

COMPARISONS OF D/R MODELS OF EQUILIBRIUM ADSORPTION OF BINARY MIXTURES OF ORGANIC VAPORS ON ACTIVATED CARBONS

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Introduction

A variety of equations and sets of equations (“models”) have been proposed for calculating total and component equilibrium adsorption capacities of mixtures of vapors on activated carbons. The bases for such multicomponent adsorption models are always the adsorption isotherm equations and parameters of individual components. Many isotherm equations have been proposed for describing adsorption isotherm data (Freundlich, Langmuir, Langmuir/Freundlich, Dubinin/Radushkevich, Polanyi, Kisarov, Vacancy Solution Model, and Johns). The Dubinin/Radushkevich adsorption isotherm equation [1] is the most versatile, proven, and useful model for predicting, as well as describing, equilibrium adsorption capacities of organic vapors on ordinary commercial activated carbons [2]. For specialized carbons the more general Dubinin/Astakhov equation [3] with an additional parameter can be used. These Dubinin equations have the advantages of including: a) carbon property parameters, b) vapor property parameters, and c) temperature.

Therefore, only mixture models based on the Dubinin/Radushkevich (D/R) adsorption isotherm equation were included in this study. The single vapor D/R equation for n moles adsorbed (e.g., mol/g) in equilibrium with its vapor pressure (or concentration in any consistent units) p can be expressed as:

$$n = \frac{W_o}{V_m^o} \exp \left[- \left(\frac{RT}{\beta E_o} \right)^2 \left\{ \ln \left(\frac{p_{sat}}{p} \right) \right\}^2 \right] \quad (1)$$

where W_o (cm^3/g) is the micropore volume of the adsorbent and E_o (kJ/mol) is its reference adsorption energy; V_m^o (cm^3/mol) is the liquid molar volume of the adsorbate, β is its affinity coefficient (relative to the reference), and p_{sat} is the vapor pressure of its unadsorbed bulk form at temperature T . One of the best features of the D/R equation is the inclusion of the affinity coefficient, which allows the application of the parameters of micropore volume and reference adsorption energy measured with one vapor to predict adsorption capacities of other vapors. A thorough review with compilations and correlations of affinity coefficients has been published [4], which makes single vapor isotherms easily predictable. Benzene is usually chosen as the reference vapor ($\beta = 1.0$).

In searching and reviewing the diverse and scattered literature we recognized the need to summarize proposed multicomponent models and publish them together in one place. Since they have been validated based on different and limited data sets (often for light gases, not vapors of condensable chemicals), we also saw a need to compare models with a common set of multivapor data.

Models Tested

Mixed D/R Isotherm Equations: The simplest extensions of the D/R equation to mixtures of miscible components involve mole fraction (x_i) weighting of affinity coefficient (β_i), partial liquid molar volume (V_{mi}), and adsorption potential ($\epsilon_i = RT \ln[p_{si}/p_i]$) parameters of the components i to calculate total molar capacity, n_T , for the mixture. This was first proposed by Bering et al. [5]:

$$n_T = \frac{W_o}{V_{mT}} \exp \left[- \left(\frac{\epsilon_T}{\beta_T E_o} \right)^2 \right] \quad (2)$$

$$\begin{aligned} \text{where } \beta_T &= \sum x_i \beta_i \\ V_{mT} &= \sum x_i V_{mi} \\ \epsilon_T &= RT \sum x_i \ln(p_{si}/p_i) \end{aligned}$$

This equation will be called the Bering1 model.

Bering et al. [5] also proposed an alternative in which the relative partial pressures of the components of the mixture are set equal to the ratio of the sum of the pressures of the components to the sum of the standard state pressures. For a binary mixture this is:

$$\frac{p_{s12}}{p_{12}} = \frac{p_{s1} + p_{s2}}{p_1 + p_2} \quad (3)$$

The corresponding D/R equation for a multicomponent mixture is:

$$n_T = \frac{W_o}{V_{mT}} \exp \left[- \left(\frac{RT}{\beta_T E_o} \right)^2 \left(\ln \left(\frac{\sum p_{si}}{\sum p_i} \right) \right)^2 \right] \quad (4)$$

This equation will be called the Bering2 model.

