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**Theoretical Aspects of
Multicomponent Adsorption Equilibria
Part II: Limitations in the Application of the
Adsorbed Solution Theory**

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13. ABSTRACT (<i>Maximum 200 words</i>) Theoretical aspects of multicomponent adsorption equilibria are investigated with a focus on the thermodynamically based Adsorbed Solution Theory (AST). A previously published NRL Memorandum Report 6116-97-7946 detailed the development of a computationally fast, heterogeneous, binary adsorption relation using the Langmuir isotherm with the Ideal AST (IAST) as the local, single component and mixture adsorption models. This report outlines the limitations in the AST when applied to systems which contain components demonstrating unfavorable adsorption isotherms. Investigation of organic/water mixture data on activated carbon produces erroneous excess areas of mixing as calculated by the AST. Theoretical studies involving both the Freundlich and constant separation factor isotherms reinforce the calculations from the organic/water mixture AST work-up. The combination of these results indicate that care should be taken when applying the AST to systems that contain one or more unfavorably adsorbed components.			
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TABLE OF CONTENTS

INTRODUCTION	1
ADSORBED SOLUTION THEORY	1
Background	1
ANALYSIS OF PRIOR EXPERIMENT	2
Theory.....	4
Freundlich Isotherm.....	5
Constant Separation Factor Isotherm.....	6
CONCLUSION	8
REFERENCES	9

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NOMENCLATURE

A_s	= Area of the Adsorbent
b	= Langmuir isotherm fitting parameter (1/MPa)
$F(\epsilon)$	= Cumulative (integral) energy distribution
$f(\epsilon)$	= Single probability density function
$g(\epsilon_1, \epsilon_2)$	= Joint probability density function
H, L	= Exponential curve fitting parameters
K, u	= Freundlich parameters
m	= σ_2^2/σ_1^2
N	= Global amount adsorbed (moles/kg)
n	= Amount adsorbed in local homogeneous patch (moles/kg)
P	= Partial pressure (MPa)
Q	= Saturation adsorption value (moles/kg)
R	= Universal gas constant (kJ/mole•K or MPa•L/mole•K)
R_i	= Constant separation factor isotherm parameter
T	= Temperature (K)
X	= Adsorbed phase mole fraction
Y	= Vapor phase mole fraction
Z	= Total number of components in the mixture

GREEK LETTERS

γ_i	= Activity coefficient in the adsorbed phase
ϵ	= Adsorption site energy (kJ/mole)
μ_p	= p^{th} central moment of a probability density function
π	= Spreading pressure
ρ	= Site matching parameter or covariance of the probability density function
σ	= Square root of the variance of a probability density function
σ^e	= Excess area of mixing (kg/mole)
ϕ	= Fugacity coefficient
ψ	= Spreading pressure function $\pi A_s/RT$ (moles/kg)

LIMITATIONS IN THE APPLICATION OF THE ADSORBED SOLUTION THEORY

INTRODUCTION

The need exists for a method to accurately model mixture adsorption equilibria. This need arises not only from an academic desire to understand the fundamentals of the adsorption process, but also from the more pragmatic requirement to provide the nucleus of mathematical models which describe dynamic adsorption systems. In the course of generating results for a dynamic adsorption system using accepted mathematical models, adsorption isotherm relationships are generated hundreds of thousands of times. This points to the importance of generating equilibrium adsorption data with a minimum of computational burden and a high degree of accuracy.

Several models have been developed to describe adsorption systems. The simpler models often are limited in their applicability and accuracy, while the more complicated systems become too cumbersome or unsolvable under some conditions. Several of the models are ultimately correlative in nature. While these models provide important information in understanding the mixture adsorption process, their utility is limited due to the paucity of, and difficulty in obtaining, mixture adsorption data. As a result, models that can predict mixture adsorption from single component adsorption data are becoming more popular.

