phenylsulfoxide/Cyclohexane/Silica with Different AS Coating Levels at 25°C
- Figure 13. Adsorption Isotherms for the Systems of Quinoline/Cyclohexane/Silica with Different AS Coating Levels at 25°C
- Figure 14. Adsorption Isotherms for the Systems of Benzophenone/Cyclohexane/Silica with Different ASI Coating Levels at 25°C
- Figure 15. Adsorption Isotherms for the Systems of Benzylbenzoate/Cyclohexane/Silica with Different AS2 Coating Levels at 25°C
- Figure 16. Adsorption Isotherms for the Systems of Pyrene/Cyclohexane/Silica with Different Asl Coating Levels at 25°C
- Figure 17. Acid and Base/Hydrogen Bonding Interactions among Model Compounds, AS Agents and Silanol Groups in Organic Medium
- Figure 18. Effect of Solvent on the Adsorption of Benzoic Acid onto Uncoated Silica at 25°C
- Figure 19. Effect of Solvent on the Adsorption of Phenol onto Uncoated Silica at 25°C
- Figure 20. Effect of Solvent on the Adsorption of Benzoic Acid onto 0-2 wt% AS1 Precoated Silica at 25°C
- Figure 21. Effect of Solvent on the Adsorption of Benzoic Acid onto 0-2 wt% AS2 Precoated Silica at 25°C
- Figure 22. Effect of Solvent on the Adsorption of Phenol onto 0-2 wt% ASI Precoated Silica at 25°C
- Figure 23. Effect of Solvent on the Adsorption of Phenol onto 0-2 wt% AS2 Precoated Silica at 25°C
- Figure 24. Adsorption/Desorption Behavior of Benzoic Acid onto/from 0-2 wt% ASI Precoated Silica at 25°C
- Figure 25. Adsorption/Desorption Behavior of Benzoic Acid onto/from 0-2 wt% AS2 Precoated Silica at 25°C
- Figure 26. Adsorption/Desorption Behavior of Phenol onto/from 0-2 wt% ASI Precoated Silica at 25°C
- Figure 27. Adsorption/Desorption Behavior of Phenol onto/from 0-2 wt% AS2 Precoated Silica at 25°C

- Figure 28. UV Calibration Curves for Two Commercial AS Agents in Dichloromethane Solutions
- Figure 29. Calibration Curve for AS1 in Water Solution
- Figure 30. Calibration Curve for AS2 in Water Solution
- Figure 31. Calibration Curve for Benzoic Acid in Water Solution
- Figure 32. Calibration Curve for Phenol in Water Solution

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Christine W. Curtis and Young W. Jeon

I. INTRODUCTION

One of major causes of asphalt pavement failure has long been recognized as the stripping of asphaltic binder from the aggregate surface due to water intercession at the asphalt-aggregate interface. This stripping phenomenon is attributed to the influence of polar water molecules on the wetting and adhesion of a relatively nonpolar asphalt onto a polar stone surface. When a stone has been soaked with water, the asphaltic binder is not able to wet the stone surface until the surface water has been removed in some way. Even when binders have already adhered to the stone surface, there still exists a possibility that water penetrated through the asphalt film may displace the binder molecules adhered to the stone surface and result in damage to the surface because of traffic stresses.

Mathews (1962) reported that using cationic surfactants as anti-stripping (AS) agents promoted adhesion between asphalt and aggregate and effectively reduced damage due to water. The cationic surfactants used contained long-chain alkyl or alkenyl groups and at least one primary amine group: for example, n-alkylamine, N-alkyl-substituted trimethylene diamine, and imidazoline. The substantive action of these surfactants when added to the bulk asphalt is to migrate to the aggregate as the adsorbing cathodic surface. These oil-soluble cationic surfactants, upon migration to and adsorption by an aggregate surface, displace the surface water, render the surface hydrophobic and lipophilic, and facilitate asphalt adsorption onto the surface.

Dybalski (1982), however, pointed out that those surfactants containing amine groups might react with acidic components present in asphalt to form amides which were inactive with the aggregate surface. In a typical hot mix, furthermore, only approximately 30-40 percent of the surfactant added could migrate to the aggregate surface due to the high viscosity of asphalt and short period of heating time (less than 3 hours). Consequently, a method to apply the AS agents directly to the aggregate was proposed.

The objectives of the present study are to precoat silica which represents a model siliceous aggregate with two commercially available AS agents and to investigate the adsorption/desorption behavior of asphalt model functionalities onto/from the precoated silica. The silica precoating was attained by adsorbing an AS agent onto dry silica using dichloromethane as solvent at 25°C and by washing the adsorbed silica several times with pure dichloromethane to remove any weakly adsorbed fraction. The asphalt model functionalities were selected based on the work accomplished by Petersen et al. (1982) who estimated the amount of each chemical functional group present in asphalt by employing differential infrared spectrometry and selective chemical reactions. The adsorption of the model functionalities onto precoated silica was performed using cyclohexane as an adsorption medium.

In this study, the acidic model compounds, benzoic acid and phenol, exhibited strong competition for the silica precoated with AS agents in an organic phase as compared to the other nonacidic compounds. Thus, the adsorption of benzoic acid and phenol onto uncoated and precoated silica was further investigated in aqueous and organic environments to evaluate the effect of different solvents on the adsorption of the acidic model compounds onto the silica. In addition, the desorption of the acidic model compounds preadsorbed on the precoated silica was examined by placing them into bulk water at 25°C. For the present study, the quantitation of amount adsorbed or desorbed was made by using UV spectroscopy and gravimetric analysis.

II. EXPERIMENTAL

Materials Used in Adsorption Studies

Two commercially available anti-stripping agents were used. They contained polyamines as their major constituent (Yoon 1987), but the exact chemical composition of the AS agents was not known because they are proprietary products. They were used as received. The seven model compounds representing chemical functionalities present in asphalt used in these studies were: benzoic acid (purity = 99+ %), quinoline (99+ %), phenylsulfoxide (97 %), phenol (99+ %), benzophenone (99+ %), benzylbenzoate (99+ %), and pyrene (99+ %), all supplied by Aldrich. The organic solvents used were dichloromethane for the AS agents and cyclohexane (99+ %, spectrophotometric grade, Aldrich) for the model compounds. Distilled water was also used as an aqueous solvent for the acidic model compounds, phenol and benzoic acid. The liquid model compounds and the organic solvents were dried by adding activated 4A molecular sieves while the solid compounds were dried in a vacuum desiccator. The adsorbent used was a silica gel purchased from Fisher and manufactured by Davison Chemical Division, W.R. Grace and Company. The silica gel was dried before use at 150°C for 24 hours to remove physisorbed water and organics from the silica surface.

Equipment

A Model 3528CC microprocessor controlled orbit shaker manufactured by Lab-line Instruments, Inc. was used to perform a liquid phase adsorption experiment. The orbit shaker features an automatic control of temperature (from 15 to $60 \pm 0.65^\circ\text{C}$), speed (0 to 500 ± 2 rpm), and shaking time (0 to 99.9 hours). The platform in the shaker accommodates up to 32 flasks (125 ml) so that multiple experiments can be performed simultaneously. For the present study, adsorption temperature, speed, and shaking time were controlled to be $25 \pm 0.65^\circ\text{C}$, 250 ± 10 rpm, and 60 min, respectively.

Procedure

(1) Preparation of Precoated Silica

For preparation of precoated silica, an AS agent was dissolved into dichloromethane to make solutions with various initial concentrations up to 10 g/L. The insoluble fraction of the AS agent was removed by vacuum filtering the solution through Whatman 934 AH glass microfilters. The solution concentration after filtration was corrected by subtracting the insoluble fraction from the initial amount of the AS agent introduced. The flasks containing AS agent solution were mounted on the platform of the orbit shaker and left for an hour to allow the solution temperature to equilibrate at the set temperature of 25°C. Then, 2 g dried silica were introduced into 95 ml of AS agent solution, and the solution mixture was stirred for one hour which was a sufficient period of time for attaining equilibrium for adsorption. Samples of 5 ml aliquots were taken before and after adsorption by filtering them through 0.22 micron MSI Teflon membrane filters. In order to remove any weakly adsorbed AS fraction, the preadsorbed silica was washed three times with 100 ml of pure dichloromethane. Samples were taken after each one hour washing. Then, the wet silica was collected by carefully decanting off the washing solvent, transferred into a vacuum desiccator, and then dried at room temperature for 24 hours.

(2) Adsorption of Model Compounds onto Precoated Silica

For model compound adsorption onto the precoated silica, a model compound was dissolved into cyclohexane to make solutions with various initial concentrations up to 15 g/L. The batches of sample solution were mounted on the platform of the orbit shaker and left for an hour to allow the solution temperature to reach the set temperature of 25°C. Then, 0.5 g precoated silica was added into 95 ml of model compound solution, and the solution mixture was agitated by the orbit shaker for one hour which was a sufficient period of time for attaining equilibrium. Samples of 5

ml aliquots were taken before and after adsorption.

(3) Adsorption onto Precoated Silica from Aqueous Solution

In order to adsorb acidic model functionalities (benzoic acid and phenol) onto precoated silica in an aqueous environment, the dichloromethane washed, precoated silica was washed four times with distilled water to obtain a strongly adsorbed AS agent fraction which was impervious to water. The weakly adsorbed fraction was so quickly removed that equilibrium was attained within 30 minutes. Thus, one hour was used as an equilibrium time for washing the precoated silica. The wet solids were collected by carefully decanting off the wash solution. They were then brought into contact with benzoic acid or phenol in water solutions containing different initial concentrations for adsorption. The solution mixtures were agitated by the orbit shaker for one hour which was a sufficient period of time for attaining equilibrium. Samples of 5 ml aliquots were taken before and after adsorption.

(4) Desorption of Acidic Compounds from Precoated Silica by the Introduction of Bulk Water

The wet solids obtained in section (3), which retained an AS agent fraction which was impervious to water, were dried for 48 hours in a vacuum oven whose temperature was controlled to be between 30 and 50°C under a continuous nitrogen purge. 0.5 g dried precoated silica was then transferred to 95 ml benzoic acid or phenol in cyclohexane solutions with various initial concentrations for adsorption. The solution mixtures were agitated by the orbit shaker for one hour. Samples of 5 ml aliquots were taken before and after adsorption. For each batch, the wet precoated silica preadsorbed with benzoic acid or phenol was collected by carefully decanting off the bulk cyclohexane solution and dried in a vacuum desiccator at room temperature for 24 hours. Then, the dried solids were placed into 100 ml distilled water and stirred by the orbit shaker for one hour at 25°C to evaluate the amount of stripping from the AS agent coated silica. Samples of 5 ml aliquots were taken after desorption.

Analysis

In this study, all samples taken in the adsorption experiment were analyzed by ultraviolet (UV) spectroscopy using a Model 250 Gilford UV-visible spectrometer. For all test compounds, the characteristic wavelengths used are summarized in Table 1. Quantitation was based on the Beer's law, $A = abc$, where A , a , b and C denote UV absorbance, absorptivity (L/g cm), cell pathlength (cm), and solution concentration (g/L), respectively. The calibration curves for AS agents and model compounds were developed using standard solutions of known concentrations and showed good conformity to the Beer's law as given in Appendix A. From the absorbance readings, the solution concentration as well as the amount adsorbed for each case was calculated by using the following equations:

Table 1. Wavelengths of UV Maxima Used for Test Compounds

Test Compound/Solvent	Wavelength (nm)
AS1/Dichloromethane	270
AS2/Dichloromethane	270
AS1/Water	280
AS2/Water	277
Phenol/Water	270
Benzoic Acid/Water	273
Quinoline/Cyclohexane	274
Phenylsulfoxide/Cyclohexane	252
Phenol/Cyclohexane	271.5
Benzoic Acid/Cyclohexane	274
Benzophenone/Cyclohexane	250
Benzylbenzoate/Cyclohexane	247
Pyrene/Cyclohexane	295

(1) AS Agent Loading on Silica from Organic Solution

$$C/C_o = \text{Abs}/\text{Abs}_o$$

$$AW = V(C_o - C)$$

$$DW = VC_D = V(\text{Abs}_D/a)$$

$$\sigma = A - D$$

where,

C_o = initial solution concentration (g/L)

C = equilibrated solution concentration (g/L)

Abs_o = UV absorbance of initial solution

Abs = UV absorbance of equilibrated solution

A = amount adsorbed per gram silica (g/g silica)

W = quantity of silica used (g)

V = solution volume (L)

D = amount desorbed per gram silica (g/g silica)

C_D = solution concentration resulting from washing (g/L)

Abs_D = uv absorbance of wash solution

a = absorptivity of AS agent (L/g*cm)

σ = amount of AS loading on silica attained by removing the weakly adsorbed fraction (g/g silica)

(2) Model Compounds Adsorption from Organic Solution

$$C/C_o = \text{Abs}/\text{Abs}_o$$

$$AW = V(C_o - C)$$

where,

- C_o = initial solution concentration (g/L)
- C = equilibrated solution concentration (g/L)
- Abs_o = UV absorbance of initial solution
- Abs = UV absorbance of equilibrated solution
- A = amount adsorbed per gram silica (g/g silica)
- W = quantity of silica used (g)
- V = solution volume (L)

(3) AS Agent Loading on Silica after Washing with Distilled Water

It was found to be very difficult to measure the exact amount of the AS agent loading on silica because the AS agents (especially ASI) contained a relatively large amount of water-insoluble fraction. The water-insoluble fraction not only contains very volatile components but is also subject to degradation in air. Therefore, the quantitation of the insoluble fraction was difficult and could not be made accurately. Thus, a range of the AS agents loading on silica was estimated by making spectroscopic and gravimetric analyses. The detailed procedure for the estimation of the AS agent loadings on silica is given in Appendix B.

