EDGEWOOD

CHEMICAL BIOLOGICAL CENTER

U.S. ARMY SOLDIER AND BIOLOGICAL CHEMICAL COMMAND

ECBC-CR-023

PREDICTING ADSORPTION EQUILIBRIA OF MIXTURES: COMPARISON OF POTENTIAL THEORY AND IDEAL ADSORPTION SOLUTION THEORY
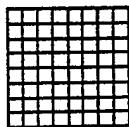
David T. Croft
David K. Friday

Guild Associates, Inc.
Baltimore, MD 21236

October 1999

19991122 115

Guild
Associates, Inc.

Aberdeen Proving Ground, MD 21010-5424

DTIC QUALITY INSPECTED 4

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1999 October	Final; 97 Dec - 99 Jun

4. TITLE AND SUBTITLE
Predicting Adsorption Equilibria of Mixtures: Comparison of Potential Theory and Ideal Adsorption Solution Theory

5. FUNDING NUMBERS
C-DAAM01-96-C-0043

6. AUTHOR(S)
Croft, David T., and Friday, David K.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Guild Associates, Inc., 5022 Campbell Boulevard, Baltimore, MD 21236

8. PERFORMING ORGANIZATION REPORT NUMBER
ECBC-CR-023

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
DIR, ECBC,* ATTN: AMSSB-RRT-PF, APG, MD 21010-5424

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
COR: David E. Tevault, AMSSB-RRT-PF, (410) 436-3860
* When this work started, the U.S. Army Edgewood Chemical Biological Center (ECBC) was known as the U.S. Army Edgewood Research, Development and Engineering Center (ERDEC).

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The Dubinin-Radushkevich (DR) Equation has been used successfully to correlate and predict pure-component adsorption equilibria for a variety of vapors on microporous, carbonaceous adsorbents. Two methods are examined to apply the predictive advantages of the DR Equation to describe multicomponent adsorption equilibria: (1) the method of Grant and Manes, and (2) the method of Myers and Prausnitz. These methods are equivalent whenever the Gibbs adsorption isotherm is satisfied. The DR Equation for mixtures has the "correct" limits whenever more than one component is adsorbed. The thermodynamic theory of mixtures is used to determine if pure-component isotherm data is consistent with the Gibbs adsorption isotherm.

14. SUBJECT TERMS
Adsorption equilibria
Adsorbed mixtures

15. NUMBER OF PAGES
19

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

Blank

PREFACE

The work described in this report was authorized under Contract No. DAAM01-96-C-0043. This work was started in December 1997 and completed in June 1999.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release. Registered users should request additional copies from the Defense Technical Information Center; unregistered users should direct such requests to the National Technical Information Service.

Blank

CONTENTS

Blank

PREDICTING ADSORPTION EQUILIBRIA OF MIXTURES: COMPARISON OF POTENTIAL THEORY AND IDEAL ADSORPTION SOLUTION THEORY

1. INTRODUCTION

The Dubinin-Radushkevich (DR) Equation is useful for correlating, as well as predicting pure-component adsorption equilibrium data for adsorbates that are liquids at the adsorption temperature. It is useful because (1) it is a relatively simple equation that fits adsorption equilibria data of non-polar organic adsorbates reasonably well over a practical range of concentrations and temperatures, (2) the theory on which it is based provides a means of predicting adsorption equilibrium using liquid properties of the adsorbate,[1] and (3) the theory can easily be extended to predict the adsorption equilibrium of mixtures.[2,3] A second approach used to predict adsorption equilibria of adsorbed mixtures from pure-component data is the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.[4] The IAST is rarely used with the DR Equation.[5] This work will show that the DR Equation can be successfully incorporated into the IAST framework.