This study will investigate one of the more popular mixture adsorption theories, the Adsorbed Solution Theory (AST) (Myers and Prausnitz, 1965), and its ability to predict mixture adsorption from single component data. In an effort to isolate pure theory from the effects and inherent errors associated with experimental data, this project was divided into two tasks: A) The development of a computationally fast adsorption isotherm model that can be applied to systems which demonstrate energetic heterogeneity; B) Limitations in the application of the adsorbed solution theory. NRL Memorandum Report 6116-97.7946 (Matuszko and Lamontagne, 1997) detailed the development of part A. This report (part B) will cover the complications and problems encountered when applying the AST to systems that have unfavorably adsorbed components. Since this work focuses primarily on the AST, a short background section of this theory is provided. For an in-depth explanation of AST as applied to this problem, the reader is referred to Matuszko and Lamontagne (1997).

ADSORBED SOLUTION THEORY

BACKGROUND

The Adsorbed Solution Theory (AST) is the most widely used model to describe

adsorption of gas phase mixtures. The AST is a translation of three dimensional solution thermodynamics to the two dimensions of an adsorbed surface. Three dimensional properties such as pressure and volume become the two dimensional properties, spreading pressure and area. In addition, mixing properties associated with nonidealities, such as activity coefficients and excess volume, become adsorbed phase activity coefficients and excess area. The popular theories for incorporating nonidealities into the adsorption system detailed in Matuszko and Lamontagne (1997), assume that, while the overall mixture interactions may be affected by the adsorbent surface, the relative interactions between adsorbates remain the same as those found in a liquid mixture. It is expected, therefore, that adsorbed mixtures should behave similarly to the analogous liquid mixtures.

The adsorption of water and organic mixtures is a case where the translation from solution properties to adsorption properties is of particular interest. As liquids, water and organic mixtures are so highly non-ideal that two separate phases are formed. The translation of this extremely non-ideal behavior to the adsorbed phase has not provided adequate results (Matuszko, 1992), and therefore requires a more thorough investigation.

To simplify the investigation of nonidealities, Talu and Zwiebel (1986) developed a method which strips all but the most basic assumptions governing adsorbate/adsorbate interactions from the AST. The only inherent assumption in the method is that the adsorption system can be described with spreading pressure dependent activity coefficients. Otherwise, all assumptions arising from the choice of a theory for describing excess Gibbs free energy, and hence activity coefficients and excess area of mixing, are removed. This method is a powerful tool in elucidating the exact relationships between adsorbates. The method involves the direct calculation of mixture spreading pressures from binary data and uses them to generate adsorbed phase activity coefficients and excess areas of mixing. These mixing parameters are then used to predict the performance of ternary or other systems which have no mixture data.

This analysis uses Talu and Zwiebel's (1986) method to generate adsorbate/adsorbate interaction parameters for a mixture of perfluorocyclobutane (PFCB) and water on BPL activated carbon. The purpose of this effort is to determine the effect the adsorption process has on the overall value of the activity coefficients and excess area of mixing. While it is accepted that the relative values of these parameters remain the same as those found in a liquid mixture, the overall impact of the adsorption process remains unknown. In addition, as a byproduct of the results of this analysis, a mathematical investigation is made into the application of the AST to an organic/water adsorption system.

ANALYSIS OF PRIOR EXPERIMENT

Adsorption isotherm data for perfluorochlorobutane (PFCB) and water on BPL activated carbon at room temperature were obtained from Matuszko and LeVan (1994). The apparatus and procedure used for the experiments is described in Farris *et al.* (1993). The

data were taken at a constant vapor phase mole fraction so that experimental mixture spreading pressures could be obtained by direct integration of the data. In addition, the experiments were controlled so that each point would fall on the adsorption leg of the water adsorption hysteresis loop. These data can be found in Table 1.