(4) Desorption of Acidic Model Compounds from Precoated Silica by Introduction of Bulk Water

$$D_w W = V c_w = V(\text{Abs}_w/a_w)$$

where,

- D_w = amount desorbed by water (g/g silica)
- W = quantity of silica used (g)
- V = solution volume (L)
- C_w = concentration of water solution established by desorption (g/L)
- Abs_w = UV absorbance of water solution
- a_w = absorptivity of model compound in water solution (L/g*cm)

III. RESULTS AND DISCUSSION**Selection of Model Functionalities**

Petersen et al. (1982) determined the amounts of chemical functional groups found in original asphalt and asphalt fractions by using the technique of differential infrared spectrometry and selective chemical reactions as shown in Table 2. All functionalities contained at least one heteroatom (S,N,O). These polar functionalities were found in strongly adsorbed fractions at a concentration level of about 3.5 times as much as in original asphalt, indicating that those heteroatoms played an important role in asphalt-aggregate interfacial chemistry. Based on these results, the following model compounds were selected: benzoic acid representing carboxylic acid; phenol, phenolics; phenylsulfoxide, sulfoxides; quinoline, N-bases; benzophenone, ketones; benzylbenzoate, esters; and pyrene, polynuclear aromatics. The molecular structures of these model functionalities are given in Figure 1.

Table 2. Amounts and Concentrations of Chemical Components in Original Asphalts and Their Fractions

Asphalt Fraction	Percent of Original Asphalt	Total Nitrogen	Pyrrolic NH	Phenolic OH	Ketones	Carboxylic Acids	Anhydrides	2-Quinolones	Sulfoxides	Sum ²
Original Asphalt	100	543 (210:1010) ⁵	160 (50:420)	42 (20:100)	44 (0:210)	14 (0:52)	0.1 (0:1)	21 (14:29)	21 (10:36)	685.1
Strongly Adsorbed Fraction ³	1.1	849 (100:2780)	85 (10:340)	320 (10:840)	375 (230:690)	264 (120:450)	134 (70:270)	85 (50:110)	534 (230:900)	2,561
Strongly Adsorbed Fraction Not Displaced with Water ⁴	1.05	884 (100:2900)	83 (0:340)	318 (0:840)	381 (230:700)	264 (120:430)	133 (60:260)	84 (50:140)	521 (220:900)	2,585

1. Source: TRB 843, 1982, pp. 95-104. (All values are an average of 8 data values reported for 8 different asphalts and aggregates.)

2. Summation of functional groups minus pyrrolic NH that contributed to total nitrogen.

3. Fraction retained on aggregate after benzene extraction.

4. Fraction retained on aggregate after benzene extraction and water stripping tests.

5. (Max:Min) range of data values.

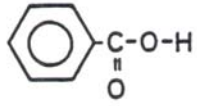
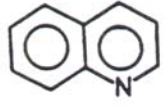
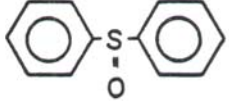
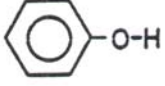
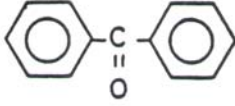
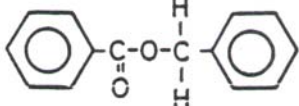

<u>Model Compounds</u>	<u>Molecular Structure</u>
Benzoic Acid	
Quinoline	
Phenylsulfoxide	
Phenol	
Benzophenone	
Benzylbenzoate	
Pyrene	

Figure 1. Model Compounds Selected

Adsorption Isotherms of AS Agents

The AS agents were precoated onto silica from a dichloromethane solution. Figure 2 presents the adsorption isotherms for the AS agents/Dry silica systems using dichloromethane as solvent at 25°C. AS1 exhibited a Langmuir type monolayer adsorption which was characterized by the formation of a plateau at high concentrations, whereas AS2 did not show an asymptote but a continuously increasing adsorption with the increase of concentration. Two crossover points were created by the two adsorption isotherms; one occurred at about 1 g/L and the other at about 8 g/L. That is, AS2 showed larger adsorption than did AS1 at concentrations below 1g/L while the reverse was observed between 1 and 8 g/L. At high concentrations above 8 g/L, however, AS2 was again more adsorbed onto dry silica than AS1.

The Langmuir equation was applied to the adsorption data of both AS agents as seen in Figure 3. The Langmuir model used has the form of $C/A = C/A_m + 1/bA_m$ where C , A , A_m , and b denote equilibrium concentration, amount adsorbed per gram silica, saturated monolayer amount, and a constant, respectively (Brooks, 1958). As expected, the Langmuir equation modeled the adsorption data of AS1 ($r = 0.993$) better than that of AS2 ($r = 0.974$). Monolayer amounts of AS1 and AS2 were obtained as 0.138 and 0.139 g/g silica from the Langmuir plot, respectively.

Adsorption of Model Compounds on Precoated Silica in Organic Phase

Seven model functionalities were adsorbed onto AS1 and AS2 precoated silica using cyclohexane as an adsorption medium at 25°C. The seven model compounds used were phenol, benzoic acid, phenylsulfoxide, quinoline, benzophenone, benzylbenzoate, and pyrene. The adsorption of benzoic acid and phenol was enhanced with the precoating of the AS agents on silica, whereas the other functionalities underwent a large reduction in their adsorption due to the precoated AS agents.

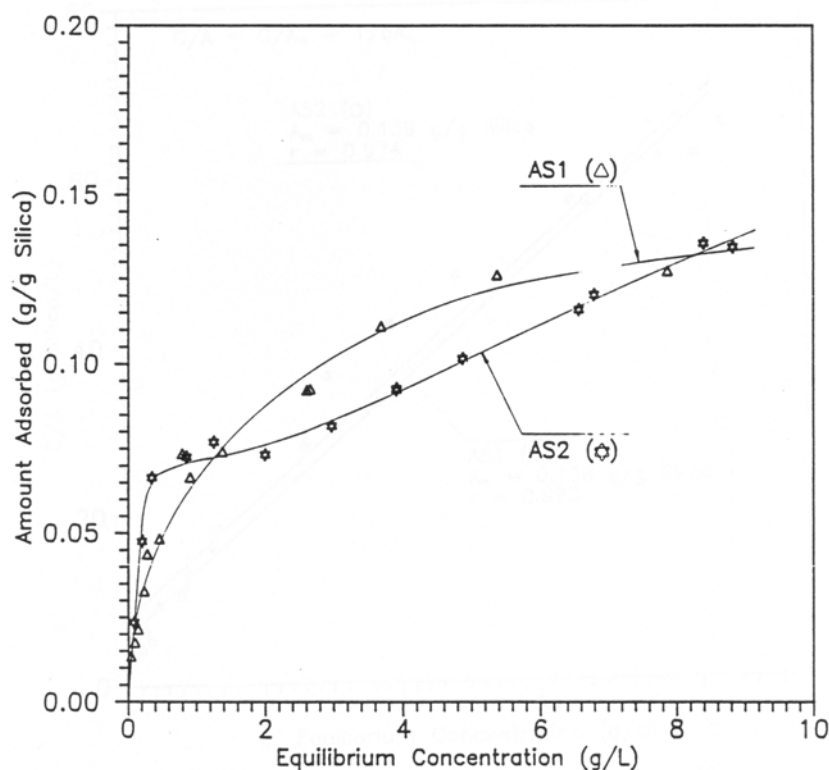


Figure 2. Adsorption Isotherms for Two Commercial Anti-Stripping Agents/Dichloromethane/Silica Systems at 25°C

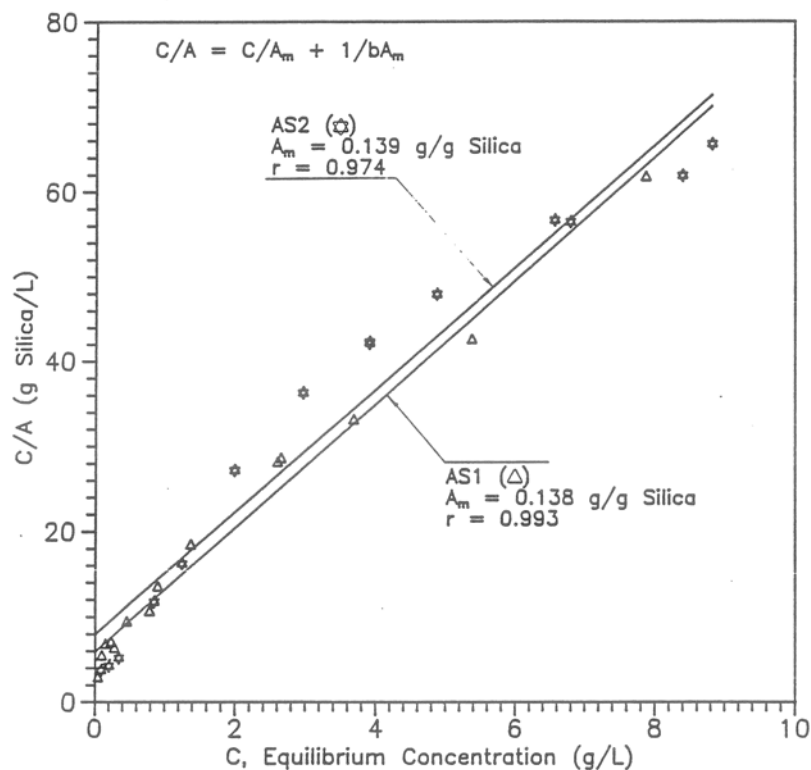


Figure 3. Langmuir Plot of Two Commercial Anti-Stripping Agents at 25°C

(1) Enhanced Adsorption of Acidic Compounds

Enhanced Adsorption by Precoated AS1. Benzoic acid was adsorbed onto precoated silica with 6.3 wt% AS1 loading as illustrated in Figure 4. The circles represent uncoated silica adsorption while triangles indicate precoated silica adsorption. As shown, benzoic acid was more adsorbed to precoated silica than to uncoated silica. Both isotherms showed similar behaviors: adsorption quickly increased at low concentrations and reached a level plateau at high concentrations, featuring the Langmuir type monolayer adsorption. The Langmuir equation was applied to both sets of isotherm data, yielding good conformity to the model with a correlation coefficient of 0.999 as shown in Figure 5. The monolayer amount was increased from 0.110 g/g for uncoated silica to 0.140 g/g for 6.3 wt% AS1 coated silica.

Phenol was adsorbed onto precoated silica with various AS1 loadings as given in Figure 6. The phenol adsorption demonstrated different behavior compared to the benzoic acid adsorption. A crossover occurred between the adsorption isotherms for uncoated and precoated silica, indicating that at low concentrations the adsorption of phenol was inhibited while at high concentrations it was enhanced by the precoated silica. The crossover point shifted to a lower concentration value with the increased loading of AS1 on the silica. In Figure 7 the Langmuir model was applied to the isotherm data for uncoated and for precoated silica with 7.0 wt% AS1 loading. As predicted, the adsorption of phenol onto precoated silica did not show good conformity to the model ($r = 0.983$) compared to uncoated silica adsorption ($r = 0.999$). However, the enhanced adsorption of phenol at high concentrations can be interpreted by the increase in monolayer amount from 0.131 g/g for uncoated silica to 0.186 g/g for 7.0 wt% AS1 coated silica.

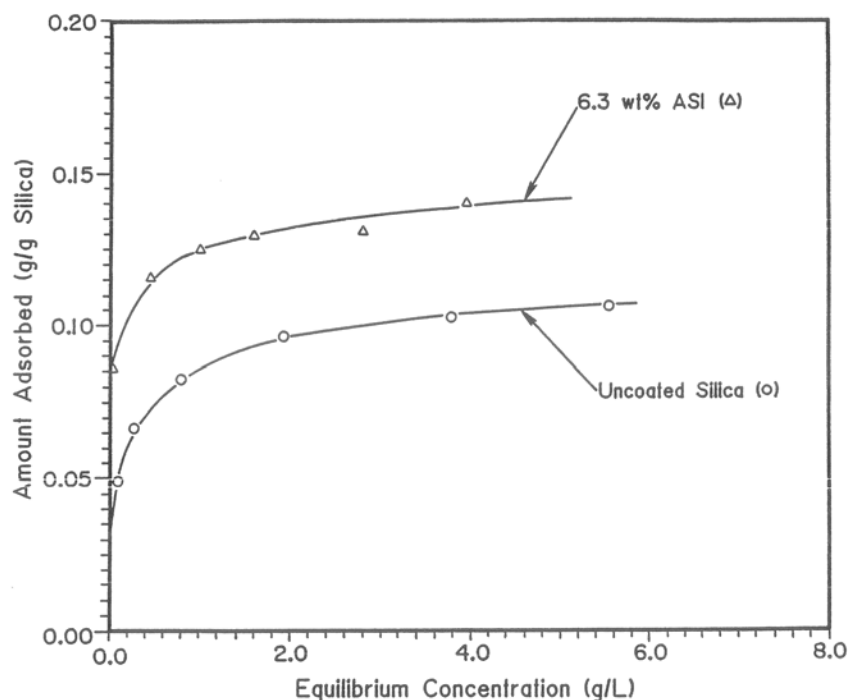


Figure 4. Adsorption Isotherms for the Systems of Benzoic Acid/Cyclohexane/Silica with Different ASI Coating Levels at 25°C