The DR Equation is based on a theory developed by Polanyi[6] where he proposes that the important intermolecular interactions controlling the adsorption process are electronic dispersion forces. Further, he states that the magnitude of the electronic dispersion forces is both independent of temperature and proportional to the molecular polarizability of the adsorbate. The adsorption potential is, likewise, independent of temperature. In addition to the discussion of intermolecular interactions and the adsorption potential, Polanyi notes that in the limit of low surface coverage, adsorption isotherms should be linear. In more recent literature, this is commonly referred to as Henry's Law.[1,4,7,8,9,10]

Building on Polanyi's work, Dubinin[11] found that many adsorbates have potential curves of similar shape, and he proposed a relationship having two adjustable parameters to fit these data. This is the basis of the well-known Dubinin-Radushkevich (DR) Equation. Polanyi also proposes approximating the molar polarizability using the molar volume, thus providing a means of predicting the parameters of the DR Equation from readily available physical properties of the adsorbate. The DR Equation has proved to be very useful for making practical estimates of adsorption equilibria,[1,12,13,14,15,16] but it is often criticized for lacking a Henry's Law limit.[10,17]

The practical advantage of the Polanyi-Dubinin theory approach is that it is *predictive*. If adsorption equilibria data for an adsorbate-adsorbent pair is available, then the adsorption isotherm for a similar adsorbent on the same adsorbent can be estimated knowing the ratio of the molar volumes of the two adsorbates.[18] In keeping with Dubinin's original work, estimates have also been made using a ratio of a function of molar polarizability.[19] A second advantage is that the same theory can be used to predict adsorption equilibria of mixtures. The

7

theory has some limitations. Perhaps the most significant is that the DR Equation and its relatives do not possess a Henry's Law limit.

Based in part on work reported by Lewis, et al.,[2] Grant and Manes[3] discuss a correlation for predicting equilibria of mixed vapor adsorption. This approach is based on Potential Theory principles only. These principles are discussed in the theory section of this paper. The paper of Myers and Prausnitz[4] also outlines a theory useful for predicting adsorption of mixtures. The IAST is well-tested and often makes good predictions.[1,4,9,14,15] Regardless of its widespread use and acceptance, the IAST is not without problems. As noted by Sircar and Myers,[7] the reference state (the spreading pressure) can become undefined when applied with some systems. This problem is especially pronounced near saturation.[7]

This work compares the multicomponent Potential Theory approach of Grant and Manes[3] with the IAST. Using the DR Equation to correlate pure-component equilibria adsorption, the IAST is compared mathematically to the results obtained from multicomponent Potential Theory. It is shown that the IAST and Potential Theory treatments of multicomponent adsorption produce identical results when the correlation coefficient of the DR Equation is proportional to the molar volume of the adsorbate. This is an assumption of the original DR Equation but has been discarded by some researchers. The significance of the Gibbs adsorption isotherm and the relationship between the Gibbs adsorption isotherm and the basic assumptions of the DR Equation are discussed. It is shown that unless the pure-component adsorption equilibria relationships satisfy the Gibbs adsorption isotherm, the IAST cannot be applied because the resulting equations have no solution. Further, when the Gibbs adsorption isotherm is satisfied, it is shown that the multicomponent Potential Theory and the IAST are equivalent.

2. IDEAL ADSORBED SOLUTION THEORY

The development of the IAST follows closely Gibbs'[20] 1906 treatment of adsorption on the surface of a liquid. Myers and Prausnitz[4] point out that thermodynamic theory sets limits on the number of degrees of freedom of a system. The phase rule for adsorption proposed is

$$(\text{degrees of freedom}) = (\text{number of components}) - (\text{number of phases}) + 3 \qquad (1)$$

where the adsorbent is considered "thermodynamically inert" (that is, it is not considered a component itself). The phase rule for adsorption specifies an additional degree of freedom over the phase rule for bulk solid-liquid-vapor systems. This degree of freedom implies the existence of an independent thermodynamic function of state. In IAST, this is the spreading pressure, π. Myers and Prausnitz write

$$p_i = x_i \, p_i^0(\pi) \qquad (2)$$

8

where p^0 is the pure-component adsorbate partial pressure, x_i is the mole fraction of the *ith* component in the adsorbed phase, and π is the spreading pressure of the mixture. The spreading pressure is defined by the Gibbs adsorption isotherm