Another approach has been taken in weighting adsorption potentials. Xie et al. [6] used:

$$\varepsilon_T = \sum x_i \ln (\gamma_i x_i p_{\text{sati}}^{\circ} / p_i) \quad (5)$$

where γ_i are activity coefficients, which in their applications for three binary mixtures (benzene-hexane, benzene-pentane, and hexane-pentane) on two carbons were apparently taken as unity. They did not use the D/R equation, but a similar one with the same weighted terms and an additional empirical parameter for micropore size distribution homogeneity. Using this weighting approach with the Bering1 Equation (2) gives:

$$n_T = \frac{W_o}{V_{mT}} \exp \left[- \left(\frac{RT}{E_o} \right)^2 \left\{ \frac{\sum x_i \ln (x_i p_{\text{sati}}^{\circ} / p_i)}{\beta_T} \right\}^2 \right] \quad (6)$$

Taking the standard reference component pressures to be $x_i p_{\text{sati}}^{\circ}$ (superscript o indicates pure component) is the same as assuming Raoult's Law and an ideal adsorbed solution (see later discussion). Therefore, Equation (6) will be referred to as the Bering1-IAS model and option.

Mixture D/R isotherm equations such as Equations (2), (4), and (6) give only the total moles of mixture adsorbed. The component distributions (e.g., as moles n_i or mole fractions x_i) must be known or determined independently by another assumption and equation.

Lewis Equation: The equation most often used to obtain moles of mixture components when total molar capacity is known or calculated is:

$$\sum \frac{n_i}{n_i^{\circ}} = 1 \quad (7)$$

where n_i° are the reference adsorbed molar capacities of the pure components and n_i are the molar capacities of the components in the adsorbed mixture. It is based on an empirical correlation obtained for adsorption from constant total pressure mixtures of hydrocarbon gases by Lewis et al. [7]. The Lewis Equation for a binary mixture in terms of mole fractions and total molar capacity (mol/g) is:

$$\frac{1}{n_T} = \frac{x_1}{n_1^{\circ}} + \frac{x_2}{n_2^{\circ}} \quad (8)$$

Xie et al. [6] proposed a volumetric form of the Lewis Equation for non-ideal mixtures:

$$\sum \frac{V_{mi} n_i}{V_{mi}^{\circ} n_i^{\circ}} = 1 \quad (9)$$

Partial molar volumes V_{mi} for each mixture composition must be obtained from independent mixing data. The Lewis Equation can also be used to calculate total molar capacity when the mole fractions are determined by another method (see below).

Since the original Lewis correlation was obtained from mixtures at constant total pressure, the reference adsorbed molar capacities n_i° should be calculated at $p_i^{\circ} = \sum p_j$, the total pressure of the components, rather than at p_i . However, Lavanchy et al. [8] and Sundaram [9] both successfully applied the Lewis Equation assuming Raoult's Law for an ideal solution for which $p_i^{\circ} = p_i / x_i$. For these cases the proper D/R standard reference pressure is $p_{si} = p_{\text{sati}}^{\circ}$, the saturation vapor pressure of the pure component i .

Polanyi Adsorption Potential Theory: One of the most popular theories relating adsorption of vapors of single pure chemicals is the Polanyi Theory [10]. Lewis et al. [7] and Grant and Manes [11] have developed it for mixtures. The latter assumed: a) a liquid-like adsorbate mixture in which the adsorption potential of each pure adsorbed component is determined by the total adsorbate volume of the mixture, b) Raoult's Law as the relationship between the partial pressure of each component and its adsorbate mole fraction, and c) the adsorbate volumes are additive. According to the Polanyi Theory all characteristic curves (adsorption capacities vs. adsorption potentials) on a given adsorbent are superimposable to form a single curve by using correlating divisors for the adsorption potentials. This correlating divisor can be a) molar volume calculated at the boiling point corresponding to adsorption pressure [7], b) normal boiling point molar volume [11], or, more generally, c) the affinity coefficient β of Dubinin [1,3]. This theory for mixtures states that:

$$\left(\frac{RT}{\beta_1} \right) \ln (x_1 f_{1s} / f_1) = \left(\frac{RT}{\beta_2} \right) \ln (x_2 f_{2s} / f_2) = \text{etc.} \quad (10)$$

Fugacities f_i (and f_{is} for saturated vapors) used by Grant and Manes for high-pressure gases can be replaced with partial (and saturated vapor) pressures p_i or concentrations C_i at normal atmospheric conditions.