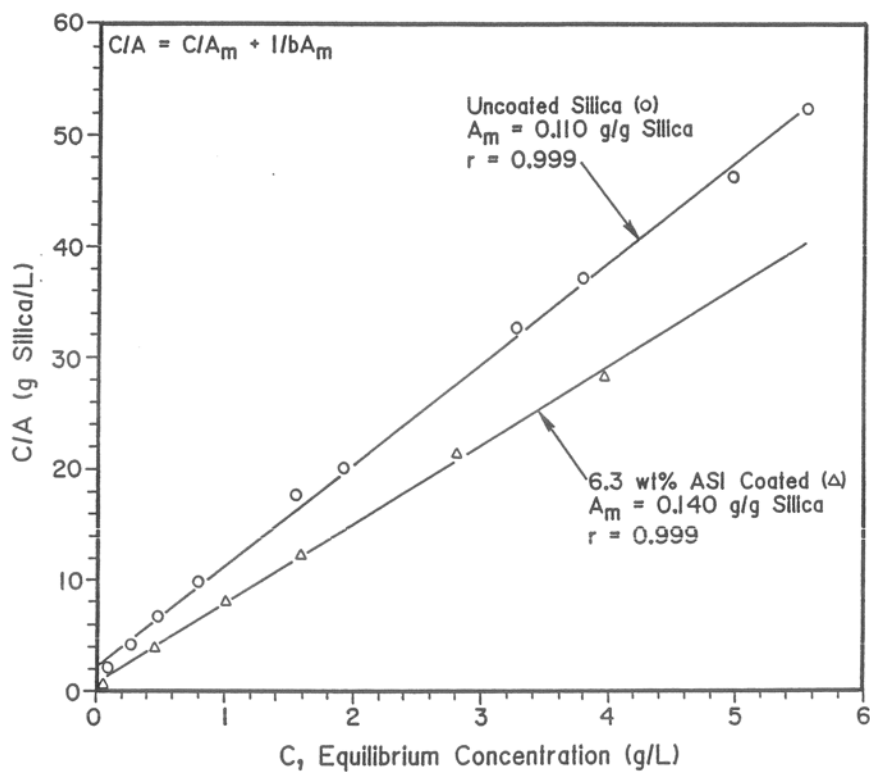


Figure 5. Langmuir Plot from Adsorption Isotherms for the Systems of Benzoic Acid/Cyclohexane/Silica with Different ASI Coating Levels at 25°C

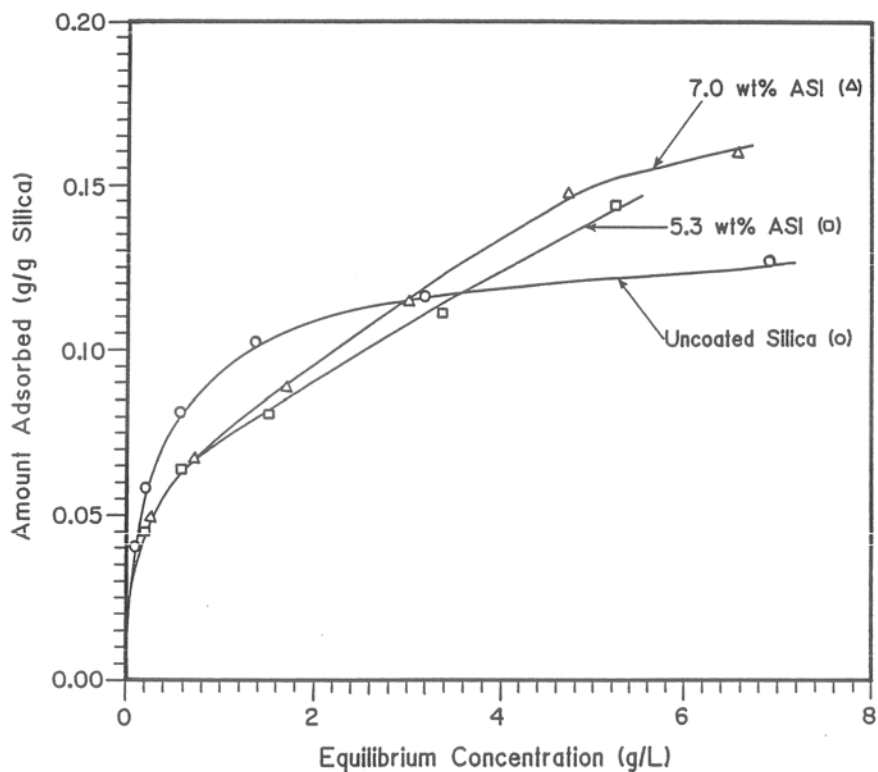


Figure 6. Adsorption Isotherms for the Systems of Phenol/Cyclohexane/Silica with Different ASI Coating Levels at 25°C

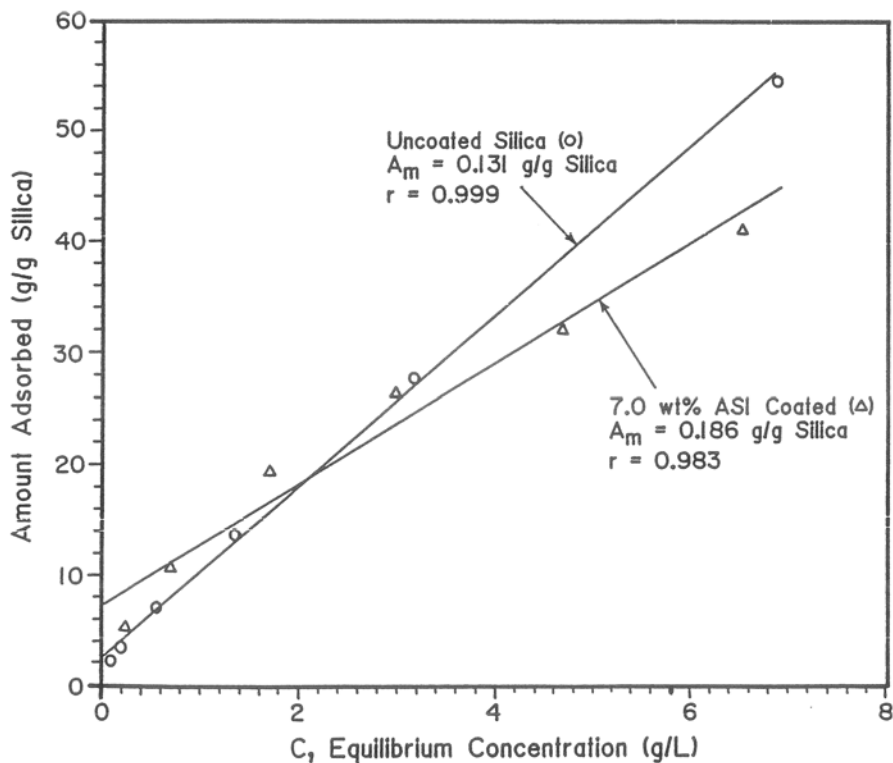


Figure 7. Langmuir Plot from Adsorption Isotherms for the Systems of Phenol/Cyclohexane/Silica with Different ASI Coating Levels at 25°C

Enhanced Adsorption by Precoated AS2. Figure 8 illustrates the adsorption of benzoic acid onto silica precoated with various loadings of AS2. The precoated silica with a loading of 6.5 wt% AS2 promoted to a nearly equal extent the adsorption of benzoic acid over the entire range of concentration tested. However, the 10 wt% AS2 coated silica exhibited an increasing promotion with increasing concentration: that is, a small enhancement in adsorption of benzoic acid at low concentrations and a larger enhancement in adsorption at higher concentrations. The amount of benzoic acid adsorbed onto 10.0 wt% AS2 coated silica was lower than that onto the 6.5 wt% AS2 coated silica at concentrations below 2.2 g/L, whereas the opposite was observed for the concentrations above 2.2 g/L. The three sets of adsorption isotherm data were fitted to the Langmuir model showing a good conformity to the model with a correlation coefficient of 0.998 or better (Figure 9). When compared to uncoated silica adsorption, the monolayer amount of benzoic acid was increased with the increasing of AS2 loading: 0.110 g/g for uncoated, 0.165 g/g for 6.5 wt% AS2 coated, and 0.190 g/g for 10 wt% AS2 coated silica.

Figure 10 presents adsorption isotherms of the phenol/AS2 coated silica systems. The adsorption of phenol onto precoated silica exhibited different behavior compared to uncoated silica adsorption; the latter showed a Langmuir type monolayer adsorptive behavior, whereas the former exhibited a continuous increase in adsorption with the increase of concentration. There occurred crossovers between the adsorption isotherms, indicating that at low concentrations phenol was less adsorbed onto precoated silica than onto uncoated silica, but at high concentrations the opposite was observed. Figure 11 illustrates the Langmuir plots of the three sets of isotherm data. As shown, the data points of phenol for precoated silica deviated from a linear curve although correlation coefficients are relatively high; however, those for uncoated silica form a straight line with a correlation coefficient of 0.999. The monolayer amount of phenol increases with the increase of AS2 loading on the silica: 0.131 g/g for uncoated, 0.153 g/g for 7.0 wt% AS2 coated, and 0.173 g/g for 9.8 wt% AS2 coated silica.

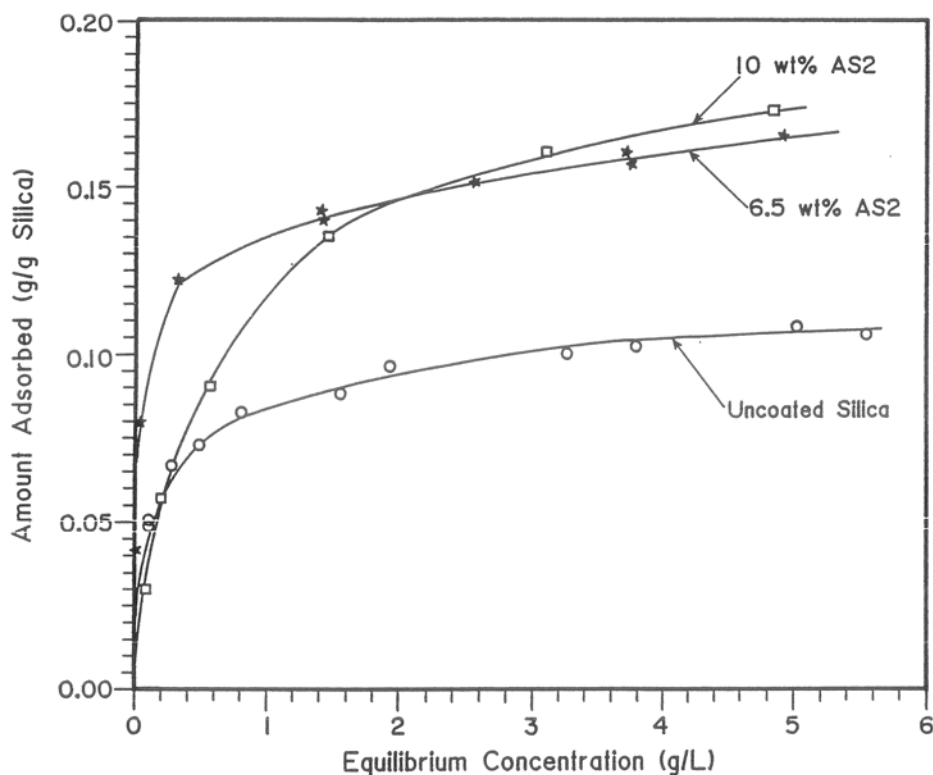


Figure 8. Adsorption Isotherms for the Systems of Benzoic Acid/Cyclohexane/Silica with Different AS2 Coating Levels at 25°C

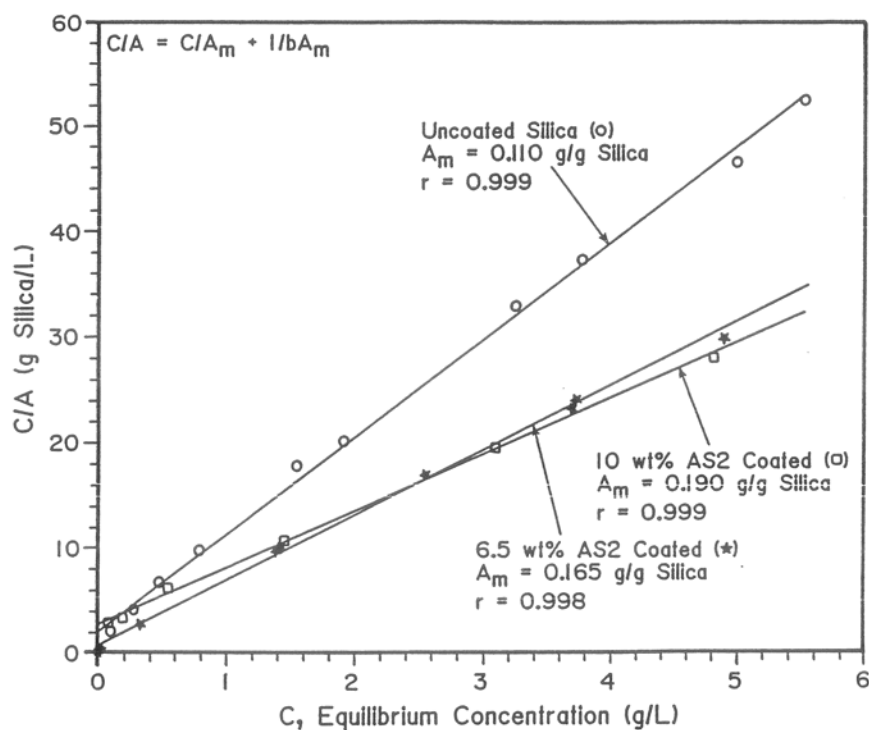


Figure 9. Langmuir Plot from Adsorption Isotherms for the Systems of Benzoic Acid/Cyclohexane/Silica with Different AS2 Coating Levels at 25°C