$$\frac{\pi A}{RT} = \int_0^{p^0} \frac{n}{p} dp \tag{3}$$

where A is the adsorption area. It is assumed that no change in adsorption area will occur with mixing, so one may express A in terms of pure-component areas and adsorbed phase mole fractions:

$$A = A_1^{\,0} x_1 + A_2^{\,0} x_2 + A_3^{\,0} x_3 \ldots \qquad \text{(constant } T \text{ and } \pi\text{)} \tag{4}$$

Since the adsorbed-phase area is inversely proportional to the adsorbed-phase concentration, one may write

$$\frac{1}{n_t} = \sum \frac{x_i}{n_i^{\,0}} \tag{5}$$

where n_t is the total number of moles adsorbed. The $n_i^{\,0}$ are pure-component adsorbed-phase concentrations which correspond to the spreading pressure of the mixture. The $n_i^{\,0}$ are expressed as implicit functions of the spreading pressure by Equation 3. As is well documented, the IAST makes good predictions, even in some cases where the adsorbates would not be expected to form ideal solutions in the liquid phase.[4]

An example of the IAST using Langmuir pure component isotherms is now given to emphasize a point that was not emphasized by Myers and Prausnitz; the theory places a restriction on the pure-components isotherms. The single component Langmuir isotherms are

$$\ln p_1 = \ln \frac{\theta_1}{\left(1 - \theta_1\right)} - \ln k_1 \tag{6a}$$

$$\ln p_2 = \ln \frac{\theta_2}{\left(1 - \theta_2\right)} - \ln k_2 \tag{6b}$$

where fractional surface coverage $\theta_i = n_i / m_i$ is the adsorbed concentration, and m is the monolayer capacity. Equations 6a and 6b are inserted into Equation 3 to determine the relationship between the adsorbed phase concentration and the spreading pressure of the mixture.

$$\frac{\pi A}{RT} = m_1 \int_0^{\theta_1^0} \theta_1 \, d\frac{\theta_1}{1-\theta_1} = m_2 \int_0^{\theta_2^0} \theta_2 \, d\frac{\theta_2}{1-\theta_2} \tag{7}$$

Equation 7 can be valid only if θ_1^0 is equal to θ_2^0 and m_1 is equal to m_2. For pure-component Langmuir isotherms, equal mono-layer coverages are required for thermodynamic consistency[9] and are consistent with the site-specific assumption used in deriving the Langmuir equation. Using the equal mono-layer coverage restriction demonstrated in Equation 7 (all n_i^0 are equal) one may apply the IAST simply by multiplying Equation 5 by $n_i * n_i^0$ to give the following:

$$n_1^0 = x_1 n_t + x_2 n_t = n_1 + n_2 \tag{8}$$

Another important conclusion that can be drawn from Equation 7 is that θ^0 is a unique function of π.

3. POTENTIAL THEORY

The Potential Theory is in part a thermodynamic theory; but, in addition to thermodynamics, it considers the nature of the intermolecular forces acting in the adsorption process.[6] The adsorption potential is defined as the difference between the chemical potential (the chemical potential was defined by Gibbs[20]) of a substance in the adsorbed state and its chemical potential in a state free from the influence of an adsorbent. The state the adsorbed substance assumes uninfluenced by the adsorbent is taken as the reference state:

$$\varepsilon = \mu - \mu^{ref} \tag{9}$$

In addition to the thermodynamics, it is assumed that the adsorption potential can be expressed by an equation in the following form:

$$\varepsilon = \beta F(\theta) \tag{10}$$

The adsorbent contribution $F(\theta)$ varies depending on the fraction of the adsorption space filled θ, while the adsorbate contribution is characterized by a constant β. Equation 10 follows from the assumption regarding the nature of intermolecular interactions important in the adsorption process: the interactions are due to electronic dispersion.

