A Literature Review of

THE ADSORPTION OF
ASPHALT FUNCTIONALITIES
ON AGGREGATE SURFACES

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"Chemistry of Bonding and Competitive Adsorption of Asphalt Functionalities on Aggregates"

by

Young W. Jeon and Christine W. Curtis
Auburn University, Alabama

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DISCLAIMER

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THE ADSORPTION OF ASPHALT FUNCTIONALITIES ON AGGREGATE SURFACES

INTRODUCTION

Asphalt is the most commonly used material in pavement construction today because of its high engineering performance capabilities such as elasticity, adhesion, and water resistance. Asphalt is known to be a complicated colloidal system of hydrocarbon materials which are composed of asphaltenes, resins, and oils(1). Thus, in many cases, asphalt could be defined as a colloidal suspension of asphaltenes in oils with resins acting as agents to prevent coagulation of the asphaltenes, the most polar, heaviest fraction of asphalt. The chemical composition of the asphaltenes has been elucidated as a combination of polyaromatic, alicyclic, and alkyl moieties containing heteroatoms such as oxygen (O), nitrogen (N) and sulfur (S). Metals such as nickel and vanadium, normally in the form of porphyrin complexes, are also present in asphaltenes(2).

Today's asphalt is produced mainly by the refining of crude oil. To alter or improve its physical and chemical properties, asphalt is subsequently treated by blending, air blowing, or adding additives. More than 70 percent of all asphalt produced in the United States is consumed for highway construction(3). Asphalt is a tarry, cementitious material which is usually fairly hard at ambient temperatures; when heated, it softens and flows. Asphalt is incorporated into aggregates in its liquid state at a hot mix processing and, upon cooling, hardens binding the aggregates together, and forming an asphalt-aggregate concrete.

The interface between the asphalt and aggregate has been the focus of much attention to determine the chemical factors that influence bonding between the two materials. Since a phase discontinuity occurs at the interface, the chemistry occurring there is strongly correlated to the integrity of the asphalt-aggregate concrete layer. The study of asphalt adsorption onto the surfaces of model and actual aggregates has been made to understand the chemistry of interfacial bonding between asphalt and aggregates(4-10). In order to examine the adsorptive interaction more specifically, asphalt was separated into the fractions of asphaltenes, polar aromatics and saturates(11) and their adsorption behavior was determined and compared to that of bulk asphalt. Furthermore, the composition of asphalt was elucidated by identifying the chemical functional group types present in fresh and aged asphalts using differential infrared spectrometry combined with selective chemical reactions(12).

The adsorption of asphalt functionalities onto actual aggregates (granite, quartzite, and limestone) was performed by Plancher, et al.(6). The relative affinity of these functionalities was determined based on the amount of adsorption from single-component solutions. However, the single-component adsorptive behavior does not fully predict the competitive adsorptive behavior of asphalt, the complicated mixture, on aggregates in an actual pavement environment. Although Curtis, et al.(13) investigated the adsorption of bi-functional groups on silica, the result was observed only at the single level of concentration rather than a range of concentrations. Thus, to truly understand multicomponent adsorption equilibria of asphalt functionalities with aggregates surfaces, a full range of concentrations must be studied. Higher levels of multiple compounds are also valuable. This information along with a predictive model will yield valuable information regarding adsorption of actual components from asphalt.

In conjunction with the statements mentioned above, the present literature review has been initiated to search for pertinent methodologies, theoretical and technical, and to conduct the single - and multi-component adsorption equilibria of the asphalt-aggregate systems. In addition, this review included the infrared study of adsorption occurring in situ at the liquid/solid interface, which will provide information on the adsorption mode of asphalt functionalities on oxide surfaces.

OBJECTIVE/PURPOSE

This literature review was conducted to determine the current state of knowledge of the theoretical and technical aspects of adsorption and how adsorption of polar functionalities influences the chemistry of the asphalt-aggregate interface. The information obtained from this literature review is used in conjuction with SHRP A-003B research to understand the chemistry occurring at the asphalt-aggregate interface.

SCOPE

This review covers the following topics:

1. Thermodynamics of Adsorption at the Solid/Liquid Interface
2. Adsorption Isotherms for Single-Solute Liquid Systems
3. Multicomponent Equilibria
4. Chemistry of Adsorption
    - Adsorbates
    - Experimental Procedures
    - Modelling of Adsorption Processes
    - Adsorbate-Adsorbent Interactions
    - Adsorption Mode
5. Significance to SHRP A-003B Research

NOTATION

The notation used for the literature review is given here for ready reference.

NOTATIONS

A = molar Helmholz free energy

$\hat{A}$ = UV absorbance

$\bar{A}$ = area under a gas chromatographic (GC) peak

C = solution concentration at equilibrium

$C_{m,i}$ = solution concentration of species i in a solution mixture

$C^{o}_{m,i}$ = initial concentration of species i in a solution mixture

G = molar Gibbs free energy

H = molar Enthalpy

$\hat{H}$ = differential enthalpy

K = equilibrium constant

K = degree in Kelvin

M = mass of adsorbent

P = total pressure

R = ideal gas constant

R_f = response factor for GC analysis

S = molar entropy

T = absolute temperature

U = molar internal energy

V = total solution volume

W = weight of a chemical species in GC analysis

a = Langmuir constant

$\hat{a}$ = activity

$\tilde{a}$ = specific surface area of adsorbent

b = Langmuir constant

f = fugacity

f^o = fugacity at standard state

i = integer variable

j = integer variable

k = constant in Equation (26)

m = constant in Equation (21)

n = number of moles

$\tilde{n}$ = total number of species in a solution mixture

p = cell pathlength

q = amount adsorbed on a unit mass of adsorbent

q_m = monolayer capacity

q_T = total amount adsorbed from the mixture

$q_{m,i}$ = adsorbed phase concentration of species i

r = constant in Equation (26)

x = mole fraction in a solution phase

z = mole fraction in an adsorbed phase

Λ = Wilson parameter

Φ = change in Helmholz free energy per unit mole of solvent

Ψ = dimensionless parameter in Equation (24)

α = constant in Equation (20)

β = constant in Equation (20)

γ = activity coefficient

δ = constant in Equation (21)

ϵ = absorptivity

ζ = constant in Equation (20)

$1/\eta$ = Freundlich constant

κ = Freundlich constant

μ = chemical potential

ν = peak frequency of infrared band

ξ = constant in Equation (21)

π = spreading pressure

ρ = constant in Equation (23)

THEORETICAL ASPECTS

1. Thermodynamics of Adsorption at the Solid/Liquid Interface

The thermodynamic approach to the study of equilibrium can be applied to adsorption equilibria just as to any other phase equilibrium. The only general assumption is that the adsorbed layer can be treated as a distinguishable phase in the thermodynamic sense. It is possible to adopt two somewhat different but entirely consistent perspectives in applying thermodynamic principles to adsorption equilibrium. The surface layer, consisting of adsorbate, may be considered as a single phase having the general properties of a solution. Alternatively, the adsorbent may be considered as thermodynamically inert. By these assumptions the adsorbed layer may be regarded as a distinct phase and the effect of the adsorbent is confined to the creation of a force field, the detailed nature of which need not be specified.