Grant and Manes [11] used the additivity of molar volumes:

$$V_T = n_T \sum x_i V_{mi} \quad (11)$$

and the sum of mole fractions x_i in the adsorbate equal to unity to calculate the numbers of moles of each component adsorbed. However, this assumption of additivity is not a necessary part of the Polanyi mixture theory. Mixture isotherm equations, the Lewis Equation, Molar Proportionality, or any other way of calculating or measuring total adsorbed molar capacity can be combined with the mole fractions obtained from Equation (10) to get molar capacities of mixture components.

Ideal Adsorbed Solution Theory (IAST): Myers and Prausnitz [12] are credited with the thermodynamically

consistent Ideal Adsorption Solution Theory, sometimes called the Myers-Prusnitz theory. They assumed Raoult's Law and the concept of equality of spreading pressures Π_i for each component:

$$\Pi_i = \frac{RT}{A} \int_0^{p_i^o} \frac{n_i^o}{p_i} dp_i \quad (12)$$

where n_i^o is the number of moles of pure component i in the adsorbed phase obtained from a pure component isotherm for a vapor pressure p_i . The value of p_i^o is that corresponding to the spreading pressure. A is the specific area of the sorbent. Grant and Manes [11] stated that their adsorption theory for mixtures and the IAST are practically equivalent if the correlating divisor is molar volume.

A major difficulty with the IAST model is the requirement that the adsorption isotherms (actually, the n_i/p_i ratios as functions of p_i) be accurately defined to zero pressure and capacity, so that they can be integrated. Some have used Freundlich and other isotherm equations with this property or have fit the lower coverage portion of experimental or theoretical isotherms with empirical equations that can be integrated analytically. Sundaram [9] truncated a logarithmic expansion of the inverted D/R Equation (1) to get the Henry's Law limit and apply the IAST. Alternately, Grant and Manes [11] pointed out that the integration difficulties for the IAST could be overcome by using any Polanyi-type correlation. Subsequently, Lavanchy et al. [8] derived analytical solutions for the integrations of the Dubinin/Radushkevich and Dubinin/Astakhov equations to calculate spreading pressures. Their D/R-Ideal Adsorbed Solution equation for spreading pressure is:

$$\Pi_i = \left(\frac{W_o \beta_i E_o \sqrt{p}}{2V_{mi} RT} \right) \left(1 - \operatorname{erf} \left[\left(\frac{RT}{\beta_i E_o} \right) \ln \left(\frac{x_i p_{sati}^o}{p_i} \right) \right] \right) \quad (13)$$

where erf is the classical error function, which can be approximated [16] by a series:

$$\operatorname{erf}(x) = \frac{2}{\sqrt{p}} \left(x - \frac{x^3}{3} + \frac{x^5}{10} - \frac{x^7}{42} + \frac{x^9}{216} - \dots \right) \quad (14)$$

In applying this model, spreading pressures for the components are balanced by adjusting the mole fractions, which must add up to unity.

A volumetric form of the IAST can be called the Volumetric Adsorbed Solution Theory (VAST). Since molecules of mixture components occupy different volumes, their evaporation rates and corresponding pressures should be proportional to volume fractions, not mole fractions (all intermolecular interactions being

equal). Also, since activated carbon is a volume filling sorbent, we should have a "filling pressure", rather than a spreading pressure. Equation (13), then, can be used to equate filling pressures and calculate volume fractions, which can be converted to mole fractions by knowing partial molar volumes in the corresponding mixture.

As with the Polanyi Adsorbed Potential Theory, which also gives adsorbed mixture component distributions, the IAST and VAST require a second equation to determine total and component adsorbed capacities.

Exclusion Theories: Models based on exclusion assume that each adsorbate in a mixture reduces the sorbent available for adsorbing the other(s). In Molar Exclusion the adsorbates reduce the number of surface sites or area; in Volume Exclusion they reduce adsorption volume. The adsorbates are still considered independent and existing as if they are in the pure state; only the area or volume to be filled is less for each because of the presence of the other. Doong and Yang [14] proposed a Volume Exclusion Model for the D/R equation, such that for component 1 of a binary mixture:

$$V_1 = (W_o - V_2) \exp \left[- \left(\frac{RT}{\beta_1 E_o} \ln \frac{p_{s1}}{p_1} \right)^2 \right] \quad (15)$$

where V_1 and V_2 are the micropore volumes occupied by adsorbed mixture components 1 and 2 from the total micropore volume W_o . If the D/R isotherms for the pure components show significantly different micropore volumes, W_{o1} and W_{o2} , these can be used. Benefits of the Doong/Yang simple volume exclusion model include: a) solvable by simple matrix solutions without the need for iteration, even for multiple components, and b) yielding both distributions and quantities of adsorbed mixture components without a second equation.