Building on the work of Lewis, et al.,[2] Grant and Manes apply the Potential Theory to treat multicomponent adsorption. Because $F(\theta)$ of Equation 10 is independent of properties of the adsorbate, the ratio ε / β must also be independent, and, therefore, the same for all adsorbates of the mixture.[3] Grant and Manes, much like Myers and Prausnitz,[4] list a series of

equations, which when solved, simultaneously (usually numerically) predict multicomponent equilibrium from unconstrained and not necessarily related pure-component isotherms. Grant and Manes briefly discuss the conditions under which their theory is equivalent to the IAST but do not mention any required relationship between pure-component isotherms used with their theory. Belfort[21] discusses similarities between the Grant and Manes and IAST, but due to an error in a derivation, reached an incorrect conclusion that the theories were equivalent regardless of relationships between pure-component isotherm equations.

4.   MULTICOMPONENT (MIXTURE) EQUILIBRIA ADSORPTION USING THE IAST WITH PURE-COMPONENT DR EQUATIONS

Even though the DR Equation lacks a Henry's Law limit, it is still possible to use it with the IAST.[17] As an example, the DR Equation for pure-component adsorption equilibria is applied to the IAST pure-component relationships. The DR Equation can be expressed in terms of adsorbate partial pressure:

$$\ln p_1 = \frac{\beta_1 E}{RT}\left[-\ln \theta_1\right]^{1/2} + \ln p_1^{sat} \tag{11a}$$

$$\ln p_2 = \frac{\beta_2 E}{RT}\left[-\ln \theta_2\right]^{1/2} + \ln p_2^{sat} \tag{11b}$$

The fraction of the adsorbed space filled is related to the spreading pressure by substituting Equations 11a and 11b into Equation 3 to get

$$\frac{\pi A}{RT} = \frac{\beta_1 E}{RT} n_1^{sat} \int_{\infty}^{\sqrt{-\ln\theta_1^0}} \theta d\sqrt{-\ln\theta} = \frac{\beta_2 E}{RT} n_2^{sat} \int_{\infty}^{\sqrt{-\ln\theta_2^0}} \theta d\sqrt{-\ln\theta} \tag{12}$$

where the fraction of the adsorption space filled, $\theta_i, = n_i / n_i^{sat}$, n is the adsorbed concentration, and n^{sat} is the adsorbent capacity. The subscript refers to the component number. As with the Langmuir equation, the function of θ in the integral is non-linear, and in order to be valid, all θ_i^0 must be equal ($\theta_i^0 = \theta_2^0$). This is consistent with the assumptions of the Potential Theory for mixtures and similar to the restriction imposed on the Langmuir pure component isotherms in Equation 7. Equation 12 now requires the following relationship be true.

$$\frac{\beta_1}{\beta_2} = \frac{n_2^{sat}}{n_1^{sat}} \tag{13}$$

The adsorbed-phase concentration at saturation is defined as

$$n_i^{sat} = W_0/V_{m,i} \tag{14}$$

where W_0 is a constant representing the capacity of a given adsorbent and is independent of the adsorbate and V_m is the molar volume of the adsorbed phase. Equation 14 requires that the ratio of the correlative coefficients, β_1 and β_2, are equal to the ratio of the adsorbed phase molar volumes V_{m1} and V_{m2}. Unlike the case with the Langmuir isotherm, the saturation capacity of adsorbates can differ for each pure-component DR Equation. This, too, is consistent with the theory on which the equations are based. In place of a site-specific assumption, the Potential Theory assumes the adsorbate fills an adsorption space and the amount of space filled is related to the molar volume of the adsorbed phase.