(1) Spreading Pressure

A fundamental differential equation for the change of Helmholz free energy for a bulk solution phase may be written

$$dA = - SdT - PdV + \Sigma\mu_i dn_i \qquad (1)$$

If we consider an adsorbed phase, designated by superscript a, as a solution of n_i^a moles of adsorbates and n_s^a moles of solvent, equation (1) becomes[14]

$$dA^{1a} = -S^{1a}\, dT - PdV^{1a} + \Sigma\mu_i^a\, dn_i^a + \mu_s^{1a}\, dn_s^a \qquad (2)$$

We may also write for the adsorbed phase in the absence of adsorbates:

$$dA^{0a} = -S^{0a}\, dT - PdV^{0a} + \mu_s^{0a}\, dn_s^a \qquad (3)$$

and by subtraction of (3) from (2) we obtain

$$dA^a = -S^a\, dT - PdV^a - \Phi\, dn_s^a + \Sigma\, \mu_i^a\, dn_i^a \qquad (4)$$

where $A^a \equiv A^{1a} - A^{0a}$, $S^a \equiv S^{1a} - S^{0a}$, $V^a \equiv V^{1a} - V^{0a}$ and $-\Phi \equiv \mu_s^{1a} - \mu_s^{0a}$.

The measuring of the variable Φ requires further consideration(15);

$$\Phi \equiv \mu_s^{0a} - \mu_s^{1a} = -(\partial A^a / \partial n_s^a)_{T,\, V^a,\, n_i^a} \qquad (5)$$

It is evident that Φ represents the change in the Helmholtz free energy per unit mole of solvent due to the spreading of the adsorbate over the surface of the adsorbent introduced. For adsorption on a two-dimensional surface, the surface area $\bar{a}$ is directly proportional to n_s^a so that we may write

$$\Phi \, dn_s^a = \pi d\bar{a} \qquad (6)$$

where π is the two-dimensional spreading pressure defined by $\pi = -(\partial U^a / \partial \bar{a})_{S^a,\, V^a,\, n_i^a}$ which corresponds to the difference in surface tension between a pure solvent-solid interface and a solution-solid interface at the same temperature.

(2) Gibbs Adsorption Isotherm

The Gibbs adsorption isotherm can be derived from equation (4) by following essentially the same logic as the derivation of the Gibbs-Duhem equation. The term PdV^a can be neglected since the volume of the adsorbed phase is negligible in comparison with the volume of the bulk solution phase. At constant temperature and neglecting the term PdV^a, equation (4) becomes

$$\begin{aligned} dA^a &= -\Phi \, dn_s^a + \Sigma \, \mu_i^a \, dn_i^a \qquad (7) \\ &= -\pi d\bar{a} + \Sigma \, \mu_i^a \, dn_i^a \end{aligned}$$

By Euler's theorem, equation (7) can be integrated to give

$$A^a = -\pi\bar{a} + \Sigma \, \mu_i^a \, n_i^a \qquad (8)$$

Differentiation of equation (8) gives

$$dA^a = -\pi d\bar{a} - \bar{a} d\pi + \Sigma \, \mu_i^a \, dn_i^a + \Sigma \, n_i^a \, d\mu_i^a \qquad (9)$$

Subtraction of equation (7) from equation (9) leads to the Gibbs isothermal adsorption equation

$$0 = -\bar{a} d\pi + \Sigma \, n_i^a \, d\mu_i^a$$

$$\text{or} \qquad \bar{a} d\pi = \Sigma \, n_i^a \, d\mu_i^a \qquad \text{(const T)} \qquad (10)$$

In dilute solution, n_i^s can be approximated by measuring the solute concentration decrease ΔC_i caused by contacting a solution of known concentration and known volume V with a known mass of adsorbent (M)$^{(14)}$:

$$n_i^s = V\,\Delta C_i/M \qquad (11)$$

(3) Energies of Adsorption

For the equilibrium of adsorption, which is interpreted by the exchange reaction between adsorbate$^{(1)}$ and solvent$^{(2)}$ molecules of equal size,

$$(1)^{\ell} + (2)^{s} = (1)^{s} + (2)^{\ell} \qquad (12)$$

the equilibrium constant is given by

$$K = \hat{a}_1^{s}\,\hat{a}_2^{\ell} / \hat{a}_1^{\ell}\,\hat{a}_2^{s} \qquad (13)$$

where $\hat{a}$ is the activity of components, and superscripts denote the surface (s) and liquid (ℓ) phases. For the cases in which both phases can be considered as ideal, activities are replaced by mole fraction, and thus

$$K = x_1^{s}\,x_2^{\ell} / x_1^{\ell}\,x_2^{s} \qquad (14)$$

For the case of dilute solutions, K is correlated with the Langmuir equation$^{(16)}$

$$x_1^{\ell}/n_1^{s} = 1 / ((n_1^{s})_m\,(K\text{-}1)) + x_1^{\ell}/(n_1^{s})_m \qquad (15)$$

where $(n_1^s)_m$ is the monolayer capacity of component 1. A plot of x_1^{ℓ}/n_1^{s} against x_1^{ℓ} is linear, and values of $(n_1^s)_m$ and K can be deduced from the slope and intercept.

The standard free energy of adsorption is related to the equilibrium constant by

$$\Delta G^\circ = -RT \ln K \qquad (16)$$

so that values of ΔG° may in principle be calculated from adsorption data. The standard state may be chosen as the following: for a solute, the reference state of the adsorbed phase is that of the solid solute and, for solution, the concentration at which the surface becomes saturated with solute(17).

The differential heat of adsorption of component 1 is given by the following thermodynamic relation:

$$\Delta H = -RT^2 (\partial \ln \hat{a}_1 / \partial T)_{P, n_1^s, n_2^s} \qquad (17)$$

but this can be true only if n_1^s/n_2^s is independent of temperature, which is generally untrue(18). Thus, the estimation of heats of adsorption by using the Clausius-Clapeyron equation can yield misleading results. A better result is obtained by measuring the heat of immersion of the solid in solutions isothermally as a function of n_1^s.