According to Talu and Zwiebel (1986), when data are taken in the constant vapor phase mole fraction plane, the experimental spreading pressure (ψ) can be obtained from:

$$\psi = \int_0^{P_{TOT}} n_{TOT} d \ln P_{TOT} \quad (1)$$

This integral is evaluated by fitting the mixture data points from Table 1 to the curve:

$$n_{TOT} = H[\exp^{(L \cdot P_{TOT})} - 1] = H[\exp^{(L \cdot \exp(\ln(P_{TOT})))} - 1] \quad (2)$$

Where: $H = 0.12866$
 $L = 2087.2$

Equation 2 is plugged into Equation 1, integrated, and the spreading pressure for each mixture data point calculated. Once the experimental spreading pressure (ψ) is obtained for each point, the AST reference values (n_i° and P_i°) can be obtained using:

$$\psi = \int_0^{n_i^\circ} \frac{d \ln P}{d \ln n} dn \quad (3)$$

$$P_i^\circ = \mathcal{F}(n_i^\circ) \quad (4)$$

The integral in Equation 3 is solved for n_i° using Equation 4 (the single component isotherm correlation for each specie). For the purposes of this effort, a three parameter modified Antoine equation (Hacskeylo and LeVan, 1985) was used for PFCB and a four parameter polynomial was used for water. The forms for these equations are identical to those used in Matuszko (1992). The corresponding P_i° value is obtained from Equation 4. The reference values are combined with the experimental mixture values using:

$$P_i = X_i P_i^\circ \gamma_i \quad \text{-----} \quad \gamma_i = \frac{P_i}{X_i P_i^\circ} \quad (5)$$

$$\frac{1}{n_{tot}} = \sum_{i=1}^2 \frac{X_i}{n_i^o} + \sigma^e \quad \text{-----} \quad \sigma^e = \frac{1}{n_{tot}} - \sum_{i=1}^2 \frac{X_i}{n_i^o} \quad (6)$$

The values calculated for σ^e and γ_i can be found in Table 1.

TABLE 1: PFCB and Water mixture adsorption data and AST calculated results

P_1	P_2	n_1	n_2	X_i	ψ	σ^e	γ_1	γ_2
4.613e-04	1.016e-05	0.300	0.176	0.6296	0.1660	-4.6752	9.6013	11369.8
7.792e-04	1.530e-05	1.167	0.250	0.8236	0.3480	-2.5326	5.5778	13909.6
1.004e-03	2.053e-05	0.719	0.256	0.7372	0.5331	-1.2005	5.1050	6667.0
1.300e-03	2.498e-05	2.000	0.305	0.8677	0.8852	-0.8345	3.3254	6810.5
1.449e-03	2.990e-05	1.651	0.292	0.8498	1.1362	-0.4877	2.9499	4443.8
1.680e-03	3.557e-05	3.915	0.310	0.9267	1.6541	-0.3836	2.1884	4833.6
1.942e-03	4.113e-05	8.022	0.194	0.9763	2.5251	-0.2162	1.6597	6014.6
2.428e-03	4.982e-05	22.46	0.020	0.9991	5.5864	-0.0254	1.2897	15322.6

1 = Water 2 = PFCB

The most important information found in Table 1 are the calculated σ^e values. These values represent the change in adsorption area occupied by the components as a result of their interaction with the other specie. Since in an ideal mixture there is no area change on mixing, σ^e is always zero. The table shows, however, that σ^e is always negative for PFCB and water on BPL carbon. Negative σ^e values indicate that the mixture is occupying less adsorption space than would an ideal solution. This result would indicate that PFCB and water associate and attract each other in the adsorbed phase and therefore occupy less adsorption space. Considering that, in the liquid phase, PFCB and water are highly non-ideal and form two separate phases, the results above seem incorrect and require further investigation.

THEORY

To address the excess area anomaly found with PFCB and water, a more thorough investigation into the fundamentals of the AST was initiated. An approach was developed to examine the implications, in general, of using the AST on a mixture which displayed unfavorable single component adsorption behavior. Both Freundlich and constant separation factor isotherms are considered below.