The conclusions drawn from Equation 12 make completing the IAST derivation using the pure component DR Equations straightforward. Multiplying both sides of Equation 5 by n_t gives the following result:

$$1 = \frac{n_1}{n_1^0} + \frac{n_2}{n_2^0} \tag{15}$$

Dividing denominator and numerator of each term of the sum of Equation 15 by n^{sat}, results in

$$1 = \frac{\theta_1}{\theta_1^0} + \frac{\theta_2}{\theta_2^0} \tag{16}$$

and since $\theta_1^0 = \theta_2^0$, one may derive the following relationship:

$$\theta^0 = \theta_1 + \theta_2 \tag{17}$$

Thus, as expected for an ideal solution, the fraction of the adsorption space filled is equal to the sum of the fractional filling of the components of the mixture.

The general form of the multi-component DR derived from DR pure-component isotherms is

$$p_i = x_i p^0(\theta^0) = x_i p_i^{sat} \exp\left[\frac{V_{m,i}E}{RT}\sqrt{-\ln\left(\sum \theta_j\right)}\right] \tag{18}$$

where the summation is over all j components, including component i. This relation gives the adsorbate partial pressure in terms of the adsorbed-phase concentration and the temperature.

The multi-component form of the DR Equation given by Yang[1,22] is

12

$$n_t = \frac{W_0}{\sum x_i V_{m,i}} \exp\left[-\frac{kT^2}{\left(\sum x_i \beta_i\right)^2}\left(\sum x_i \ln\frac{p^{ref}}{p_i}\right)^2 \right] \qquad (19)$$

where n_t is the total adsorbed-phase concentration, W_0 is the adsorbent capacity, V_{mi} is the adsorbed-phase volume of the ith component, $k = 1/E^2$ is the constant that characterizes the adsorbent, β_i is the correlative coefficient of the ith adsorbate and the mole fractions in the adsorbed phase are related by $\Sigma x_i = 1$. Algebraic manipulation reveals that Equation 19 and Equation 18 are identical if $\beta_i = V_{m,i}$. Since Equation 13 shows that indeed $\beta_i = V_{m,i}$, then one can conclude that the multi-component formulation of Yang and the IAST are equivalent as long as $\theta_1^0 = \theta_2^0$.

An important result obtained from both the Langmuir and the DR derivations is that it is possible to determine p^0 as a function of θ^0 of the mixture as opposed to π. We, therefore, can write Equation 2 in the equivalent form:

$$p_i = x_i\, p_i^0\left(\theta^0\right) \qquad (20)$$

5.   THERMODYNAMIC CONSISTENCY

5.1   Potential Theory and the Gibbs Adsorption Isotherm.

The Gibbs adsorption isotherm written for pure-component adsorption (Equation 5) plays an important role in the IAST. This equation requires that there be a relationship between pure-component isotherms in order for them to be used successfully in making IAST predictions. The relationship between the IAST and the Potential Theory can be illustrated further by expressing it in Potential Theory notation and evaluating the integral. Making the appropriate substitutions, Equation 5 becomes

$$[\pi A] = W^0 \int_{\varepsilon_{p=0}}^{\varepsilon_{p=p_i^0}} \theta\, d\left(\tfrac{\varepsilon}{\beta_i}\right) \qquad (21)$$

where $\theta = \beta_i n_i / W^0$ and $\varepsilon_i = -RT \ln\dfrac{p_i}{x_i\, p^{0,sat}}$. It has been shown that for non-linear adsorption equilibria, the spreading pressure must be a unique function of the fraction of the adsorption space filled. This is the case when the differential, $d\left(\tfrac{\varepsilon_i}{\beta_i}\right)$, of Equation 21 is of the form $d\,F(\theta)$. Integrating Equation 21, keeping in mind that T is held constant, results in the following:

13

$$\varepsilon_i = \beta_i F(\theta^0, T) + \beta_i G(T) \tag{22}$$

If the potential is assumed to be independent of temperature and if $G = 0$, Equation 22 is identical to Equation 10 of the Potential Theory; thus the Potential Theory is consistent with the Gibbs adsorption isotherm. Furthermore, when using the IAST, the functions $F(\theta, T)$ and $G(T)$ must be the same functions for all pure components of the mixture. If they are not, the pure-component isotherms are mutually inconsistent with the Gibbs adsorption isotherm, and there will be a region of the concentration space where the spreading pressure will become undefined.