The heat of adsorption provides a direct measure of the strength of the bonding between adsorbate and surface. Adsorption from the liquid phase is generally exothermic, as may be shown by a simple thermodynamic argument. Since the adsorbed molecule has at most two degrees of translational freedom on the surface and since the rotational freedom of the adsorbed species must always be less than that of the bulk phase molecules, the entropy change on adsorption ($\Delta S = S_{ads} - S_{bulk}$) is necessarily negative. In order for significant adsorption to occur, the free energy changes on adsorption (ΔG) must also be negative and since $\Delta G = \Delta H - T\Delta S$ this requires ΔH negative, or exothermic adsorption. Hence ΔG is an indication for the extent of adsorption, and the strength of a bond between adsorbate and solid surface if the entropy change (ΔS) is similar for adsorbate species involved at a given temperature.

2. Adsorption Isotherms for Single-Solute Liquid Systems

A long term adsorptive interaction may require information on equilibrium properties, commonly called 'adsorption isotherms'. The adsorption isotherms derived from thermodynamic theories not only give rise to very useful thermodynamic parameters such as an equilibrium constant and a maximum adsorption capacity, but also provide bases for multi-solute adsorption equilibria predictions. For convenience in calculation, it is often desirable that these single-solute data be represented accurately by a relatively simple mathematical equation. However, the equation must satisfy a necessary thermodynamic boundary condition; at very low surface coverage the isotherm must reduce to the linear isotherm of Henry's law.

A popular adsorption isotherm for single-solute systems is proposed by Freundlich, which is expressed as

$$q = \kappa C^{1/\eta} \tag{18}$$

$$\text{or} \qquad \ln q = \ln \kappa + (1/\eta) \ln C$$

where q and C denote amount adsorbed per unit weight of solid and equilibrium adsorbate concentration, respectively, and κ and $1/\eta$ are constants. This empirical equation is suitable for highly heterogeneous surfaces and often represents typical adsorption data over a restricted range of concentration. However, the Freundlich does not obey the Henry's law at infinitely dilute concentrations.

The Langmuir equation is suited to describe the adsorptive behavior of homogeneous surfaces. The Langmuir adsorption model is established on the following hypotheses: (1) uniformly energetic adsorption sites, (2) monolayer coverage, and (3) no lateral interaction between adsorbed molecules. A mathematical expression of the Langmuir can be written

$$q = aC / (1 + bC) = bq_m C / (1 + bC) \tag{19}$$

where a and b are the Langmuir parameters and q_m denotes a monolayer capacity.

The monolayer capacity, q_m, indicates a saturated monomolecular layer of adsorbate on the surface of unit weight solid, which might be accomplished at the infinitely high adsorbate solution concentration. The adsorbed molecules in the saturated monolayer are presumably under the conditions of closest packing and maximum orientation in the interface. Most adsorbents are heterogeneous in a sense that they contain a wide range of high to low energy sites, both polar and nonpolar, as well as adsorbed impurities such as moisture and organic contaminants arising from exposure to the environment. For most systems, therefore, the assumptions of the Langmuir model are far from being realized. Nevertheless, experimental data are often fitted to the Langmuir equation and values obtained for the adsorption parameters. The Langmuir equation obeys the correct boundary condition, Henry's law.

A three-parameter isotherm model was developed by Radke and Prausnitz(14), which combined the Langmuir and the Freundlich models. The correlation leads to

$$q = \alpha C / (1 + \beta C^{\zeta}) \qquad (20)$$

where α, β, and ζ are the parameters determined by a statistical fit of experimental data. At low limiting concentrations the equation reduces to the linear isotherms of Henry's law. At high concentrations, the expression is equivalent to the Freundlich equation. For the special case of $\zeta = 1$, the model becomes the Langmuir isotherm. The Redke-Prausnitz three-parameter model generally interprets adsorption data very well.

Another well known three-parameter model was proposed by Toth(19, 20). The Toth equation reduces to Henry's law at very low concentrations and contains three adjustable parameters. The mathematical expression of the equation can be given

$$q = q_m C (\delta + C^m)^{-1/m} \qquad (21)$$

$$\text{or} \qquad q = q_m (C/\xi) [1 + (C/\xi)^m]^{-1/m}$$

where q_m, ξ, δ, and m denote empirical constants, and $\xi = \delta^{1/m}$ has the same unit as C. Toth starts with the Langmuir equation

$$q = q_m C(1/b + C)^{-1} \qquad (22)$$

For a homogeneous surface, 1/b is independent of surface coverage and related to the differential enthalpy of adsorption $\hat{H}$ by

$$1/b = \rho \exp(-\hat{H}/RT) \qquad (23)$$

where ρ, T, and R denote a constant, the absolute temperature, and the gas constant, respectively.

For a heterogeneous surface, $\hat{H}$ is not constant but varies with the surface coverage. To specify this dependence Toth introduces a dimensionless quantity Ψ defined by

$$\Psi = (d \ln C / d \ln q) - 1 \qquad (24)$$

For the Langmuir isotherm standing for a homogeneous surface

$$\Psi = bC \qquad (25)$$

but for a heterogeneous surface the relationship between Ψ and C would become more complicated. Therefore, if Ψ can be determined by isothermal adsorption data, it should be of great advantage to obtain some information on the surface heterogeneity without measuring the differential heats of adsorption experimentally. Toth suggests a function of the form

$$\Psi = k\, C^{r} \qquad (26)$$

where k and r are constants. When we set $k = 1/\delta$ and $r = m$, Toth's equation, equation (21), is obtained by integrating equation (24) according to the boundary condition $q \rightarrow q_m$ when $C \rightarrow \infty$. Setting $r = 1$ leads to the Langmuir equation while $r = 0$ the Freundlich equation. Since Ψ can be determined from experimental adsorption data obtained at one temperature, it may be used as a criterion for checking the suitability of various proposed adsorption isotherms.

3. Prediction of Multi-Component Equilibria

The problem of predicting multi-component equilibria from single-component adsorption data has attracted much attention because the experimental measurement of multi-component adsorption isotherms is time-consuming. Various approaches have been proposed for the prediction of multi-component equilibria, but there is no complete method with universally proven applicability.

(1) Langmuir Competitive Model (LCM)

The two parameter Langmuir equation, equation (19), can be easily extended to multi-component systems. The resulting expression for the isotherm is

$$q_i = (a_i\, C_i)/(1 + \sum_{j=1}^{\bar{n}} b_j C_j) \tag{27}$$

in which q_i is an amount of i-th component adsorbed onto a unit weight of adsorbent, while a_i and b_j are the Langmuir parameters determined from the single-solute adsorption isotherm of the species i or j involved.(21, 22)

Because of the limited success of the Langmuir competitive model in predicting mixture equilibria, the LCM has been modified by the introduction of a power law expression as the following(23):

$$q_i = (a_i\, C_i)/(1 + \sum_{j=1}^{\bar{n}} b_j\, C_j^{P_j}) \tag{28}$$

Although not thermodynamically consistent, this expression has been shown to provide a reasonably good empirical correlation for calculating the adsorption equilibria of multi-component systems. However, this approach should be treated with caution because of the lack of a proper theoretical foundation.