Freundlich Isotherm

Because of its mathematical simplicity, and its ability to easily represent both favorable and unfavorable adsorption isotherms, the Freundlich isotherm was selected for this model study. The Freundlich isotherm takes the form:

$$n_i = K_i P_i^{1/u_i} \quad (7)$$

When u_i is greater than 1, the isotherm is favorable, and when u_i is less than 1, the isotherm is unfavorable. To further simplify the calculations, no mixing nonidealities will be assumed (i.e. the Ideal Adsorbed Solution Theory -- IAST will be used).

The IAST calculations for a binary system have been performed by Crittenden *et al.* (1985) on a Freundlich isotherm taking the Equation 7 form. Crittenden *et al.*, after much algebra, produced the following IAST relationship:

$$P_2 = \frac{n_2}{n_1 + n_2} \left(\frac{u_1 n_1 + u_2 n_2}{u_2 K_2} \right)^{u_2} = \frac{n_2}{n_1 + n_2} \zeta^{u_2} \quad (8)$$

If a derivative with respect to n_1 is taken the equation becomes:

$$\frac{\partial P_2}{\partial n_1} \Big|_{n_2} = \left(\frac{n_2}{n_1 + n_2} \right) \left(\frac{u_1}{K_2} \right) \zeta^{u_2 - 1} - n_2 \left(\frac{1}{n_1 + n_2} \right)^2 \zeta^{u_2} \quad (9)$$

OR

$$\frac{\partial P_2}{\partial n_1} \Big|_{n_2} = \frac{1}{K_2} \left(\frac{n_2}{n_1 + n_2} \right) \zeta^{u_2 - 1} \left[u_1 - \left(\frac{1}{n_1 + n_2} \right) \left(\frac{u_1 n_1}{u_2} + n_2 \right) \right] \quad (10)$$

For normal, ideal, binary isotherm behavior, P_2 must increase if n_1 increases holding n_2 constant. In an ideal adsorbed solution, the adsorbate-adsorbate interactions should be limited to the occupation of adsorption space. Any increase in the amount adsorbed of one component takes up room and tends to crowd out the second component. For the adsorbed amount of the second component to remain unchanged, there should be an increase in the component 2 pressure. Therefore, the quantity in the brackets in Equation 10 should always be greater than zero:

$$u_1 - \left(\frac{1}{n_1 + n_2} \right) \left(\frac{u_1 n_1}{u_2} + n_2 \right) = u_1 - \left(\frac{u_1}{u_2} X_1 + X_2 \right) > 0 \quad (11)$$

OR

$$1 > \frac{X_1}{u_2} + \frac{X_2}{u_1} \quad (12)$$

If u_1 and u_2 are both greater than 1, Equation 12 is always satisfied. If, however, u_1 and/or u_2 are less than 1, then the condition may not be satisfied. If the condition is not satisfied, P_2 would decrease when n_1 is increased with n_2 held constant. This should not happen in an ideal mixture.

The calculations above should be evaluated with care. The Freundlich isotherm does not have a proper Henry's law limit and is therefore not thermodynamically consistent. How this lack of a Henry's law limit affects the ultimate result cannot be determined. For this reason, a similar set of calculations was performed on a constant separation factor isotherm.

Constant Separation Factor Isotherm

The Constant Separation Factor (CSF) isotherm is a mathematically simple type of isotherm of which the Langmuir is a sub-set. The CSF takes the form:

$$P_i = \frac{R_i P_i^{REF} n_i}{n_i^{REF} + n_i (R_i - 1)} \quad (13)$$

The CSF has a proper Henry's law limit and is thermodynamically consistent. As with the Freundlich isotherm, the CSF can represent favorable and unfavorable isotherm types by changing the value of R_i ($R_i < 1$ favorable, $R_i > 1$ unfavorable). Since no analytical IAST solution was found using the CSF, the IAST equations were solved numerically. The results of the numerical solutions can be found in Figure 1. This plot shows how P_2 varies with n_1 while holding n_2 constant for a particular set of parameters. P_2 is normalized to P_2^{PURE} which is the pure component vapor pressure calculated using $n_2 = 0.1$ in Equation 13. Thus, when P_2/P_2^{PURE} is greater than 1, the theory predicts that the mixture partial pressure for component 2 is greater than that found in pure component adsorption for the same amount adsorbed ($n_2 = 0.1$). Conversely, when P_2/P_2^{PURE} is less than 1, the theory predicts that the mixture partial pressure for component 2 is less than the analogous pure component value. In all cases, the amount adsorbed for component 2 (n_2) is fixed with the other variables (n_1 , P_1 , and P_2) allowed to change. Since the mixture calculations performed assume ideality, the two adsorbates should exhibit no attractive interactions. As a consequence, the only interaction the components have with each other should be spatial interference or the occupation of area. If the surface is loaded with one component, then the only way to add a second component is to displace an equal area of the first component to make room. When the surface is not fully loaded, the effect remains the same, but is manifested in a higher partial pressure for the first