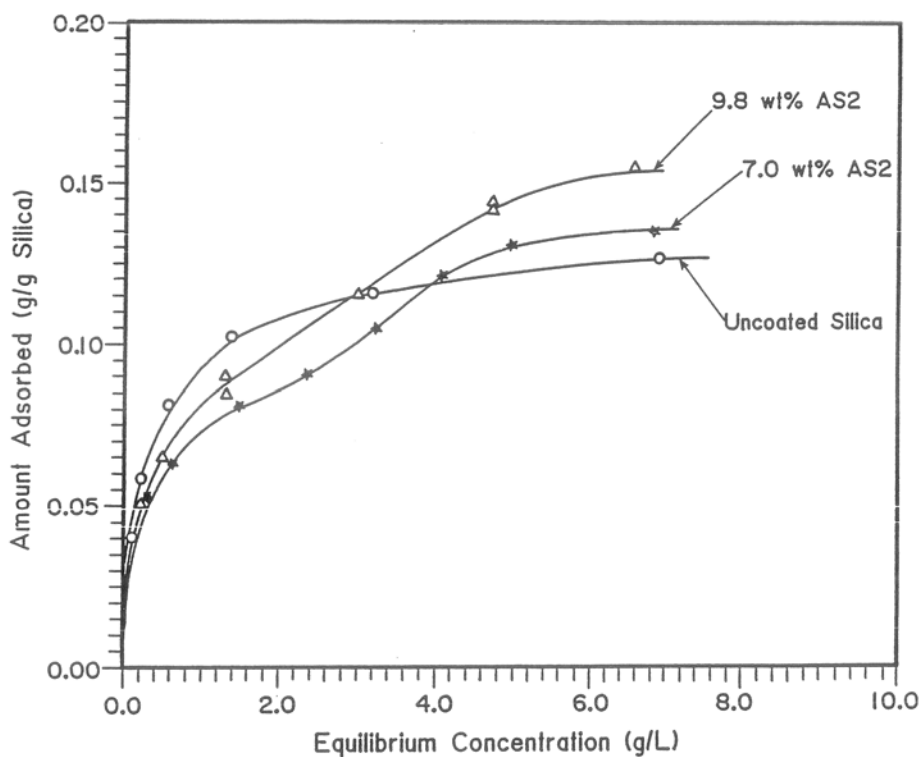


Figure 10. Adsorption Isotherms for the Systems of Phenol/Cyclohexane/Silica with Different AS2 Coating Levels at 25°C

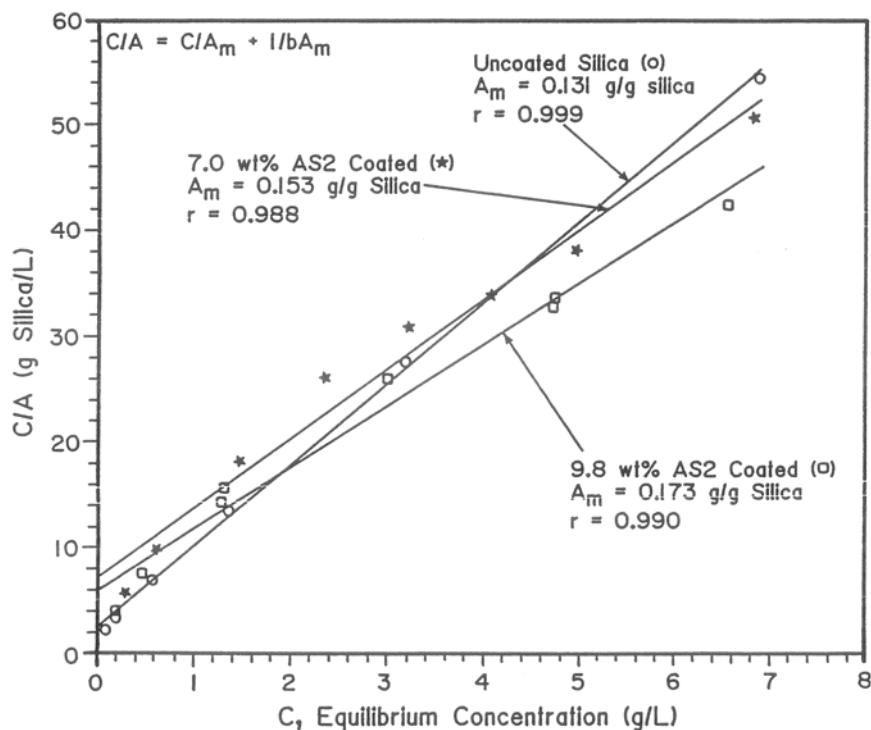


Figure 11. Langmuir Plot from Adsorption Isotherms for the Systems of Phenol/Cyclohexane/Silica with Different AS2 Coating Levels at 25°C

(2) Inhibited Adsorption of Nonacidic Compounds

Figures 12 through 16 present the adsorptive behaviors of phenylsulfoxide, quinoline, benzophenone, benzylbenzoate, and pyrene. All of the five model functionalities showed a large decrease in adsorption due to the precoated silica. As mentioned earlier, AS agents are composed of polyamines as a primary constituent. Amine groups have free electron pairs and thus can act as a Lewis base, i.e. a proton acceptor or an electron pair provider (Drago and Matwiyoff 1968). However, none of these five model compounds has a free proton to release so that they remain unreactive with the basic AS agents. As a result, the adsorption of these nonacidic functionalities onto the silica surface was inhibited by the preadsorbed AS agent molecules. As compared to uncoated silica adsorption, the amount of decrease in adsorption due to the 6-7 wt% AS1 precoated silica was 92 percent for quinoline, 82 percent for phenylsulfoxide, 89 percent for benzophenone and 90 percent for pyrene when determined at an equilibrium concentration of 5 g/L. Also the amount of decrease in adsorption due to the 6-7 wt% AS2 precoated silica was 86 percent for quinoline, 78 percent for phenylsulfoxide and 93 percent for benzylbenzoate as shown in Table 3.

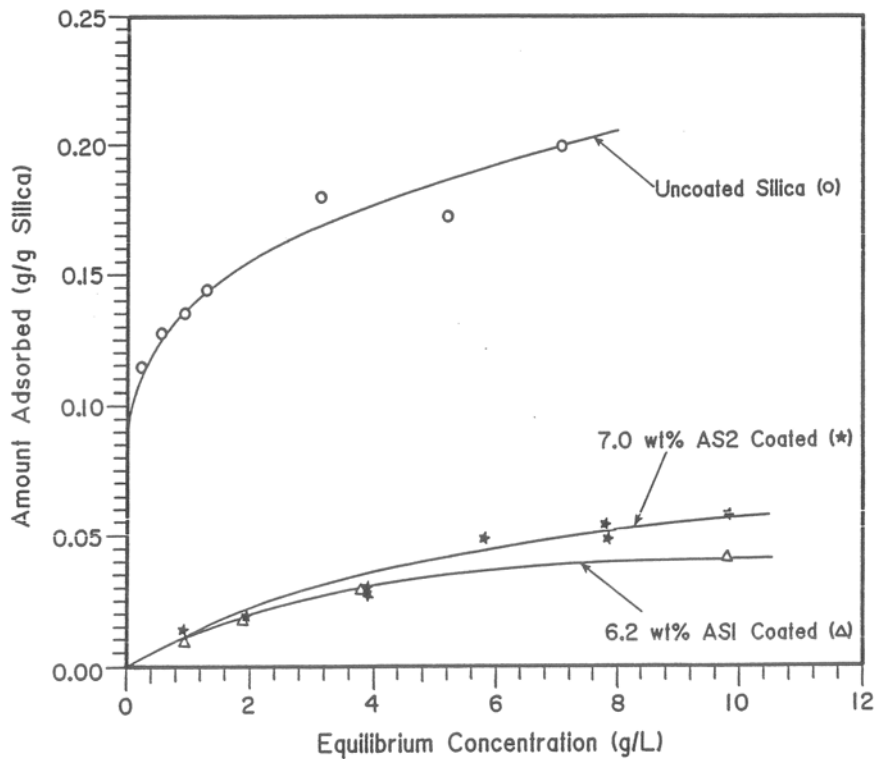


Figure 12. Adsorption Isotherms for the Systems of Phenylsulfoxide/Cyclohexane/Silica with Different AS Coating Levels at 25°C

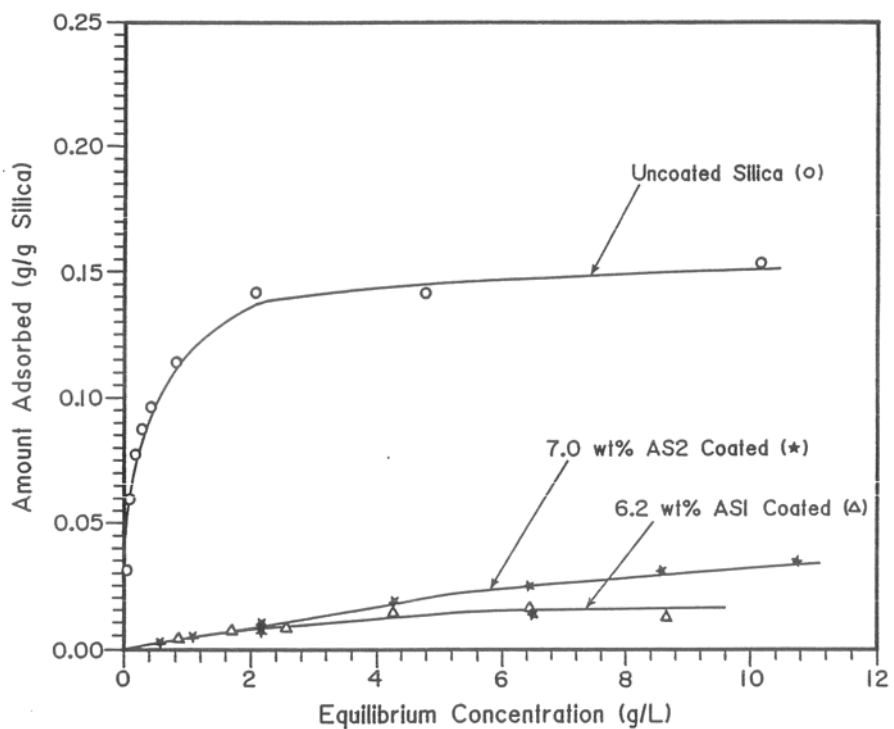


Figure 13. Adsorption Isotherms for the Systems of Quinoline/Cyclohexane/Silica with Different AS Coating Levels at 25°C

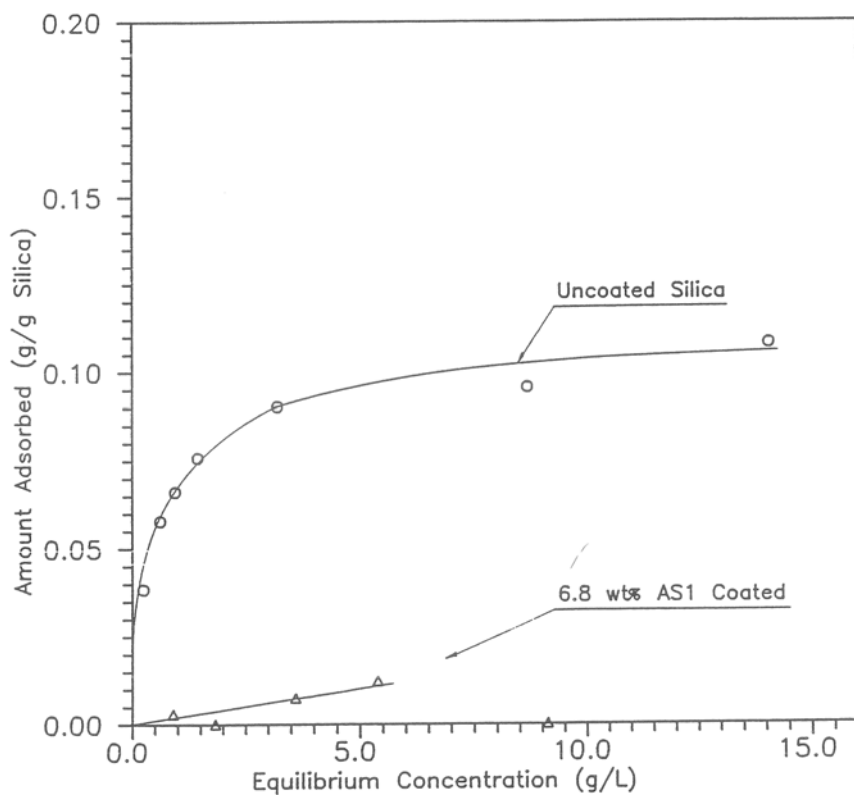


Figure 14. Adsorption Isotherms for the Systems of Benzophenone/Cyclohexane/Silica with Different AS1 Coating Levels at 25°C