Jain and Snoeyink(24) proposed another modification of the LCM to be applied for the adsorption of bicomponent organic ions onto active carbon. The modified equation was developed based on the hypothesis that when $q_{m1} \neq q_{m2}$ the number of adsorption sites without competition was equal to the quantity $(q_{m1} - q_{m2})$, where $q_{m1} > q_{m2}$. The equations are written

$$q_1 = [(q_{m1} - q_{m2})b_1C_1]/(1 + b_1C_1) + (q_{m1}b_1C_1)/(1 + b_1C_1 + b_2C_2) \tag{29}$$

$$q_2 = (q_{m2}b_2C_2) \,/\, (1 + b_1C_1 + b_2C_2) \tag{30}$$

where q_1 and q_2 are amount of component 1 and 2 adsorbed per unit weight of adsorbent at equilibrium concentration C_1 and C_2, respectively, while q_{m1}, q_{m2}, b_1 and b_2 are the Langmuir constants derived from single-component systems. However, this model is expected to be valid only when a fraction of the adsorption occurs without competition; that is, when the layer of the two adsorbates is unable to enter the small pores of a porous adsorbent or when an adsorbent selectively prefers one of the two solutes because of specific adsorbate-adsorbent interactions.

(2) Ideal Adsorbed Solution (IAS) Theory

If the adsorbed phase is thermodynamically ideal, it is possible to derive the equilibrium relationships for an adsorbed mixture directly from the single-component isotherms using the method developed by Myers and Pransnitz(14, 25). From the assumption of the ideal adsorbed solution phase and phase equilibria, a set of necessary relationships can be drawn for calculating multi-component equilibria. A spreading pressure (π) may be evaluated by integrating the Gibbs adsorption isotherm of a single-component system:

$$\pi_i = RT/\bar{a} \int_0^{Ci} [q_i(C_i) / C_i]\, dC_i \qquad \text{(Constant T)} \qquad (31)$$

where C_i and q_i = the solution- and solid-phase concentrations of component i at equilibrium; $\bar{a}$ = the specific surface area of the adsorbent; R = the universal gas constant; and T = the absolute temperature.

Equivalence of the spreading pressures of all the solutes in the mixture gives

$$\pi_1 = \pi_2 = \ldots\ldots = \pi_n$$

$$\text{or} \quad \int_0^{C1} (q_1/C_1)\, dC_1 = \int_0^{C2} (q_2/C_2)\, dC_2 = \ldots = \int_0^{Cn} (q_n/C_n)\, dC_n \qquad (32)$$

other equations needed for the IAS calculation are(21)

$$C_{m,i} = z_i C_i \qquad (33)$$

$$\sum_{i=1}^{n} z_i = 1 \qquad (34)$$

$$q_i = f(C_i) \qquad (35)$$

$$1/q_T = \sum_{i=1}^{\bar{n}} z_i/q_i \qquad (36)$$

$$q_{m,i} = z_i q_T \qquad (37)$$

$$q_{m,i} = [(C^0_{m,i} - C_{m,i})\, V] \,/\, M \qquad (38)$$

in which $C_{m,i}$ and $q_{m,i}$ = respectively, the solution- and solid-phase concentration of species i in the mixture; z_i = the mole fraction of species i in the adsorbed phase; q_T = the total amount adsorbed from the mixture; $\bar{n}$ = the total number of species in solution; $C^0_{m,i}$ = the initial concentration of species i; V = the volume of solution; and M = the dosage of adsorbent. Equation (35) is used to represent the functional relationship between q and C in the single-solute systems. Equation (38) was not presented in the original IAS calculation procedure described by Radke and Prausnitz$^{(14)}$. An examination of equations (32) through (38) gives the following:

1. There are a total of $(5n + 1)$ equations.
2. $C^0_{m,i}$, V, M, and $q_i = f(C_i)$ are knowns.
3. The unknown variables are $C_{m,i}$, $q_{m,i}$, z_i, C_i, q_i, and q_T, comprising a total set of $(5\bar{n} + 1)$ unknowns.

These $(5\bar{n} + 1)$ independent equations with $(5\bar{n} + 1)$ unknowns should give rise to a unique solution, without requiring the use of experimental data for calculation purposes. At first sight the hypothesis of ideal behavior in the adsorbed phase seems highly improbable, but it has been shown that a number of systems follow this model very closely$^{(14, 21)}$.

(3) Correlations for Nonideal Adsorbed Phase

It has been reported that multi-component systems which adsorb strongly and which are chemically dissimilar are deviated from the predictions of the IAS model due to nonidealities of the adsorbed phase. Jossens, et al.$^{(20)}$ observed that deviations from the IAS model were strongly related to the acidities of adsorbate molecules and a surface coverage: the larger a deviation, the higher the acidity of an adsorbate (equivalently, the lower the pKa value of an adsorbate) as well as the higher a surface coverage. Radke and Prausnitz(14) included this nonideality by defining an activity coefficient for the adsorbed phase

$$\gamma_i^{a} (T, \pi, z_i) = f_i^{a} / z_i f_i^{a0} \qquad (39)$$

in which γ_i^{a} = adsorbed-phase activity coefficient; z_i = adsorbed phase invariant mole fraction of solute i; f_i^{a} = adsorbed-phase fugacity of solute i; and f_i^{a0} = adsorbed-phase fugacity of solute i at standard state. Suwanayuen and Danner(26, 27) extended this concept and obtained the composition dependence of the activity coefficient by using the Wilson equation

$$\ln\gamma_k = 1 - \ln\left[\sum_{j=1}^{\bar{n}} z_j \Lambda_{kj}\right] - \sum_{i=1}^{\bar{n}} \left[(z_i \Lambda_{ik}) / \left(\sum_{j=1}^{\bar{n}} z_j \Lambda_{ij}\right)\right] \qquad (40)$$

where Λ's are the Wilson parameters. The main advantage of this equation is that a multicomponent adsorption activity coefficient can be calculated if all relevant binary parameters are known. These correlations for the nonideality of the adsorbed phase can make it possible to predict asymmetric adsorption phase diagrams as well as azeotrope formation.