5.2   Henry's Law for the DR Equation.

The DR Equation is criticized for lacking a Henry's Law limit.[17] Henry's Law for adsorption requires that in the limit as the vapor-phase concentration approaches zero, adsorption isotherms must be linear. The Langmuir equation has a Henry's Law limit. In this section the limiting behavior of the DR Equation for ideal mixtures is explored. Parameters for a hypothetical binary DR Equation are shown in the Table below. Several Henry's Law plots of predictions of this binary equation are shown in the Figure. Whenever some of Component 2 is adsorbed, the predicted isotherm of Component 1 becomes linear as its concentration approaches zero. Thus, the Henry's Law is satisfied at all times as long as at least two components are adsorbed.

Table. Mixture Parameters For The DR, $V_m = \beta$.

Component	W^0 (ml/kg)	β (ml/mol)	E (J/ml)
1	500	100	100
2	500	200	100

6.   DISCUSSION

It is important to note that when F is independent of temperature and $G = 0$, the basis of the Polanyi Potential Theory, Equation 22 is identical to Equation 10. The Potential Theory, therefore, conforms to the restrictions imposed by the Gibbs adsorption isotherm. The Gibbs adsorption isotherm, however, is less restrictive than the Potential Theory and allows also for a function of temperature. This is because the IAST does not assume anything regarding the nature of the intermolecular interactions involved in adsorption.

The pure-component DR Equation does not have a Henry's Law limit, but the multicomponent DR does. If there is more than one adsorbate, and Component 2 is maintained
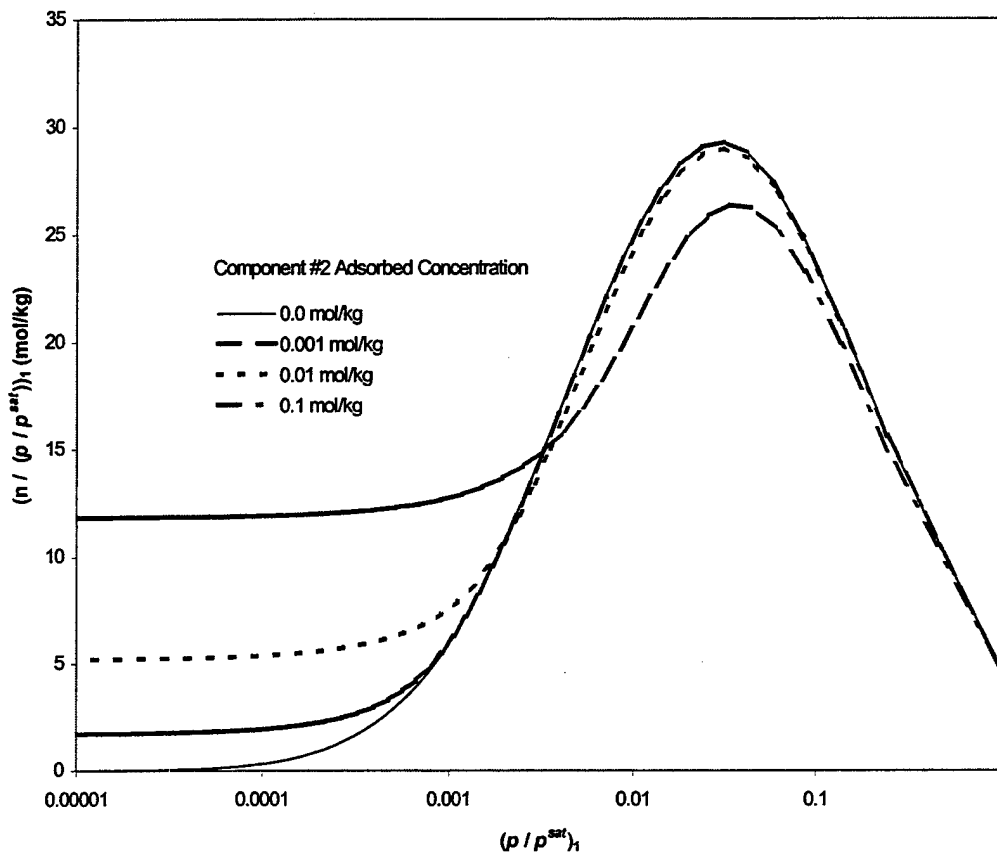
14