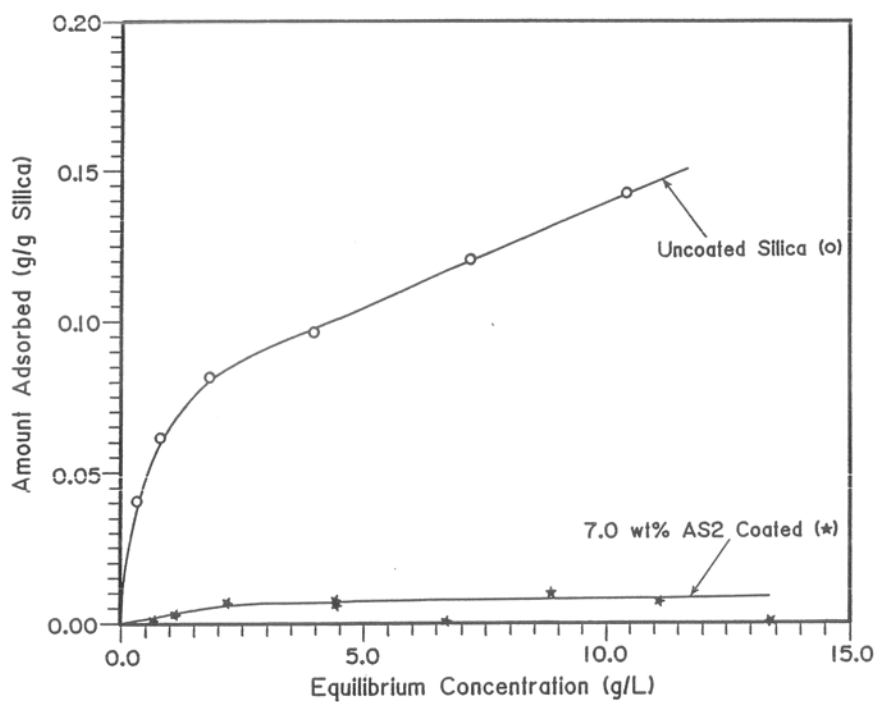


Figure 15. Adsorption Isotherms for the Systems of Benzylbenzoate/Cyclohexane/Silica with Different AS2 Coating Levels at 25°C

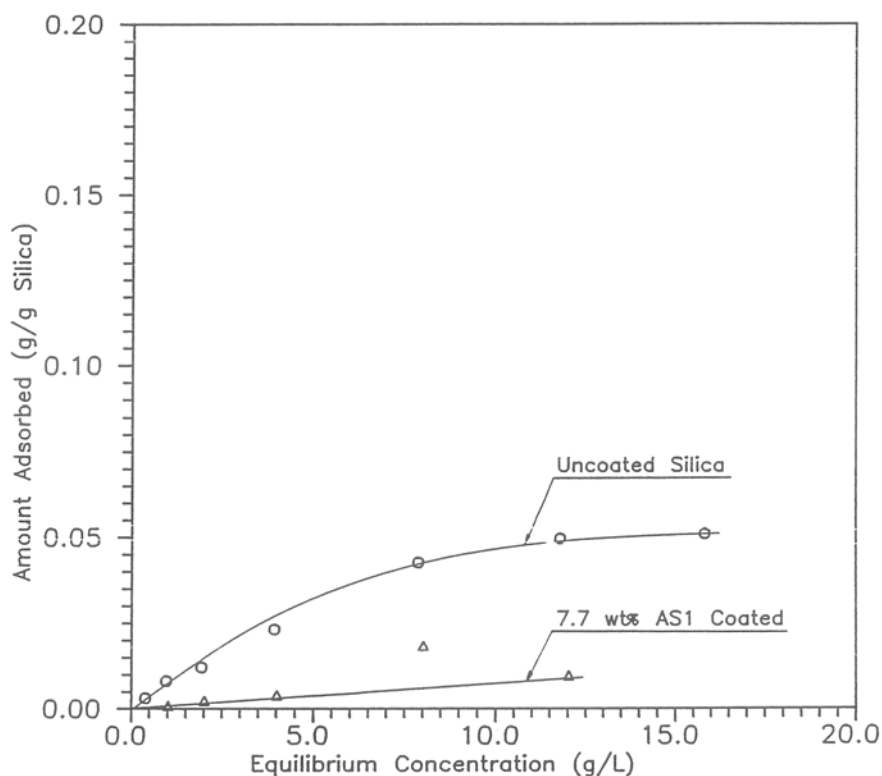


Figure 16. Adsorption Isotherms for the Systems of Pyrene/Cyclohexane/Silica with Different AS1 Coating Levels at 25°C

(3) Interaction between AS agents and Model Compounds

Table 3 summarizes the effect of precoated silica on the adsorption of model functionalities based on amount adsorbed determined at an equilibrium concentration of 5 g/L and 25°C. Only acidic compounds, benzoic acid and phenol, showed enhanced adsorption for the precoated silica. The other model functionalities underwent more than 80 percent reduction in their adsorption onto the precoated silica when compared to uncoated silica adsorption. The largest increase in benzoic acid adsorption of 57 percent was attained with 6-7 wt% AS2 coated silica while the largest increase in phenol adsorption of 25 percent was shown by 6-7 wt% AS1 coated silica. The adsorption data of benzoic acid fitted the Langmuir model better than those of phenol as illustrated in Table 4. For both benzoic acid and phenol, the monolayer amounts derived from the Langmuir plots generally increased with the increase of an AS agent loading on the silica.

Figure 17 presents a proposed mechanism for an acid-base interaction between acidic compounds and AS agents. An acidic functionality donates a proton to a basic amine group of an AS agent. Thus, the acidic molecule is negatively charged while the amine group has a positive charge by forming a quaternary ammonium ion. As a result, there exists a charge attraction between the acidic molecule and the ammonium ion. This acid-base interaction may explain the enhancement in the adsorption of acidic compounds, benzoic acid and phenol, onto the precoated silica with AS agents. Benzoic acid and phenol are also adsorbed onto the silanols of the silica surface unoccupied by the precoated AS agents through the formation of hydrogen bonding in an organic medium.

Table 3. Effect of Precoated AS Agents on Silica on the Adsorption of Asphalt Model Functionalities

Asphalt Functionality	Amount Adsorbed (G/G Silica) ¹		
	Uncoated Silica	6 - 7 Wt% AS1 Coated Silica	6 - 7 Wt% AS2 Coated Silica
Benzoic Acid (Carboxylic Acid)	0.105	0.140 (33%) ²	0.165 (57%)
Phenol (Phenolic)	0.120	0.150 (25%)	0.130 (8%)
Quinoline (N-base)	0.145	0.012 (-92%)	0.020 (-86%)
Phenylsulfoxide (Sulfoxide)	0.185	0.034 (-82%)	0.040 (-78%)
Benzophenone (Ketone)	0.095	0.010 (-89%)	---
Benzylbenzoate (Ester)	0.103	---	0.007 (-93%)
Pyrene (Polynuclear Aromatic)	0.030	0.003 (-90%)	---

1. Determined at an equilibrium concentration of 5 G/L and 25°C

2. % Change in adsorption = [(B-A)/A] x 100

Where A = Uncoated silica adsorption
B = AS agent coated silica adsorption

Table 4. Monolayer Amounts Derived from the Langmuir Plots of Adsorption Isotherms of Acidic Functionalities

Asphalt Functionality	Parameters	Uncoated Silica	6-7 Wt% AS1 Coated Silica	6-7 Wt% AS2 Coated Silica	10 Wt% AS2 Coated Silica
	Langmuir R Value	0.999	0.999	0.998	0.999
Benzoic Acid (Carboxylic Acid)	Monolayer (A _M) (G/G Silica) ^M	0.110	0.140	0.165	0.190
	% Change of A _M ¹	---	27	50	73
	Langmuir R Value	0.999	0.983	0.988	0.990
Phenol (Phenolic)	Monolayer (A _M) (G/G Silica)	0.131	0.186	0.153	0.173
	% Change of A _M	---	42	17	32

1. % Change in monolayer amount = [(B-A)/A] x 100

Where A = Monolayer amount of uncoated silica
B = Monolayer amount of coated silica

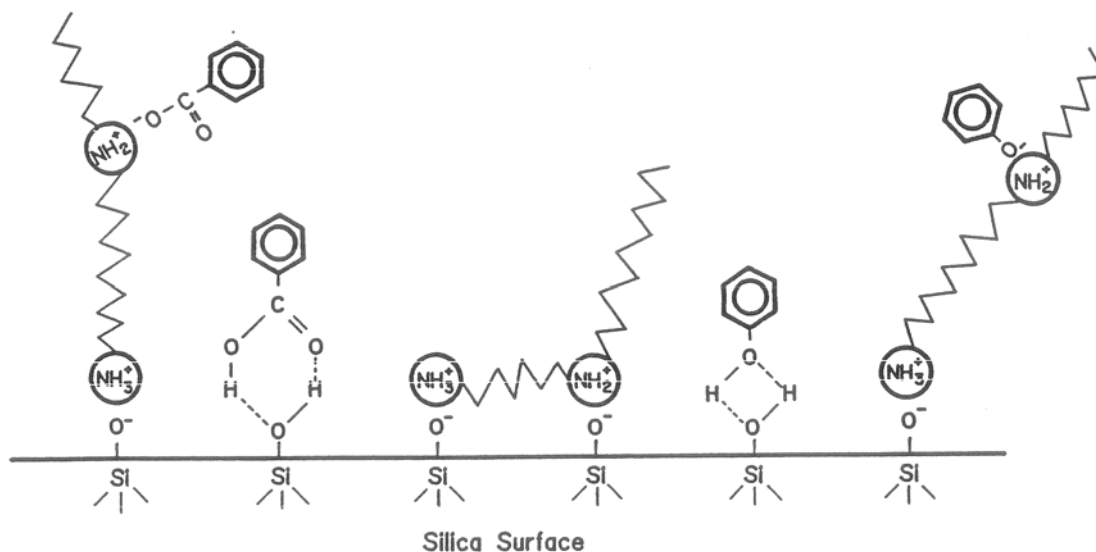


Figure 17. Acid and Base/Hydrogen Bonding Interactions among Model Compounds, AS Agents and Silanol Groups in Organic Medium

Adsorption and Desorption of Acidic Model Compounds in an Aqueous Environment

(1) Adsorption onto Uncoated Silica from Cyclohexane and Water Solutions

Figures 18 and 19 show the effect of the different solvents used as adsorption media on the adsorption of benzoic acid and phenol onto uncoated silica. Both benzoic acid and phenol were much more adsorbed onto the silica from cyclohexane solution than from water solution. In organic solution, benzoic acid and phenol exhibited high affinity for the silica, yielding adsorption isotherms of the Langmuir type, whereas their affinities were shown to be insignificant in aqueous solution. These results may be explained in the following manner. Like benzoic acid and phenol, water is a polar, oxygen containing compound, and can interact with silica surface through the formation of hydrogen bonding. Thus, competition existed between the model compounds and water for the silica. Since the model compound solutions tested were dilute, the concentration of water molecules was incomparably high relative to those of the model compounds, allowing water to show a high driving force for adsorption onto the silica surface. As a result, water molecules predominantly occupied the adsorption sites of the silica, leaving benzoic acid and phenol molecules inactive with the silica surface. In addition, benzoic acid, phenol and the silica surface can act as Bronsted acids and donate protons to water molecules which are then converted to hydronium ions in aqueous solution. The pKa values of benzoic acid and phenol in water solution at 20-25°C are 4.21 and 10.00, respectively (Perrin 1981). Thus, a small portion (a few percent) of benzoic acid and phenol initially added to water can be dissociated. Although the degree of dissociation is not significant, the dissociated model compounds as well as the silica surface involved became negatively charged and a repulsion developed between the adsorbates and adsorbent. Consequently, benzoic acid and phenol molecules were repelled from the silica surface in an aqueous environment. Thus, both factors, the high affinity of water for the silica surface and the repulsion developed due to dissociation of the model systems, led to the decrease in the adsorption of the model systems. The larger effect was due to the high affinity of water for silica.

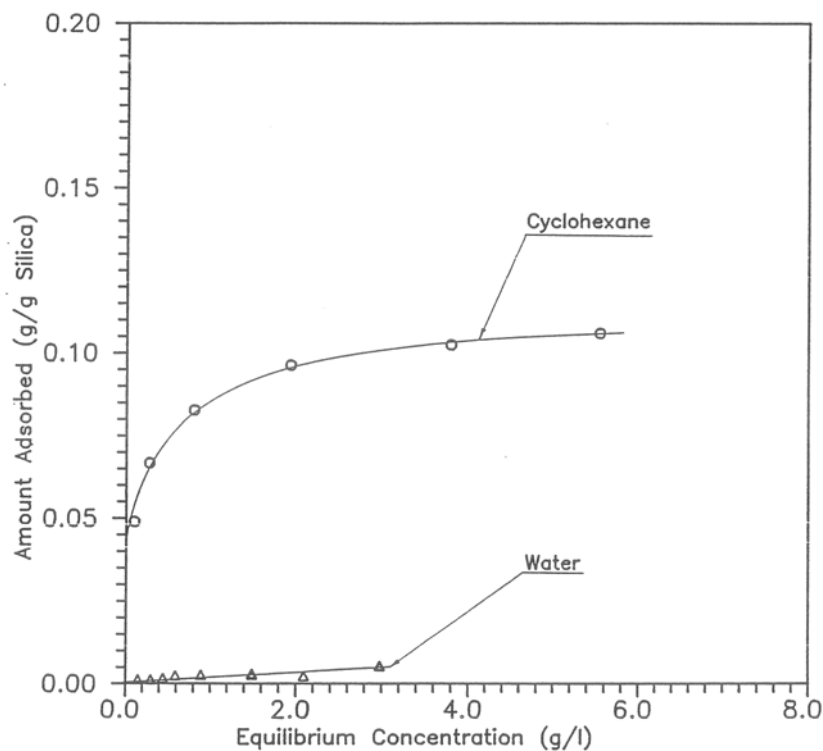


Figure 18. Effect of Solvent on the Adsorption of Benzoic Acid onto Uncoated Silica at 25°C