Proportionality Theories: The simplest model for predicting adsorption capacities of mixtures from known distributions (or distributions from total binary mixture capacity) is the Molar Proportionality Model (or Method). It incorporates the assumption that the amounts adsorbed from a vapor mixture are proportional by adsorbate mole fractions to the amounts n_i^o that would have been adsorbed from a pure vapor at the same partial vapor pressure (or concentration). In other words, the different components do not interact except to "deny" adsorption to one another. This assumes a limited number of moles (adsorption sites or surface area) can be covered (the Langmuir isotherm assumption). For a binary vapor mixture (two vapors excluding air components) the total n_T and individual amounts (e.g., mol/g) η adsorbed according to Molar Proportionality is:

$$n_T = x_1 n_1^o + x_2 n_2^o \quad (16)$$

This can easily be extended to any number of vapor components. Similarly, Volume Proportionality states:

$$V_T = z_1 V_1^\circ + z_2 V_2^\circ \quad (17)$$

Any single-vapor isotherm, including the D/R, can be used to calculate the pure vapor adsorption capacities n_i° or volumes V_i° .

Standard State Options: The Lewis, Proportionality, and Exclusion Models are all interpolations between capacities of the pure components. The pressures p_i° and/or reference standard pressures p_{si}° at which these pure component capacities n_i° are to be calculated by Equation (1) is up for discussion. The first option is the Single Vapor Isotherm (SVI), where $p_i^\circ = p_i$, the partial vapor pressure of component i in equilibrium with the mixture, and $p_{si}^\circ = p_{sati}^\circ$, the saturation vapor pressure of pure i . The second is the Ideal Adsorbed Solution (IAS) assumption, where $p_i^\circ = x_i/p_i$ or $p_{si}^\circ = x_i p_{sati}^\circ$ (not both). Similarly, the third is the Ideal Volumetric Solution (IVS), where $p_i^\circ = z_i/p_i$ for volume fractions z_i . From the Lewis correlation we also have the possibility that the reference capacities n_i° should be calculated at the total pressure, so that $p_i^\circ = \Sigma p_i$. In this paper we will explore these options with the above-mentioned models.

Comparisons

Database Selection: Criteria for selecting mixture equilibrium adsorption data for testing of predictive models required listings of: a) D/R parameters of the pure components (or data from which they could be derived); b) vapor phase pressures of components in adsorbed mixtures; c) adsorbed phase capacities and distributions; d) information on conditions, such as temperature; and e) an activated carbonaceous sorbent.

Four sources of data meeting these criteria were selected: Lavanchy et al. [8] published such data for 20 binary mixtures of chlorobenzene and carbon tetrachloride on an activated carbon at 298 °K. Stoeckli et al. [15] tabulated data for 18 benzene and 1,2-dichloroethane mixtures on the same carbon at 293 °K. Xie et al. [6] published 42 data for three binary mixtures (benzene-hexane, benzene-pentane, and hexane-pentane) on an activated carbon and a carbon molecular sieve. Hoppe and Worch [16] published gas phase pressures and adsorbed phase capacities for 13 mixtures of benzene and isopropanol at 303 °K. Although the latter did not give the D/R parameters for the pure components, they did list calculated pure component spreading pressures/RT for vapor pressures 400 – 4800 Pa. From the benzene spreading pressures and Equation (13) we calculated a best-fit reference adsorption potential of $E_0 = 10.29$ kJ/mol and micropore volume of $W_0 = 0.517$ cm³/g. This gave a total of 93 binary mixtures to study. Table 1 lists the mixtures and D/R parameters used for model comparisons. Affinity coefficients were calculated from molecular parachors.[4]

Component Molar Volumes: In applying the models discussed above a question is what to use for component molar volumes V_{mi} in adsorbed mixtures. Data on volume changes upon mixing vs. mixture composition are necessary for exact values; however, they are seldom available. On the other hand, molar volumes of pure liquids are readily calculated from liquid densities d_L and molecular weights M_w as $V_{mi}^\circ = M_w/d_L$. Doong and Yang reviewed other equations for estimating molar volumes above normal boiling points [14]. Since one goal of our work is to predict adsorption capacities of components of a wide variety of liquid mixtures using a minimum amount of input data, which must be readily available, in this paper we choose to use pure liquid molar volumes (20 – 25 °C), even for components of adsorbed mixtures.