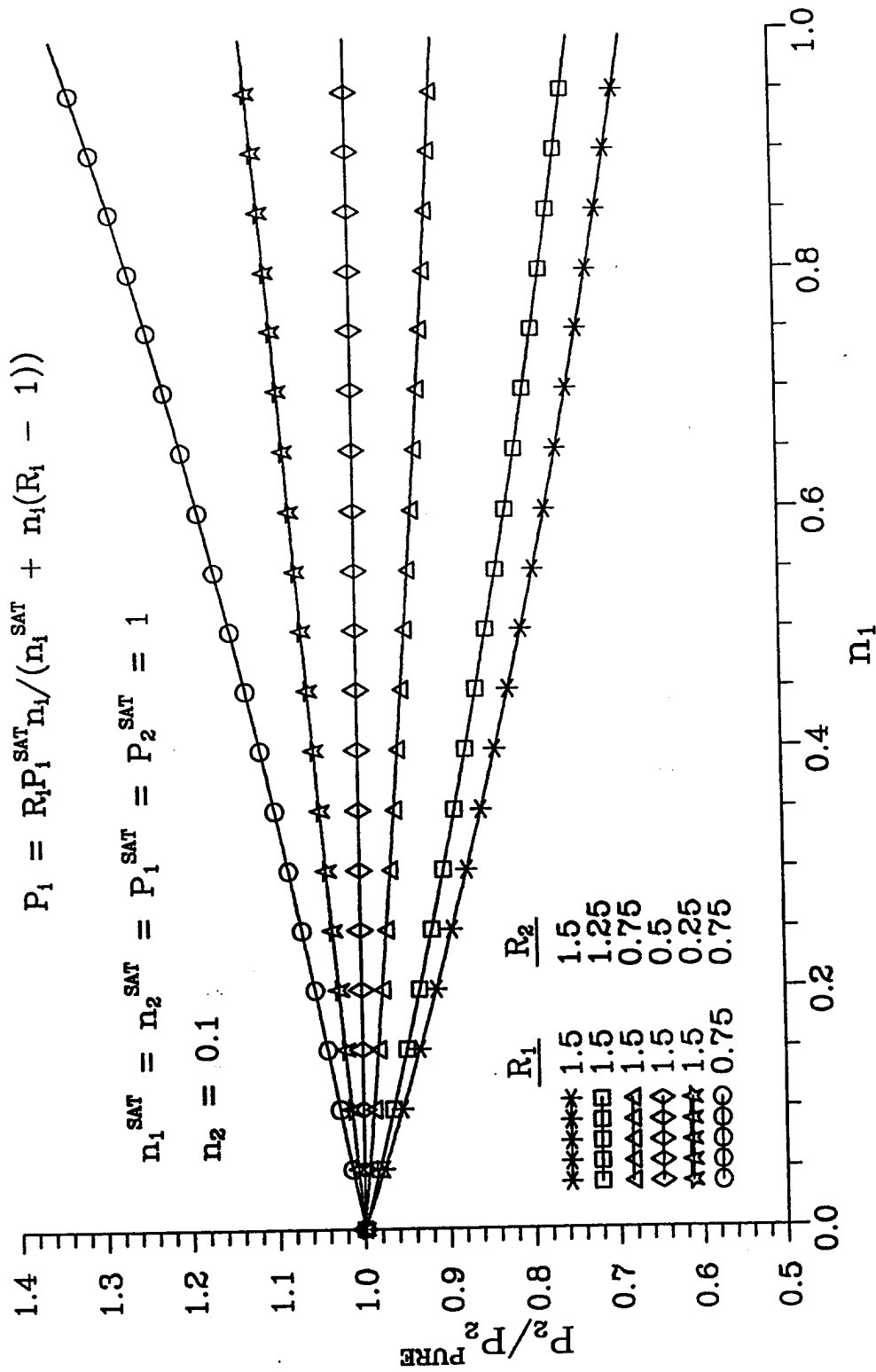


FIGURE 1: Constant Separation Factor Isotherms with Constant n_2

component to "force" the original amount to remain adsorbed. Therefore, the addition of a second component (in this case adding component 1) should crowd out the original pure component (component 2) and require a higher pressure to maintain n_2 at 0.1. As the plot shows, however, whenever one or both of the components demonstrate unfavorable adsorption ($R_i > 1$), the mixture P_2 value is lower than that found when component 2 is adsorbed as a pure component. Once again, it appears that the two components are attracting each other in the adsorbed phase. As with the Freundlich proof above, this should not happen in an ideal system.

It can be shown that, in the limiting case where the monolayer/saturation coverages of a binary system are identical, IAST calculations on an unfavorable CSF isotherm result in the following equation:

$$n_1 = \frac{Qb_1P_1e^{\epsilon_1/RT}}{1 - b_1P_1e^{\epsilon_1/RT} - b_2P_2e^{\epsilon_2/RT}} \quad (14)$$

As with the very similar form for favorable isotherms (Equation 2.2), the subscripts can be switched to create the component 2 equation. Combining the Equation 14 versions for both components, performing a little algebra, and taking a derivative as in Equations 9 and 10 produces:

$$\left. \frac{\partial P_2}{\partial n_1} \right|_{n_2} = \frac{-n_2}{b_2e^{\epsilon_2/RT}(Q + n_1 + n_2)} \quad (15)$$

This derivative must always be less than zero. As with the Freundlich analysis above, values for this derivative that are less than zero indicate that the theory is predicting an attractive action between the two components.

CONCLUSIONS

The analysis of the PFCB/water adsorption data indicates that it may be inappropriate to apply the AST to the specific adsorption system. The mathematical analyses show that the IAST should be applied with care on systems which demonstrate unfavorable single component isotherms. Indeed, these results appear to apply if any component displays unfavorable adsorption at any point in its single component isotherm that is integrated in the IAST calculations. This includes all pressures below the mixture partial pressure, and in some cases, pressures above the mixture partial pressure.

The AST models mixture adsorption by characterizing the adsorbate/adsorbent interactions through single component isotherm data, and providing adsorbate/adsorbate (as

needed) interactions through solution thermodynamics. The AST provides no mechanism to separate adsorbate/adsorbent interactions from "self interactions" of the adsorbates. In the case of water adsorption on activated carbon, or any unfavorably adsorbed component, the shape of the isotherm is a result of a greater attraction between the adsorbed molecules than between the adsorbate and the surface. As more is adsorbed, the adsorbate/adsorbate attraction becomes more dominant. Since the AST does not separate this self interaction from adsorbate/adsorbent interactions, the self interactions will be translated (along with all the other characteristics which dictate the shape of the single component isotherm) into the mixture equations. As a result, additional adsorbates will reflect this adsorbate/adsorbent interaction and therefore demonstrate an increased attraction to the surface as more of the unfavorably adsorbed component is added. In cases where adsorbate self interactions are identical for each component, and identical to the unlike adsorbate/adsorbate interactions, this effect may be appropriate. However, when components do not behave in this similar manner, the AST should be applied with care.

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