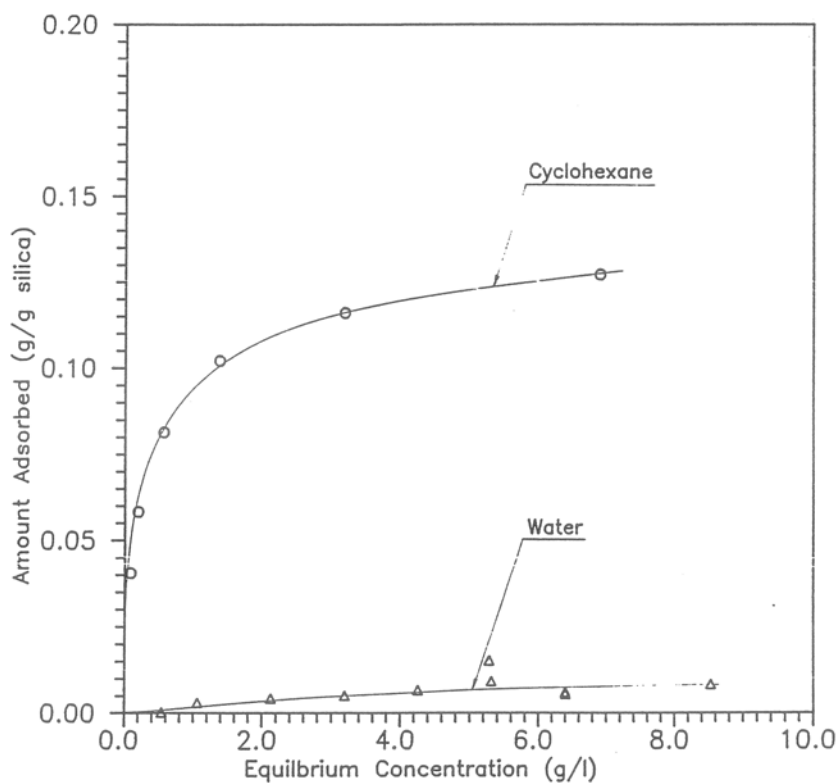


Figure 19. Effect of Solvent on the Adsorption of Phenol onto Uncoated Silica at 25°C

(2) Adsorption onto Precoated Silica from Cyclohexane and Water Solutions

Figures 20 and 21 present the effect of solvent on the adsorption of benzoic acid onto silica precoated with 0-2 wt% AS1 and AS2. The 0-2 wt% AS agents are the strongly bonded fraction which is retained on the silica after four serial washings by 100 ml distilled water and should be durable in the presence of water. As shown, adsorption of benzoic acid in cyclohexane solution was much larger than that of benzoic acid in water solution. Since monolayer amounts for AS1 and AS2 are 13.8 and 21.4 wt%, respectively, the surface coverage attained by 0-2 wt% AS agents would be low. The character of this silica surface with low coverage may be elucidated by the similarity of the three adsorption isotherms of benzoic acid in cyclohexane solution for uncoated and precoated silica as shown in Figures 18, 20 and 21. Therefore, the same explanation of water effect as given to uncoated silica adsorption can be applied to this solvent effect on the adsorption by silica with a small amount of precoating.

However, the silica precoated with AS1 and AS2 adsorbed more benzoic acid than did uncoated silica in an aqueous environment (compare Figures 18, 20 and 21). At a concentration of 3 g/L which is the maximum solubility of benzoic acid in water solution at 25°C, the amounts of benzoic acid adsorbed onto uncoated, AS1 and AS2 coated silica were 0.005, 0.026 and 0.017 g/g silica, respectively. Thus, adsorption by the precoated silica was 3.4 to 5.2 times higher than that by the uncoated silica. This behavior may be ascribed to two factors. One is that there may exist an acid-base interaction between benzoic acid and the AS agents by proton transfer. The other one is that the precoated AS agents make the hydrophilic (water-liking) silica surface become partially hydrophobic (water-disliking), allowing organic molecules to be more attractive with the silica surface in an aqueous environment (Boyd et al. 1988). Benzoic acid adsorption from both aqueous and organic solutions exhibited a flat isotherm; however, adsorption from aqueous solution reached a plateau value faster than that from organic solution.

Figures 22 and 23 illustrate the effect of solvents used as adsorption media on the adsorption of phenol onto silica precoated with 0-2 wt% AS1 and AS2. The 0-2 wt% AS precoatings are the strongly bonded fraction obtained from four serial washings by distilled water and should be impervious to water. By the same token as shown in benzoic acid case, adsorption from cyclohexane solution was larger than that from water solution. In an aqueous environment, the precoated silica adsorbed more phenol than did uncoated silica. At a concentration of 8 g/L, the amounts of phenol adsorbed onto uncoated, AS1 and AS 2 coated silica were 0.008, 0.035 and 0.038 g/g silica, respectively. Thus, adsorption by the precoated silica was 4.4 to 4.8 times larger than that by the uncoated silica. Unlike benzoic acid, however, phenol adsorption from aqueous solution did not show a plateau: it continuously increased with the increase of phenol concentration.

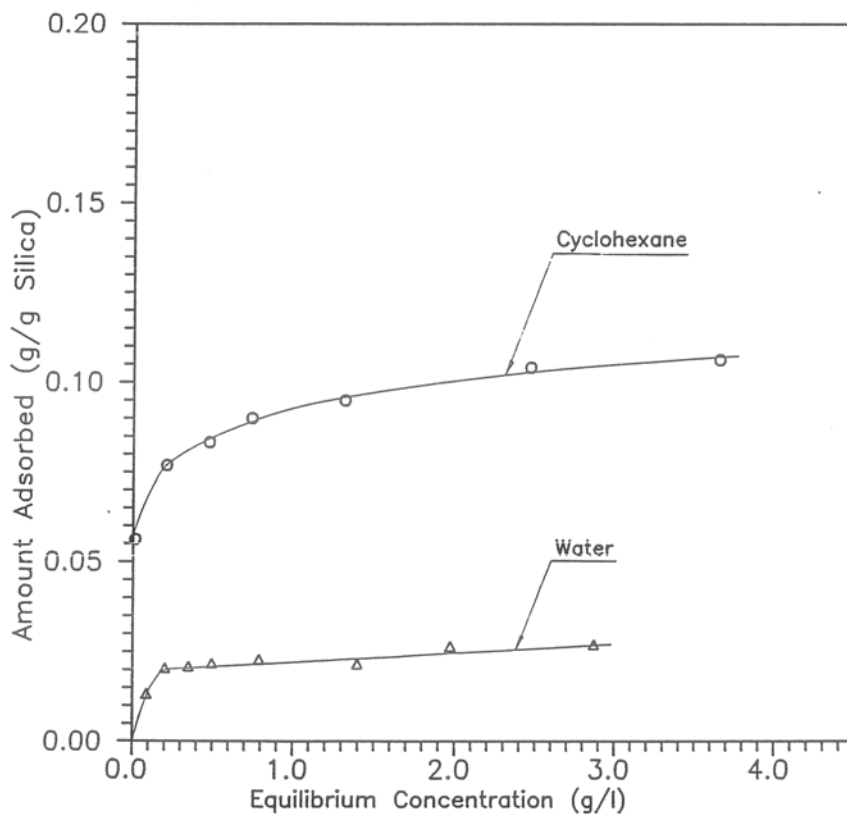


Figure 20. Effect of Solvent on the Adsorption of Benzoic Acid onto 0-2 wt% AS1 Precoated Silica at 25°C

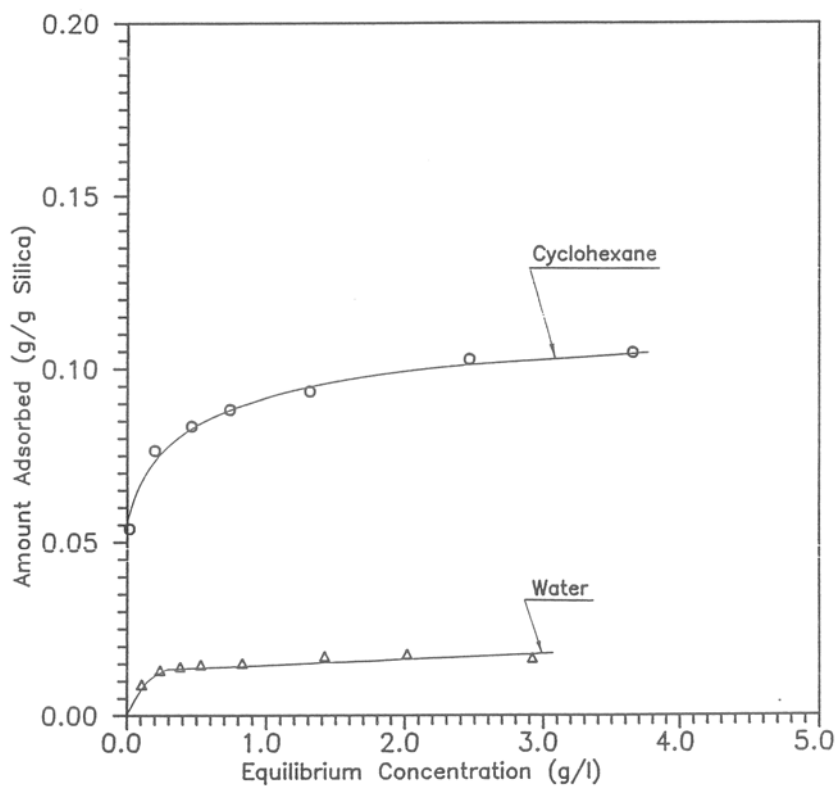


Figure 21. Effect of Solvent on the Adsorption of Benzoic Acid onto 0-2 wt% AS2 Precoated Silica at 25°C

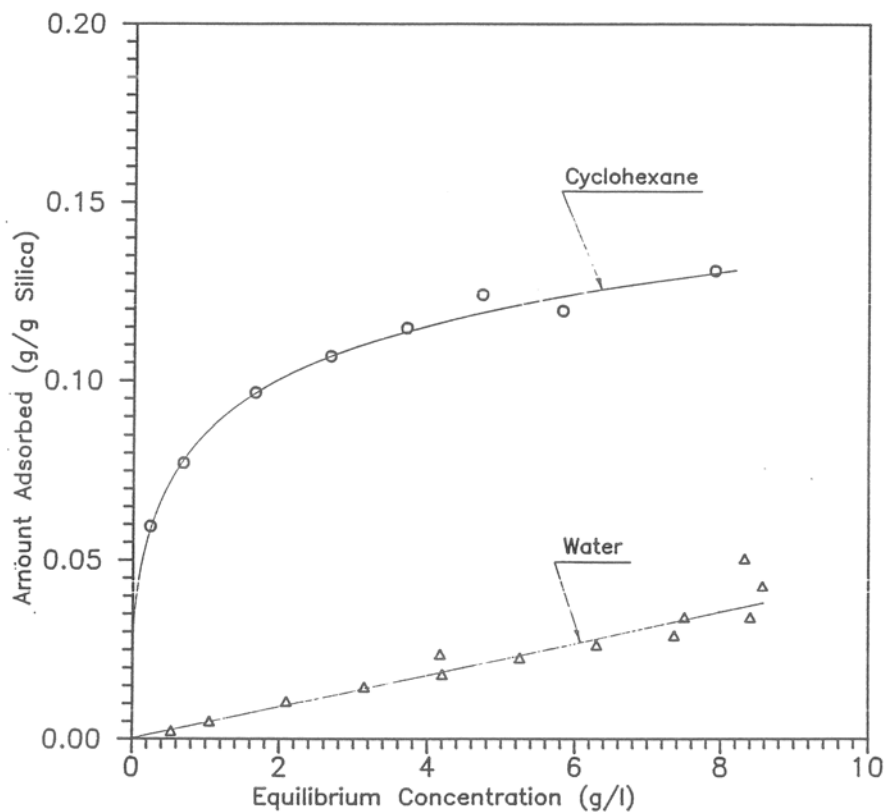


Figure 22. Effect of Solvent on the Adsorption of Phenol onto 0-2 wt% AS1 Precoated Silica at 25°C

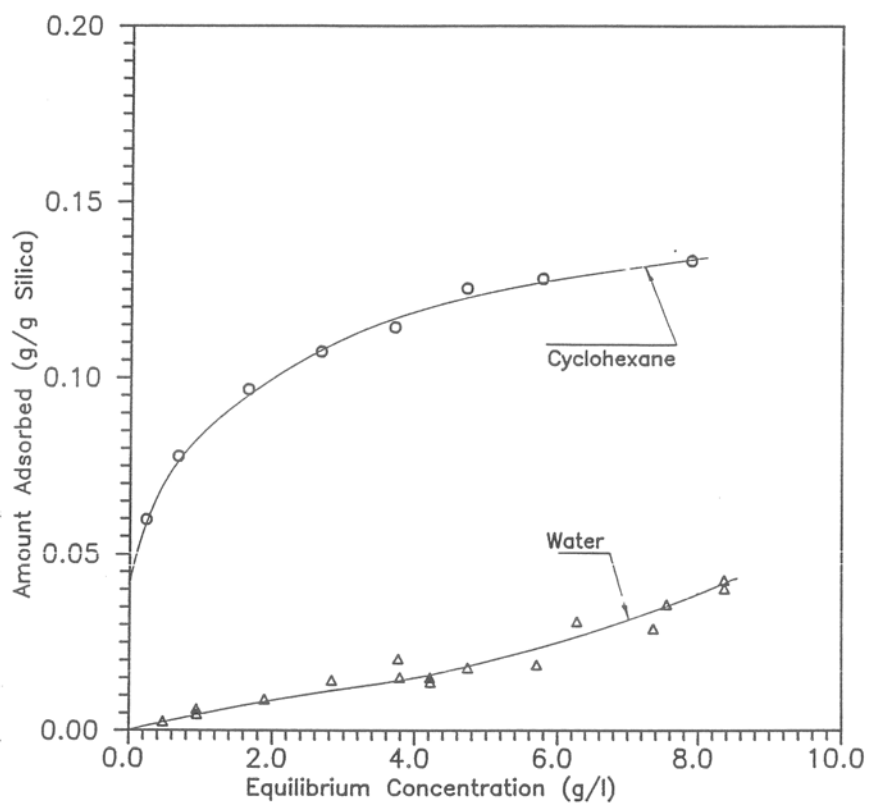


Figure 23. Effect of Solvent on the Adsorption of Phenol onto 0-2 wt% AS2 Precoated Silica at 25°C

(3) Desorption of Acidic Compounds from Precoated Silica by Introduction of Bulk Water

The desorption behavior of benzoic acid is described in Figures 24 and 25. The circles represent the adsorption of benzoic acid onto 0-2 wt% AS1 and AS2 precoated silica while the triangles denote the amount of benzoic acid retained on the silica after desorption by water. Thus, the triangles do not follow the scale of the concentration axis and simply indicate amount retained on silica after desorption for each batch tested. A large amount of stripping was observed for each batch of 0-2 wt% AS agent precoated silica which had been preadsorbed with benzoic acid due to the introduction of bulk water. The percentage stripping, defined as (amount desorbed/amount initially adsorbed) \times 100, ranged from 60 to 90 percents for both AS1 and AS2 precoated silica. The amount of benzoic acid retained on the silica after desorption by water was shown to decrease with amount of benzoic acid initially adsorbed.