TECHNICAL ASPECTS

Asphalt is often defined as a colloidal suspension of asphaltenes in oils with resins acting as agents to prevent coagulation of the asphaltenes, the most polar, heaviest fraction of asphalt. When stone chips are introduced into liquid asphalt at a hot mix processing, asphalt fractions wet the surface of the stone chips. Then, a weakly adsorbed oil fraction in the surface layer, which forms a two-dimensional single molecular layer in contact with the surface of the stone chips, may be subsequently replaced by the polar, reactive asphaltene molecules. This phenomenon can at least partially be depicted by the mechanism of adsorption occurring at the liquid solution/solid interface. Once the solution wets the surface of solid, adsorption proceeds through the subsequent replacement of solvent molecules adsorbed on the solid surface by the strongly adsorbing solute molecules. In order to effectively carry out the experiments on adsorption at the liquid/solid interface, however, we need to consider several factors which might affect the adsorption results significantly, such as adsorbates, adsorbents, experimental factors, adsorbate-adsorbent interactions and adsorption modes.

1. Adsorbates

On a molecular basis, petroleum consists of hydrocarbons and the organic compounds of sulfur (S), nitrogen (N), and oxygen (O), with metallic constituents being present, but only to a minor extent. Although the hydrocarbon content of petroleum may be as high as 97 percent, it is the heteroatomic (N, S, O) nonhydrocarbon constituents that play an important role in determining the nature and the processability of the crude oil(28). The heteroatomic molecules tend to concentrate in the high-boiling fractions of petroleum such as resid and asphalt. Heteroatomic molecules impose a significant influence on the processability of the petroleum and its fractions irrespective of their molecular size. Petersen(12) identified the chemical functional types present in fresh and oxidized asphalts using differential infrared spectrometry combined with selective chemical reactions as shown in Figure 1. They are polynuclear aromatic, phenolic, 2-quinolone-type, pyrrolic, pyridinic, sulfide, sulfoxide, anhydride, carboxylic and ketone. Anhydrides, ketones and sulfoxides are hardly found in fresh asphalts but primarily generated upon oxidation(29, 30). In selecting model asphalt-functionalities for the study of adsorption at the liquid/solid interface, the physical and chemical properties of the model compounds are to be carefully considered: for example, acidity and basicity, molecular weight and dimension, solubility in a given solvent, and others.

Asphaltenes, which are the most characteristic fraction of asphalt, are obtained from petroleum and bitumen by addition of a nonpolar solvent with a surface tension lower than 25 dynes

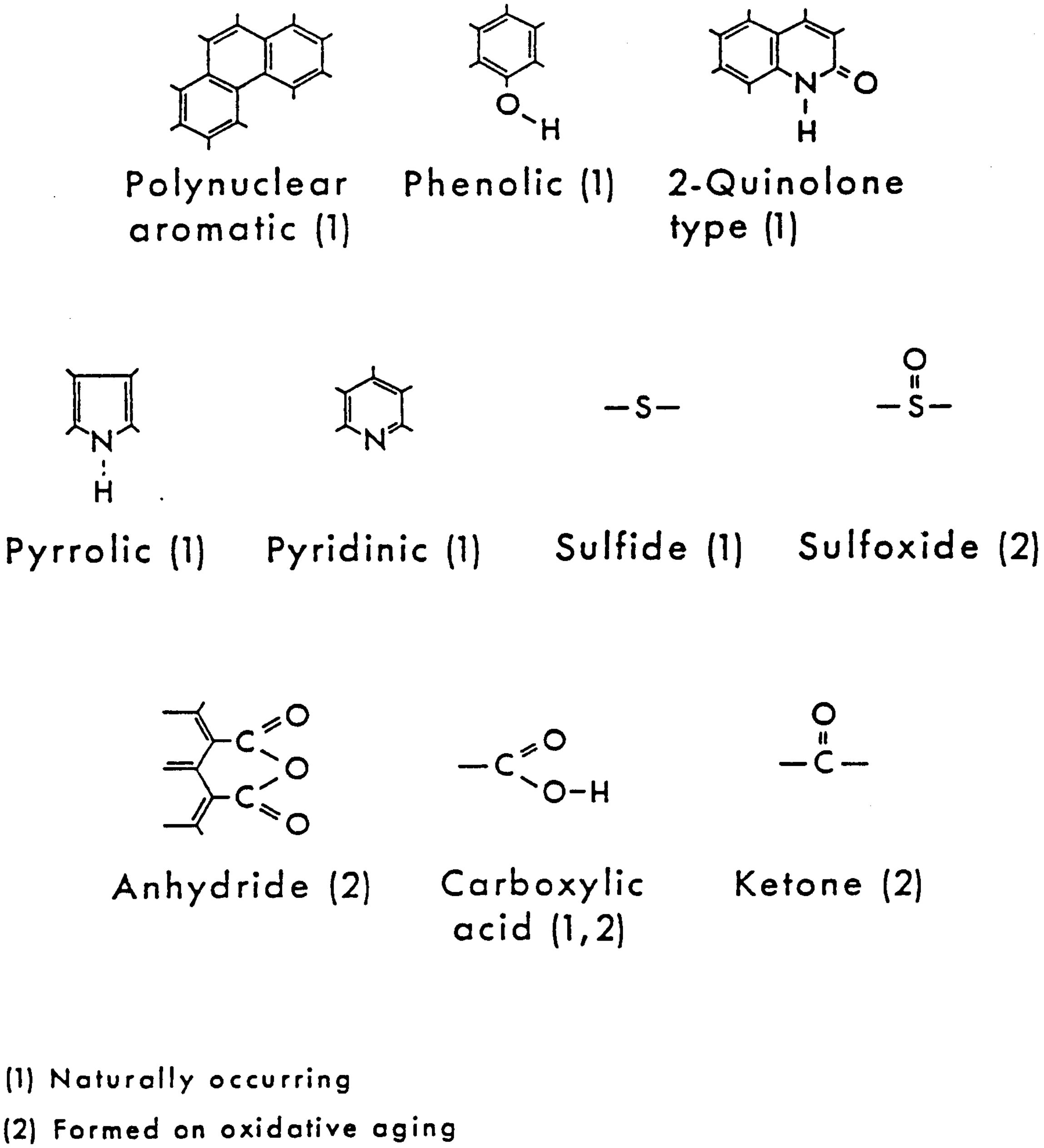


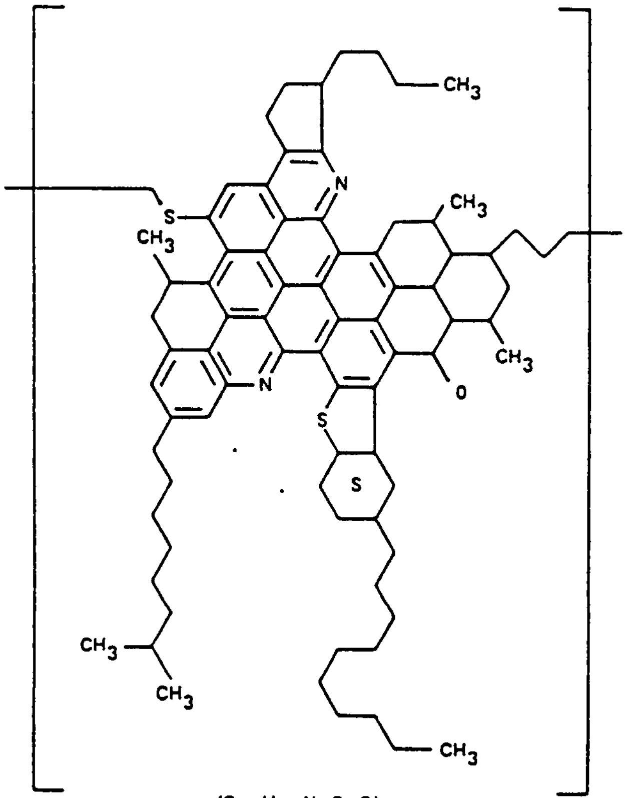
Figure 1. Examples of important chemical functionalities present in asphalt molecules