Figure. Natural Henry's Law Limit of the IAST-DR Equation for a Binary
System Consisting of Components 1 and 2.

at a finite concentration while the concentration of Component 1 is reduced to an infinitesimal
level, Component 1-Component 1 interactions will become insignificant. Component 2-
Component 1 interactions give rise to a Henry's Law limit, much as Component 1-adsorbent
interactions give rise to a Henry's Law limit for the Langmuir.

The Gibbs adsorption can be used to check the mixture data for consistency.
When doing IAST calculations, Equation 3 is used to determine the pure-component adsorbed-
phase concentration corresponding to the spreading pressure of the mixture. When there is a
unique spreading pressure of the mixture, the theory places a condition on pure-component
isotherms. Therefore, in addition to mixture isotherms, two sets of pure-component isotherm
data can be checked for consistency with the Gibbs adsorption isotherm.

An important practical consequence of this is when Equation 22 is satisfied by
analytical pure-component isotherm equations, the IAST-multicomponent form, Equation 22, is

15

also *analytical.* In many cases when pure-component isotherms are used with the IAST, numerical solutions are unnecessary.

7.   CONCLUSION

The IAST and the Potential Theory mixing rules are reviewed with particular emphasis on application with the DR Equation. It is shown that the IAST and the Potential Theory mixing rules either differ or are the same, depending on the relationship between pure-component equations with which they are applied. When Equation 22 is satisfied, the two approaches give identical results. When Equation 22 is not satisfied, results differ. Furthermore, when Equation 22 is not satisfied, the numerical method does not converge.

When the DR Equation is used with the IAST to derive an equation to describe mixture adsorption, the resulting equation has a Henry's Law limit, as well as a finite enthalpy of adsorption at low loading of a given component i as long as another component is present.

When mutually consistent pure-component isotherm equations can be solved analytically for partial pressure in terms of adsorbed-phase concentration and temperature, mixture equations derived using the IAST are also analytical.

LITERATURE CITED

1.   Yang, R.T., "Gas Separation by Adsorption Processes," In Butterworth's Series on Chemical Engineering, Butterworth Publishers, Boston, MA, 1987.

2.   Lewis, W.K., Gilliland, E.P., Chertow, B., and Cadogan, W.P., "Adsorption Equilibria - Hydrocarbon Gas Mixtures," Ind. & Chem. Engineering, Vol. 42, No. 7, p 1319 (1950).

3.   Grant, R.J., and Manes, M., "Adsorption of Binary Hydrocarbon Gas Mixtures on Activated Carbon," I&EC Fundamentals, Vol. 5, No. 4, p 490 (1966).

4.   Myers, A.L., and Prausnitz, J.M., "Thermodynamics of Mixed-Gas Adsorption," AIChE Journal, Vol. 11, No. 1, p 121 (1965).

5.   Lavanchy, A., Stockli, M., Wirz, C., and Stoeckli, F., "Binary Adsorption of Vapours in Active Carbons Described by the Dubinin Equation," Adsorption Science & Technology, Vol. 13, No. 6, p 537 (1996).

6.   Polanyi, M., "Section III. Theories of the Adsorption of Gases. A General Survey and Some Additional Remarks," Trans. Faraday Soc., Vol. 28, p 316 (1931).

7.   Sircar, S., and Myers, A.L., "Surface Potential Theory of Multilayer Adsorption From Gas Mixtures," Chemical Engineering Science, Vol. 28, p 489 (1973).

8.   Rudisill, E.N., and LeVan, M.D., "Standard States for the Adsorbed-Solution Theory," Chemical Engineering Science, Vol. 47, No. 5, p 1239 (1992).