Figures 26 and 27 present the desorption behavior of phenol from 0-2 wt% AS1 and AS2 precoated silica in an aqueous environment. For both AS1 and AS2, a large amount of stripping was observed for each batch of the precoated silica preadsorbed with phenol. Phenol preadsorbed on AS1 and AS2 coated silica was so susceptible to bulk water that more than 80 percent of the preadsorbed phenol was removed from the silica surface. In order to overcome such water susceptibility as shown by benzoic acid and phenol, the use of a long-chain polymeric functionalities and/or the formation of a chemical bond at organic-AS agent-solid interface are thought to be required (Theng 1979).

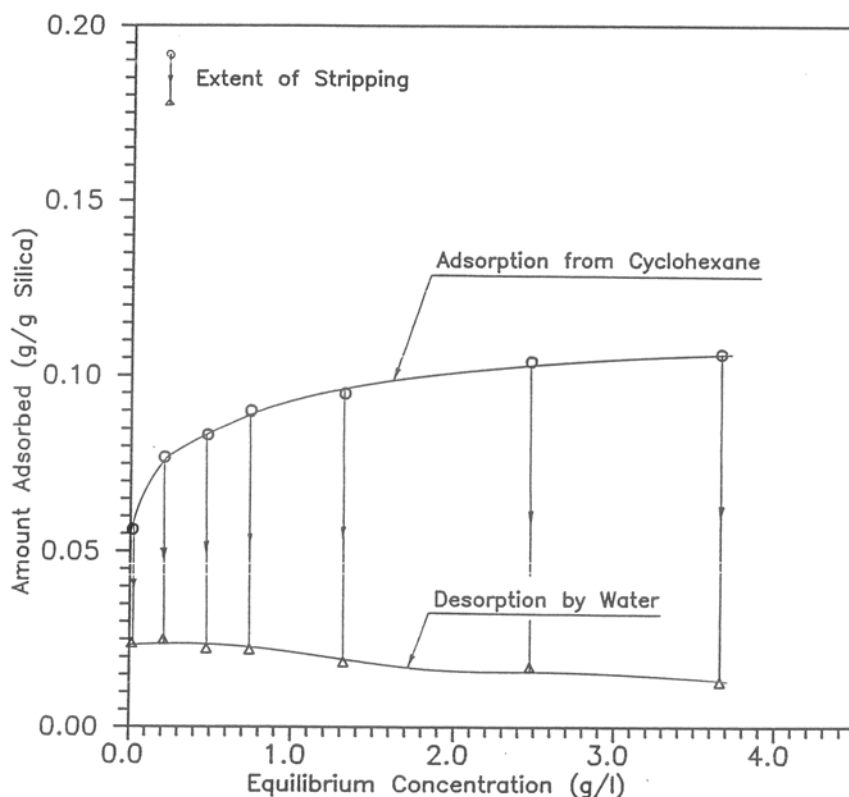


Figure 24. Adsorption/Desorption Behavior of Benzoic Acid onto/from 0-2 wt% AS1 Precoated Silica at 25°C

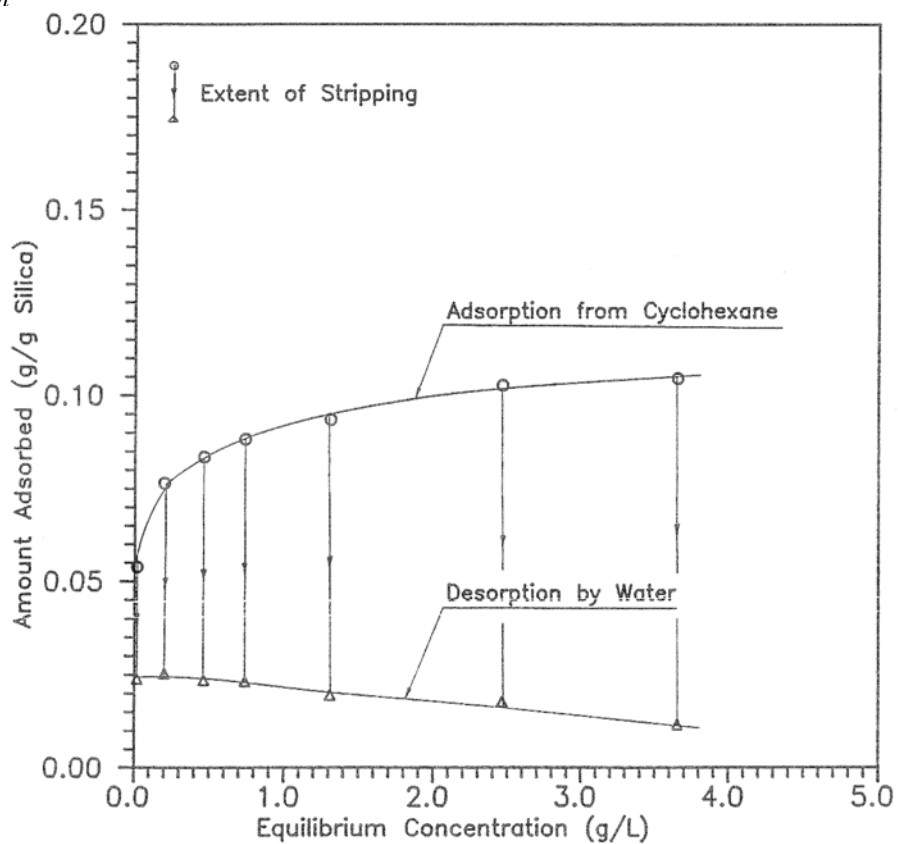


Figure 25. Adsorption/Desorption Behavior of Benzoic Acid onto/from 0-2 wt% AS2 Precoated Silica at 25°C

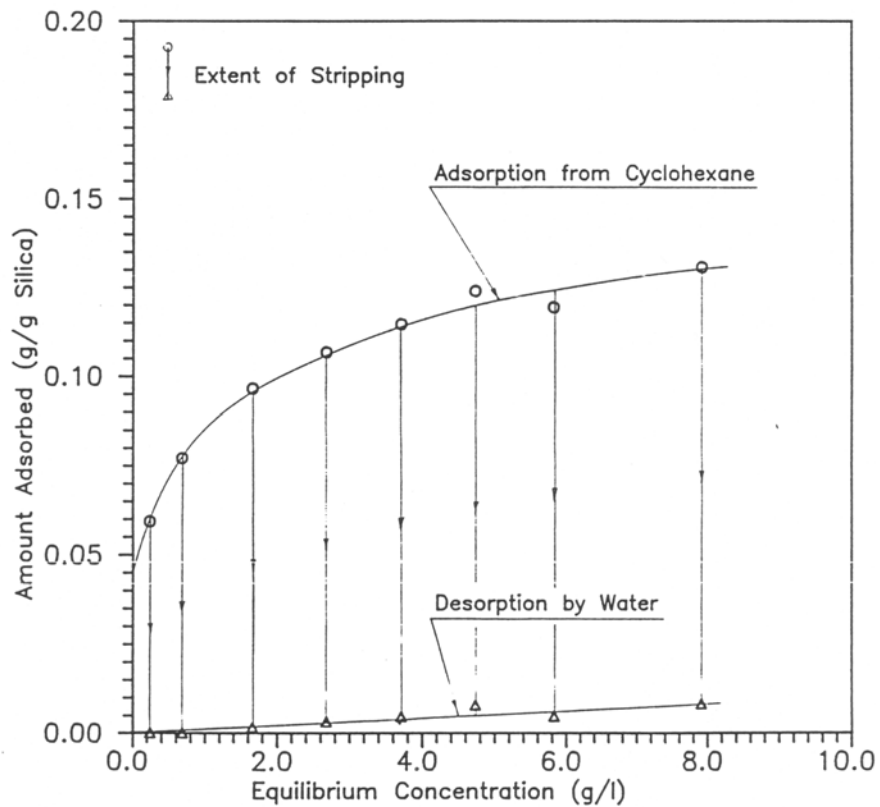


Figure 26. Adsorption/Desorption Behavior of Phenol onto/from 0-2 wt% AS1 Precoated Silica at 25°C

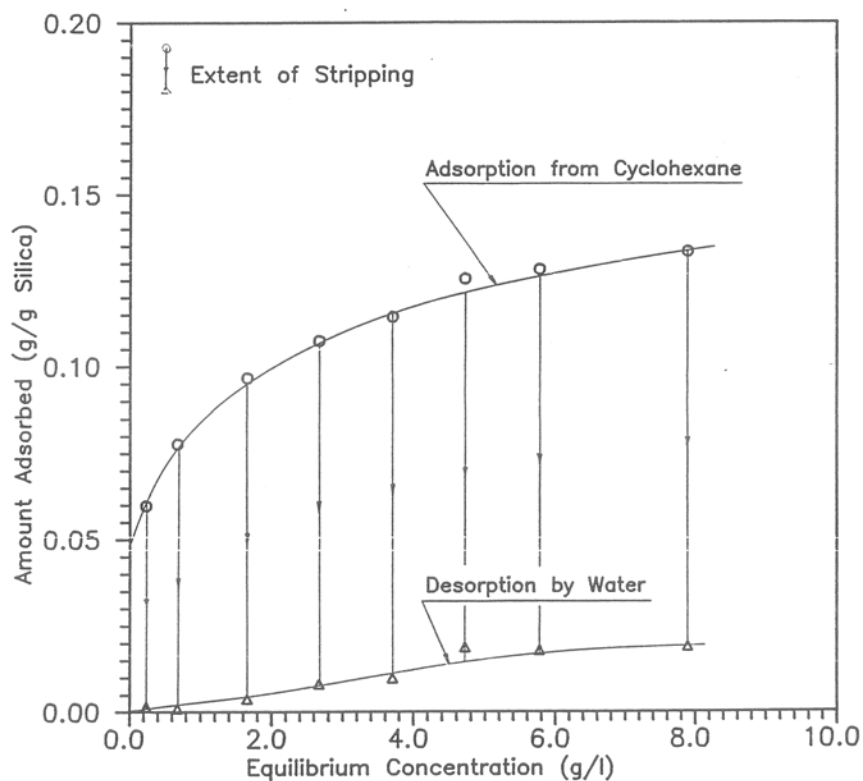


Figure 27. Adsorption/Desorption Behavior of Phenol onto/from 0-2 wt% AS2 Precoated Silica at 25°C

IV. CONCLUSIONS

The following concluding remarks may be drawn from the results obtained from the adsorption of asphalt model functionalities onto uncoated silica and silica precoated with AS agents in organic and aqueous media:

AS1 and AS2 showed a strong interaction with silica, and ASI followed the Langmuir adsorption model while AS2 exhibited multilayer adsorptive behavior when adsorbed from dichloromethane solution.

The adsorption of benzoic acid and phenol in cyclohexane solution was enhanced due to precoated AS agents on silica; however, phenylsulfoxide, quinoline, benzophenone, benzylbenzoate, and pyrene showed an inhibited adsorption compared to uncoated silica adsorption.

The enhanced adsorption of benzoic acid and phenol with AS agents can be interpreted by an acidbase interaction through which the basic amine groups of the AS agents form quaternary ammonium salts by reacting with benzoic acid and phenol as proton donors.

The adsorption of benzoic acid and phenol was significantly retarded in water solution compared to adsorption from cyclohexane solution.

Silica precoated with AS agents adsorbed more benzoic acid and phenol than did uncoated silica in an aqueous environment.

Benzoic acid and phenol preadsorbed on the precoated silica showed a high water susceptibility when they were placed into bulk water.