cm^{-1} at 25°C(31). Many investigations into asphaltene structure have given indications that asphaltenes consist of condensed aromatic nuclei that carry alkyl and alicyclic systems with heteroelements (N, S, O) scattered throughout in the molecular structure of asphaltenes(31). The hypothetical structure of a petroleum asphaltene is illustrated in Figure 2.

2. Adsorbents

Various adsorbents have been used for the study of asphalt adsorption: for example, catalysts, oxides, model and actual aggregates. As a model aggregate silica has been commonly selected because of the petrological abundance of siliceous material in most practical aggregates. Actual aggregates are usually ground into small particles with a mesh size to increase their specific surface area to the one appropriate for the adsorption study. All adsorbents are commonly conditioned in an oven at elevated temperatures as well as under atmospheric pressure or vacuum prior to use.

The surface of adsorbent imposes a significant effect on adsorption occurring at the liquid/solid interface. The chemical behavior of the adsorbent surface is related to the range of acidic and basic groups that exist on the surface. The type and number of the surface functional groups depend on the method of preparation and the treatment given prior to experimental use. For example, silica surfaces normally contain two types of hydroxyl groups: isolated (vicinal) and adjacent (geminal) silanols. However, only isolated hydroxyl groups are present on the silica surface which is preconditioned at above 600°C in vacuo.(47) Silica and graphitized carbon black are generally considered to provide (reproducible) well-defined surfaces, whereas the surfaces of graphites, charcoals, minerals, and clays are often ill-defined. The use of the reproducible materials is often required to obtain valuable and reliable information on adsorption studies. The physical structure of the surface also affects the adsorption behavior of adsorbate species. If a solid material



$(C_{79}H_{92}N_2S_2O)_3$
mol wt. 3449

Figure 2. Hypothetical structure of a petroleum asphaltene

is porous, a partial molecular sieve effect may be anticipated, thereby enhancing the adsorption of smaller components. This effect becomes particularly significant if the pores are small.

3. Experimental

There are generally two types of contact methods to examine adsorption at the solution-solid interface: batch and continuous types(32). In a batch system a known volume of sample solution is added to a known weight of solid, the mixture is stirred in a thermostated vessel until adsorption equilibrium is reached (usually several hours), and sample aliquots are then taken for analysis. In a continuous system, however, adsorbents form a fixed bed in an adsorption column which is thermostated; an adsorbate solution flows through the solid bed; the concentration of the solution changes from adsorption and is continuously monitored by an analyzing instrument. A flow-through method is schematically diagrammed in Figure 3(9). A batchwise operation may be suitable to the equilibrium study of adsorption, whereas the transient behavior of adsorption is readily evaluated by a continuous system. An adsorption temperature is usually determined to be the one far below the boiling point of a chosen solvent. The effect of pressure is of little significance in most cases.

For the analysis of adsorption from solutions, spectroscopic and chromatographic techniques are commonly employed depending upon the number and nature of adsorbate species used. In a spectroscopic analysis the quantitation of adsorption is based on the Beer-Lambert's law, $\hat{A} = \epsilon p C$ where $\hat{A}$, ϵ, p, and C denote absorbance, absorptivity, cell pathlength, and solution concentration, respectively. In a gas-liquid chromatographic analysis the quantitation is based on the method of internal standardization(33), $\bar{A}_i/\bar{A}_s = R_f\,(W_i/W_s)$, in which $\bar{A}_i/\bar{A}_s$ = an area ratio of a solute to an internal standard, W_i/W_s = a weight ratio of a solute to an internal standard, and R_f = a response factor of solute i. For both analytic methods, calibration curves are developed using the sample solutions with known concentrations and then used to measure the concentrations of unknown

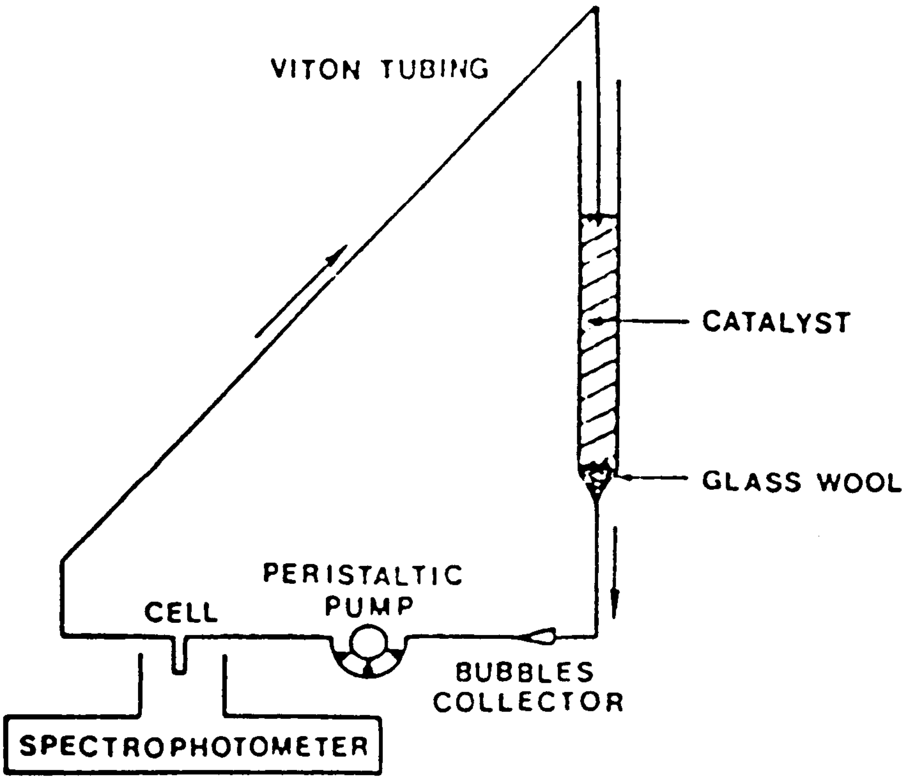


Figure 3. Continuous Adsorption Apparatus

samples. With the measured concentration values an amount of a solute adsorbed on a unit weight of adsorbent can be calculated using a mass balance equation, as shown in equation (11).