Table 1. Mixtures and D/R parameters used for calculations

Binary Mixture Components	Carbon Designation	Dubinin/Radushkevich Isotherm Parameters (Benzene Reference)			Data Source
		Micropore Volume (cm ³ /g)	Adsorption Potential (kJ/mol)	Affinity Coefficients	Ref
Chlorobenzene—Carbon Tetrachloride	Activated Carbon U-02	0.448	17.00	1.17, 1.06	8
Benzene—1,2-Dichloroethane	Activated Carbon U-02	0.448	17.00	1.00, 0.91	15
Benzene—Hexane	Carbon Mol Sieve J-1	0.469	18.70	1.00, 1.28	6
Benzene—Pentane	Carbon Mol Sieve J-1	0.469	18.70	1.00, 1.11	6
Hexane—Pentane	Carbon Mol Sieve J-1	0.469	18.70	1.28, 1.11	6
Benzene—Hexane	Activated Carbon GH-28	0.602	15.20	1.00, 1.28	6
Benzene—Pentane	Activated Carbon GH-28	0.602	15.20	1.00, 1.11	6
Hexane—Pentane	Activated Carbon GH-28	0.602	15.20	1.28, 1.11	6
Benzene—Isopropanol	Activated Carbon B-4	0.517	10.29	1.00, 0.82	16

Results and Discussion

Total Capacity Calculation Comparisons: The first test of the models discussed above with the options and data discussed above was how well their calculated total adsorbed mixture capacities compared with reported total capacities. Calculations were done for each of the 21 models and options listed in Table 2 and each of the 93 mixtures. Average and Standard Deviations from the experimental values are listed in Table 2; these represent measures of accuracy and precision, respectively.

Table 2. Total Capacity of Mixtures Calculations: Models' Average Deviations (Accuracy) and Standard Deviations (Precision) from Experimental Values for 93 Binary Mixtures.

Model and Option	Total Capacity (mmol/g)	
	Average	Std Dev
Volume Proportionality-SVI	-0.318	0.47
Volume Proportionality-IAS	0.008	0.38
Volume Proportionality-IVS	-0.003	0.38
Molar Proportionality-SVI	-0.293	0.46
Molar Proportionality-IAS	0.024	0.38
Molar Proportionality-IVS	0.032	0.38
Lewis-SVI	-0.362	0.50
Lewis-IAS	-0.008	0.38
Lewis-IVS	-0.008	0.38
Bering1-SVI	-0.304	0.47
Bering1-IAS	-0.003	0.38
Bering1-IVS	-0.001	0.38
Bering2-SVI	-0.464	0.63
Bering2-IAS	0.051	0.42
Bering2-IVS	0.043	0.42
Molar Exclusion-SVI	0.168	0.46
Molar Exclusion-IAS	0.498	0.79
Molar Exclusion-IVS	0.540	0.81
Volume Exclusion-SVI	0.168	0.46
Volume Exclusion-IAS	0.498	0.79
Volume Exclusion-IVS	0.540	0.81

SVI = Single Vapor Isotherm

IAS = Ideal Adsorbed Solution

IVS = Ideal Volumetric Solution

Table 2 shows that the best (and equivalent) precisions of the model predictions were obtained for the Volume Proportionality, Molar Proportionality, Lewis, and Bering1 models with the Ideal Adsorbed Solution and Ideal Volumetric Solution options. Of these, the Bering1 mixture isotherm Equation (2) with the Ideal Volumetric Solution option $[\epsilon_T = RT \sum z_i \ln(z_i p_{sati}^0 / p_i)]$ had the best average accuracy. The Single Vapor Isotherm option $[(\epsilon_T = RT \sum z_i \ln(p_{sati}^0 / p_i)]$ produced worse precisions and accuracies in these four models.

The Volume and Molar Exclusion models' predictions were significantly worse than those of the four best, yielding results equivalent to one another due to the assumption that molar volumes were the same in mixtures as in the pure states. Bering2 model predictions were significantly worse than those for the original Bering1 model.

Mole Fraction (Distribution) Models: The second test was of those models that can calculate distributions of adsorbed mixture components, in some cases starting with calculated or experimentally known total adsorbed molar capacities. Table 3 lists these models with options and resulting measures of accuracy and precision in applying them to data. It also lists the numbers of the 93 binary mixtures for which we were able to calculate mole fractions between 0 and 1. Only results for one component of each binary mixture were used for these measures, since the same results would be obtained for the other of each pair. To avoid the effect of which component was chosen from each binary mixture, we averaged the absolute values of model residuals (calculated minus experimental mole fraction for one of the components).