V. ACKNOWLEDGMENT

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APPENDICES

APPENDIX A

UV CALIBRATION CURVES

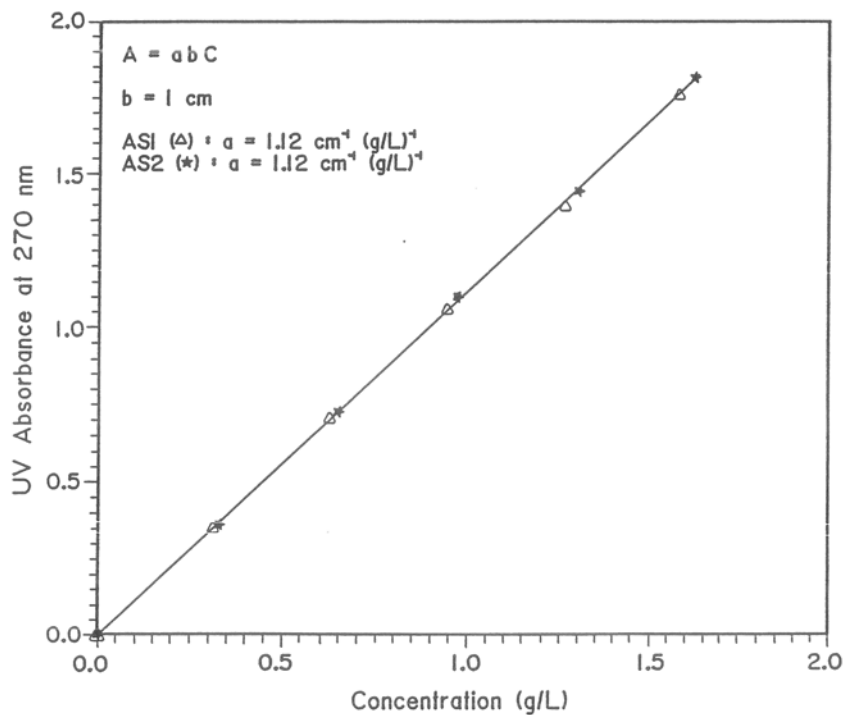


Figure 28. UV Calibration Curves for Two Commercial AS Agents in Dichloromethane Solutions

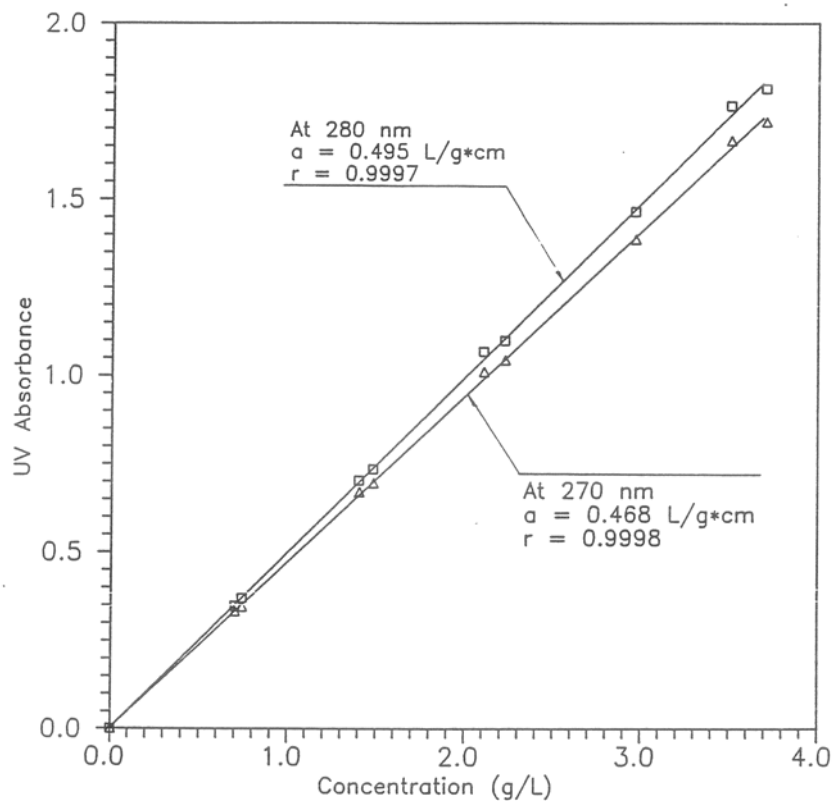


Figure 29. Calibration Curve for ASI in water Solution

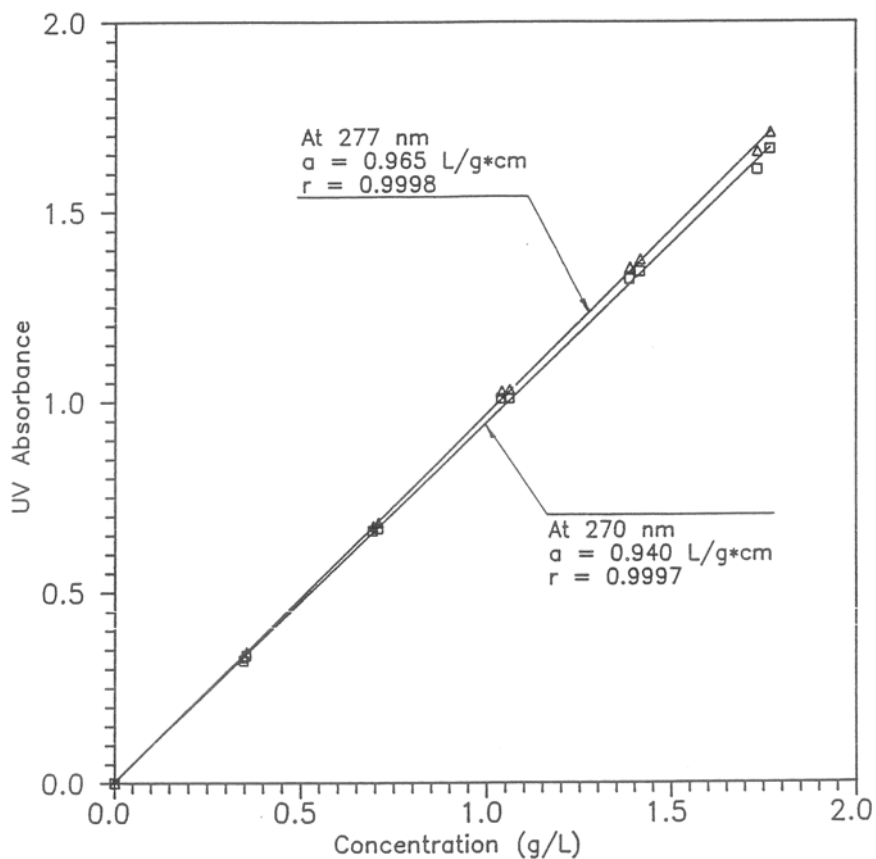


Figure 30. Calibration Curve for AS2 in Water Solution

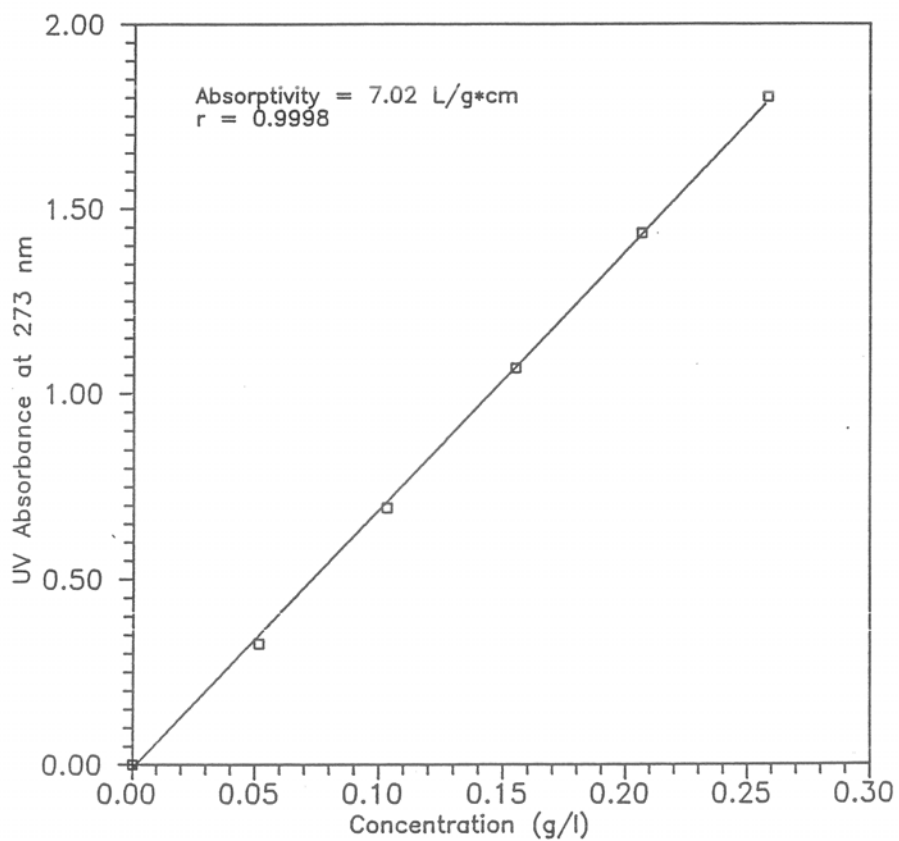


Figure 31. Calibration Curve for Benzoic Acid in Water Solution

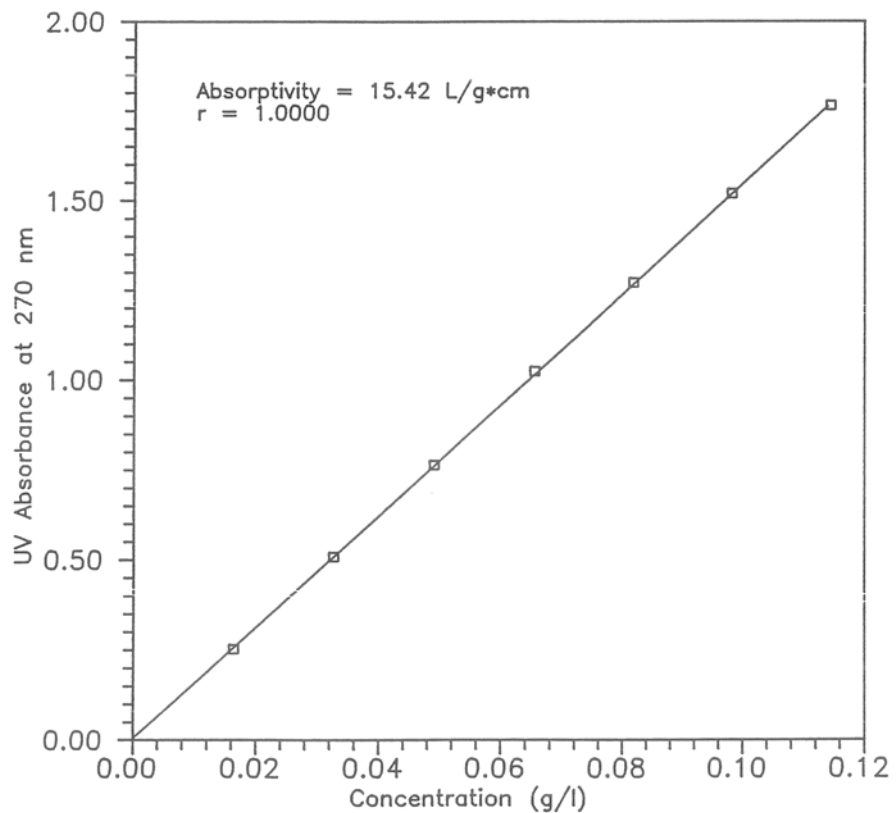


Figure 32. Calibration Curve for Phenol in Water Solution

APPENDIX B

ESTIMATION OF AS AGENT LOADINGS ON SILICA

I. Spectroscopic Analysis

(1) Solubility Measurement

The solubilities of AS1 and AS2 in distilled water are measured by quantitating their soluble and insoluble fractions at room temperature.

(a) AS1-Water Solution (100 ml)

	Trial 1	Trial 2
Amount Tested (g)	0.3922	0.4122
Soluble Fraction (g)	0.3599	0.3707
Insoluble Fraction (g)	0.0413	0.0435
Solubility (%)	89.5	89.5
Concentration (g/L)	3.509	3.707

(b) AS2-Water Solution (100 ml)

	Trial 1	Trial 2
Amount Tested (g)	0.1772	0.1806
Soluble Fraction (g)	0.1733	0.1768
Insoluble Fraction (g)	0.0039	0.0038
Solubility (%)	97.8	97.9
Concentration (g/L)	1.733	1.768

(2) UV Calibration

UV characteristic peaks are obtained by scanning sample solutions along wavelengths. UV calibration curves are then developed by measuring the UV absorbance of the sample solutions with known concentrations at wavelengths where UV peaks are observed.

(a) AS1-Water Solution

UV Peak observed at 280 nm.
 Absorptivity (a) = 0.468 L/g*cm at 270 nm
 0.495 L/g*cm at 280 nm

(b) AS2-Water Solution

UV peak observed at 277 nm.
 Absorptivity (a) = 0.940 L/g*cm at 270 nm
 0.965 L/g*cm at 277 nm

(3) Quantitation

When precoated silica is washed with distilled water, the final loadings of AS agents can be quantitated by measuring the UV absorbances of wash solutions as shown below.

Amount Precoated: 0.071 g AS1/g silica (6.6 wt%)
0.067 g AS2/g silica (6.3 wt%)

UV absorbance reading when 0.5 g precoated silica is washed with 100 ml distilled water:

UV Absorbance at 270 nm					
AS Agent	Wash 1	Wash 2	Wash 3	Wash 4	Total
AS1	0.135	0.013	0.005	0.003	0.156
AS2	0.176	0.015	0.005	0.004	0.200

For AS1, Initial Loading = (0.5) (0.066) = 0.033 g
 Amount Desorbed = $CV = (\text{Total Abs}/a)$
 = (0.156/0.468) (0.1)
 = 0.033 g
 Final Loading = (0.033 - 0.033)/0.467
 = 0.0 g AS1/g silica

For AS2, Initial Loading = (0.5) (0.063) = 0.0315 g
 Amount Desorbed = $CV = (\text{Total Abs}/a)$
 = (0.200/0.940) (0.1)
 = 0.0213 g
 Final Loading = (0.0315 - 0.0213)/0.469
 = 0.0218 g AS2/g silica
 or 2.1 wt%