4. Data Analysis and Modelling

Once data for single-component adsorption are available, they are fitted to Toth equations (24) and (26) to obtain information on selecting the most suitable adsorption model which will be the Langmuir, the Freundlich or the three parameter Toth equation. Then, multi-component adsorption equilibria can be predicted from the selected single-component adsorption models by using the Langmuir competitive model, the ideal adsorbed solution theory or other nonideal adsorption models. Experimental data for multi-component adsorption are compared with the theoretically derived results, enabling the selection of the best representing competitive adsorption model for the multi-component system of asphalt functional groups.

5. Adsorbate-Adsorbent Interactions

There are several factors influencing the nature of adsorption. In general, however, the adsorbate-adsorbent interaction can be explained in terms of the varying degrees of polarity shown by the surface and the adsorbate. For example, silica adsorbs alcohols in preference to benzene while the reverse is observed for charcoals(34). These opposing preferences may be ascribed to the highly polar nature of the silica and alcohols and the relatively nonpolar nature of the charcoal and benzene. In the absence of any specific polar group in adsorbate molecules, aromatic compounds are adsorbed more preferentially than corresponding aliphatic compounds because of the interaction between Π-electrons of aromatic systems and polar solids. Besides the polarity of an adsorption system, porosity of solids, heterogeneity of solid surfaces, limitation of solubility, and orientation of adsorbed species are also important factors to be considered in understanding adsorbate-adsorbent interactions. These factors are discussed in detail elsewhere(34).

An acid-base interaction by a proton transfer is an important mechanism in the adsorption of petroleum heavy ends onto naturally occurring stone surfaces(10, 35). Like many organic dyes, asphaltenes contain basic nitrogen groups in their molecular structures. The Broensted acidic sites of the stone surfaces tend to release protons to the basic nitrogen groups present in asphaltenes. Thus, an electrical charge attraction develops between the positively charged nitrogen group and the negatively charged stone surface. The basic nitrogen may be important in the long-range interaction between asphaltenes and the stone surface.

Another factor influencing the adsorption is an exchangeable cation(10). Naturally occurring stone surfaces contain significant amounts of exchangeable cations which determine cation-exchange capacity (CEC). The CEC is the sum of extractable bases: for example, Al + Ca + Mg + K + Na. The hydration energy of these ions is often related to differences in adsorption. The coordination of water to these exchangeable ions may influence expansibility of the silicate structure of the stone surfaces in aromatic solvents. Cations with high hydration energies will show resistance to losing structural water during a drying process and then can provide more adsorption sites for organic species. On the other hand, cations with low hydration energies will lose the structural water upon drying. The surface layers will collapse and may not be expanded by solvents. The enthalpy of hydration of these cations is in the order $Mg^{2+} > Ca^{2+} > Na^{+} > K^{+}$. A solvent carrier is also an important factor controlling the adsorption. The extent and sign of charge on the adsorbate molecules as well as the interlayer spacing of a solid surface are controlled by the solvent carrier.

Soil materials contain significant CEC which is derived primarily from clay minerals. Clays possess a net negative electrical charge which is compensated for by exchangeable cations on their surfaces. Hydration of these metal cations renders a hydrophilic nature to the mineral surfaces.

Organic cations may substitute for metal cations on the exchange sites of clays in aqueous environment. The organic cations with sizable organic moieties may modify the clay surface to become strongly organophilic. Boyd, et al.(36) observed that hexadecyltrimethylammonium [$(CH_3)_3N(CH_2)_{15}CH_3$] cations bound almost irreversibly to the clay surface through the mechanism of cation exchange.

There are other factors which become important as molecules approach the surface of solids. If large asphaltene molecules get close to the surface, van der Waals forces become significant. Also, Π-interactions of the disc-like aromatic molecules with the Bronsted adsorption sites are expected to occur by the formation of a Π-electron-proton complex(16).

Water molecules or layers of water films are often found to intervene at the organic-solid interfaces in many actual circumstances. Brooks(37) examined how organic materials accumulated on wet siliceous material surfaces in a marine environment. The adsorption of n-octadecane, stearic acid, and n-octadecylamine was performed using a high surface area nonporous silica (Aerosil) as a model siliceous substrate. It was demonstrated that the preadsorbed water films significantly retarded the adsorption of the model compounds on the silica surfaces when comparing the adsorption of n-heptane solutions onto dry silica and silica with monolayered as well as multilayered water films.

6. Adsorption Mode

The adsorption mode of organic species, which indicates the type of adsorption, the strength of adsorption, and the orientation of adsorption, has been extensively examined by employing infrared spectroscopy(38-54). The adsorbates used included aromatic and aliphatic organic molecules containing functional groups in their molecular structures; the heteroatomic species formed were comprised of the following functionalities: carboxylics, phenols, nitrogen-bases, ketones, esters, ethers, and so forth. The adsorption behavior of these adsorbates was studied using silica immersed in carbon tetrachloride or hydrocarbon solvents. In many cases, however, the use of carbon tetrachloride as a solvent was preferred because of its spectral transparency in the infrared region.

The condition of heat treatment of silica affected the mode of adsorption to a large extent. Silica pre-evacuated at above 873 K contained only isolated silanol groups on the surface, whereas both isolated and adjacent silanol groups were concomitantly present on silica pre-evacuated at below 873 K. Usually, the adjacent silanols acted as stronger adsorption sites than the isolated silanol groups. A hydrogen bonding interaction was commonly involved when polar organic species were adsorbed on the silica surfaces. The hydrogen bonding interaction was characterized by an infrared band shift $\Delta\nu_{OH}$ of -OH stretching vibrations of isolated silanol groups attributable to perturbation by the adsorbed molecules. Aromatic adsorbates formed additional Π-bonds with surface silanol groups. The band shift $\Delta\nu_{OH}$ was frequently correlated with a heat of adsorption(55, 56).