9.   Myers, A.L, "Activity Coefficients of Mixtures Adsorbed on Heterogeneous Surfaces," AIChE Journal, Vol. 29, No. 4 (1983).

10.   Giona, M., and Giustiniani, M., "Size-Dependent Adsorption Models in Microporous Materials. 1. Thermodynamic Consistency and Theoretical Analysis," Ind. Eng. Chem. Res., Vol. 34, p 3848 (1995).

11.   Dubinin, M.M., "The Potential Theory of Adsorption of Gases and Vapors for Adsorbents with Energetically Nonuniform Surfaces," Chem. Rev., Vol. 60, p 235 (1960).

12.   Malek, A., and Farooq, S., "Comparison of Isotherm Models for Hydrocarbon Adsorption on Activated Carbon," AIChE Journal, Vol. 42, No. 11, p 3191 (1996).

13.　Bulow, M., and Wappler, H.J., "Adsorption of Gas Mixtures on Solids," Journal of Colloid and Interface Science, Vol. 85, No. 2, p 457 (1982).

14.　Hacskaylo, J.J., Studies of Adsorption Equilibria, Ph.D. Dissertation, University of Virginia, Charlottesville, VA, 1987.

15.　Werner, M.D., and Winters, N.L., "A Review of Models Developed to Predict Gaseous Phase Activated Carbon Adsorption of Organic Compounds," CRC Critical Reviews in Environmental Control, Vol. 16, p 327 (1988).

16.　Mahle, J.J., Buettner, L.C., and Friday, D.K., "Measurement and Correlation of Adsorption Equilibria of Refrigerant Vapors on Activated Carbon," Ind. Eng. Chem. Res., Vol. 33, p 346 (1994).

17.　Talu, O., and Myers, A.L., "Rigorous Thermodynamic Treatment of Gas Adsorption," AIChE Journal, Vol. 34, No. 11 (1988).

18.　Ruthven, D.M., Principles of Adsorption and Adsorption Processes, John Wiley & Sons, Inc., New York, NY, 1984.

19.　Wood, G.O., Estimation of Activated Carbon Adsorption Capacities For Vapors, Los Alamos National Laboratory, MS K486, Los Alamos, NM.

20.　Gibbs, J.W., Scientific Papers, Langman and Green and Co., New York, NY, 1906.

21.　Belfort, G., "Similarity of Ideal Adsorbed Solution and Potential Theories for Adsorption from a Bulk Phase onto a Solid Surface," AIChE Journal, Vol. 27, No. 6, p 1021 (1981).

22.　Bering, B.P., Serpinsky, V.V., and Surinova, S.I., Izv. Skad. Nauk. SSSR, Otd. Khim. Nauk, 769 (1965).

GLOSSARY

E	adsorbent potential field parameter of DR equation (βE has units of J/mol)
F	general function
G	general function
p	partial pressure (Pa)
p^0	pure-component partial pressure (Pa)
p^{sat}	partial pressure at liquid saturation pressure (Pa)
n	adsorbed-phase concentration (mol/kg)
n^0	adsorbed-phase concentration corresponding to the pure-component partial pressure (mol/kg)
n^{sat}	adsorbed-phase concentration in equilibrium with the liquid saturation pressure (mol/kg)
n_t	total adsorbed-phase concentration of a mixture (mol/kg)
R	gas constant (J/mol-K)
T	temperature (K)
V_m	adsorbed-phase molar volume (cm³/mol)
W_0	adsorbent capacity (W_0/β has units of mol/kg)
x	mole fraction
y	variable

Greek

β	correlating coefficient of DR equation (βE has units of J/mol)
ε	the adsorption potential (J/mol)
πA	product of spreading pressure and adsorption area (J/mol)
θ	fraction of the adsorption space filled
θ^0	fraction of the adsorption space filled corresponding to the pure-component partial pressure

Subscript

i	property of the *ith* component