Rochester and Trebilco(53) examined the adsorption of N, N-diethylaniline on silica immersed in heptane. Silica was evacuated at 873 K under vacuum 10^{-4} N/m^2. Infrared spectra of silica immersed in N, N-diethylaniline-heptane solution are shown in Figure 4. Isolated silanol groups on silica gave an infrared band at 3705 cm^{-1} when immersed in heptane (Figure 4a). The band at 3705 cm^{-1} decreased in intensity as increasing amounts of N, N-diethylaniline were adsorbed onto the silica surface (Figure 4b-i). Concomitantly, two bands at 3620 and approximately 3380 cm^{-1} grew in intensity. The former band was assigned to the -OH stretching vibrations of silanol groups perturbed by the formation of hydrogen bonds with the aromatic Π-electron ring systems of N, N-diethylaniline molecules adsorbed on the surface. The latter band, which shifted from 3400 cm^{-1} (Figure 4c) to 3330 cm^{-1} (Figure 4i) with increasing surface coverage, was assigned to silanol groups perturbed by the formation of hydrogen bonds with the N, N-diethylamino groups of adsorbed

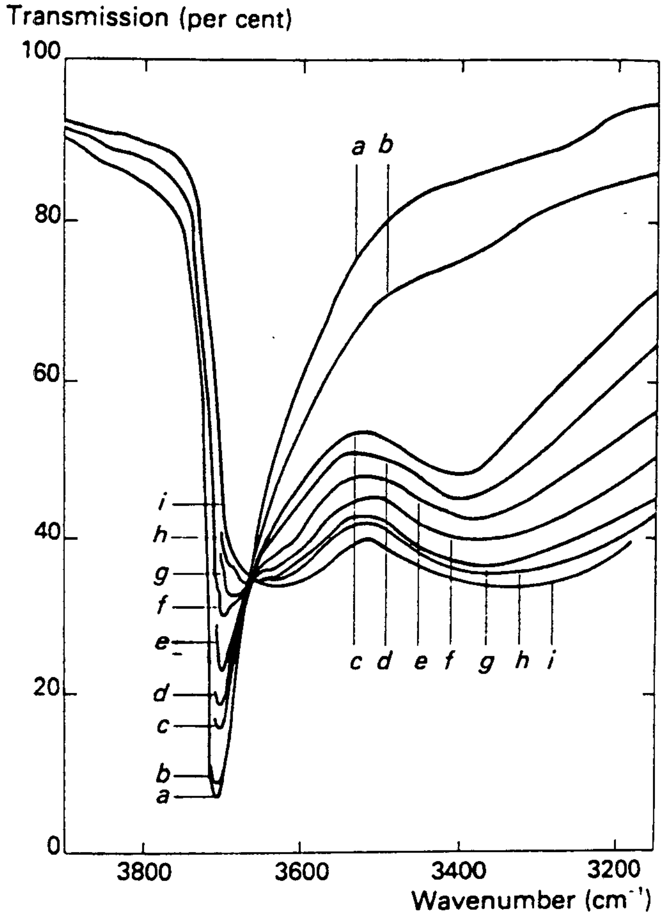
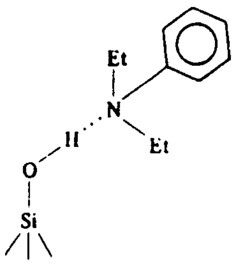
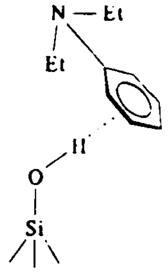


Figure 4. Infrared spectra of silica immersed in (a) heptane, (b)-(i) solutions in heptane of N, N-diethylaniline at concentrations (mmol dm^{-3}) of 1·4, 4·1, 5·5, 11,28, 41, 69 and 138 respectively

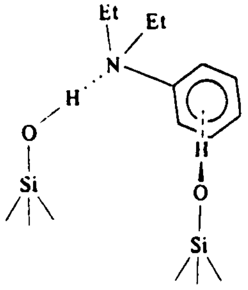
molecules. From these spectroscopic results it is thought that there exist three modes of adsorption as illustrated below.



(I)



(II)



(III)

CONCLUSIONS AND SIGNIFICANCE

Adsorption is one of the fundamental interfacial phenomena. Examining the adsorptive behavior of asphalt functional groups onto aggregate surfaces may enable us to understand the chemistry of asphalt-aggregate interactions. The classical thermodynamics of bulk solutions can be directly applicable to the adsorbed phase, facilitating the interpretation of adsorption data. For instance when single-component adsorption data are fairly well represented by the Langmuir isotherm model, some useful thermodynamic properties are derived: such as an equilibrium constant, a Gibbs free energy change, and a maximum adsorption capacity.

In the case that more than two components are involved in an adsorption process, the adsorption behavior of each component is deviated from its single-component results because of the simultaneous introduction of other components. In most cases the adsorption of each component in a multi-component system is retarded compared to that in a single-component system, but occasionally enhanced or azeotroped. Performing experiments involving multi-component adsorption onto solid surfaces is usually time-consuming. Therefore, it is valuable to predict the multi-component adsorption equilibria using only single component adsorption data. The Langmuir competitive model, the ideal adsorbed solution theory and nonideal adsorbed phase correlations may be applied to interpreting the multi-component systems of asphalt functional groups.

Adsorption mode is another useful property to investigate adsorption behavior at the liquid-oxide interface, the *in situ* spectrum of which is monitored by an infrared spectrometer. The band shift of surface hydroxyl groups of silica (SiOH), $\Delta\nu_{OH}$, is frequently correlated with the heat of adsorption indicating the strength of adsorption bond between functional groups and surface hydroxyl groups. Also, the spectroscopic results provide information on the orientation of adsorbed species at the interface (the structural arrangement of adsorbed species on the oxide surface). The analysis of adsorption mode may facilitate the in-depth understanding of the single- and multi-component adsorption behavior of asphalt functionalities and aggregate systems.

SIGNIFICANCE OF ADSORPTION TO SHRP A-003B RESEARCH

The chemistry of the asphalt-aggregate bond is significant for the long term adhesion between the asphalt and the aggregate. Two aspects of the chemistry involved at the interface can be examined. First, the chemistry of the asphalt with its strongly adsorbing component functionalities and its adhesion behavior is important in characterizing the interface. And second, the chemistry of the aggregate and how the different mineral components attract the asphaltic components are of interest.

This literature review addressed the first topic, that of adsorption. When an organic substance contacts a solid surface, then some adsorption of the organic onto the solid usually occurs.

This adsorption behavior displayed is dependent upon the chemical components of the organic substance such as asphalt, as well as on the chemistry of the adsorbent. Since the chemistry of the interaction between asphalt and aggregate must involve adsorption, studying the individual single component and the multi component adsorption of those heteroatomic species present in asphalt can lead to a more fundamental understanding of how asphalt adheres to aggregate. The thermodynamic information obtained for individual and multiple component systems can lead to a prediction of the adhesive behavior of asphalt that are either rich or lean in the respective functionalities. Not only is the amount of adsorption of a particular functionality important but also the adsorption strength of particular entities can help predict the length of pavement life and the resistance to the disruptive influences of moisture. These predictions, of course, must be examined in terms of the performance of actual pavements.

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