Table 3 shows that only four of these models were able to calculate molar distributions for all 93 mixtures: IAST, VAST, Polanyi, and Volume Exclusion-SVI. Of these, the best accuracy and precision were found for the IAST and the worst for Volume Exclusion-SVI; for VAST and Polanyi they were intermediate and very similar. The Lewis and Molar Proportionality models' calculated mole fractions are very sensitive to the values of total and reference moles input, which explains their poor performances.

One other option that was tried with the IAST and Polanyi models was mole fraction weighting of the affinity coefficient: $\beta_i = \sum x_j \beta_j$ (j includes i). This produced much worse accuracy and precision measures than using individual pure component β_i .

Combined Equation Models: The third test was to calculate both experimental distributions and experimental total capacities by combining two equation models: a) IAST, VAST, and Polanyi models were used to calculate the mole fractions of binary components; b) then the equations and options listed in the first column of Table 4 were used to calculate total and component adsorbed capacities. The latter were then compared with reported experimental values. Table 4 shows measures of accuracy (average deviations from experimental values) and precision (standard deviations).

Table 3. Molar Distribution Calculations: Models' Average Absolute Deviations (Accuracy) and Standard Deviations (Precision) of Calculated Component Mole Fractions from Experimental Values for One Selected Component of Each Binary Mixture.

	Average Absolute Value of Residuals	Standard Deviation of Residuals	Number of Mixtures that Could be Calculated
Lewis-SVI	0.659	0.267	31
Lewis-IAS	0.664	0.338	43
Lewis-Total Pressure	0.731	0.324	63
Molar Proportionality-SVI	0.662	0.280	31
Molar Proportionality-IAS	0.671	0.376	43
Molar Proportionality-Total Pressure	0.803	0.383	63
Ideal Adsorbed Solution Theory	0.054	0.071	93
Volumetric Adsorbed Solution Theory	0.072	0.090	93
Polanyi Adsorption Potential Theory	0.072	0.088	93
Molar Exclusion-SVI	0.286	0.402	88
Molar Exclusion-IAS	0.192	0.226	53
Molar Exclusion-IVS	0.195	0.229	53
Volume Exclusion-SVI	0.092	0.111	93
Volume Exclusion-IAS	0.135	0.157	88
Volume Exclusion-IVS	0.137	0.160	88

SVI = Single Vapor Isotherm
IAS = Ideal Adsorbed Solution
IVS = Ideal Volumetric Solution

Table 4. Combined Models' Average Deviations (Accuracies) and Standard Deviations (Precisions) of Calculated Component Capacities from Experimental Values for Both Components of 93 Binary Mixtures.

Model and Option	IAST		VAST		Polanyi	
	Average Deviation (mmol/g)	Standard Deviation (mmol/g)	Average Deviation (mmol/g)	Standard Deviation (mmol/g)	Average Deviation (mmol/g)	Standard Deviation (mmol/g)
Volume Proportionality -IAS	0.0144	0.318	0.0408	0.497	-0.0018	0.395
Volume Proportionality-IVS	0.0150	0.318	0.0254	0.402	-0.0176	0.449
Molar Proportionality-IAS	0.0240	0.318	0.0362	0.407	0.0108	0.391
Molar Proportionality-IVS	0.0288	0.320	0.0351	0.404	0.0143	0.391
Lewis-IAS	0.0139	0.318	0.0236	0.402	-0.0026	0.395
Lewis-IVS	0.0146	0.318	0.0252	0.402	-0.0026	0.396
Bering1-IAS	0.0139	0.318	0.0244	0.402	-0.0026	0.395
Bering1-IVS	0.0147	0.318	0.0252	0.486	-0.0018	0.395
Bering2-IAS	0.0322	0.324	0.0464	0.408	0.0056	0.401
Bering2-IVS	0.0286	0.325	0.0268	0.455	0.0018	0.403

IAS = Ideal Adsorbed Solution
IVS = Ideal Volumetric Solution

Table 4 shows that the two models with the best (and same) combination of accuracy and precision measures were the IAST-Lewis-IAS and IAST-Bering1-IAS combinations. The Polanyi model usually had better average accuracy, but worse precision. The Ideal

Volumetric Solution assumption gave no better (often worse) results than the Ideal (Molar) Adsorbed Solution assumption. Likewise, VAST was no improvement over IAST.

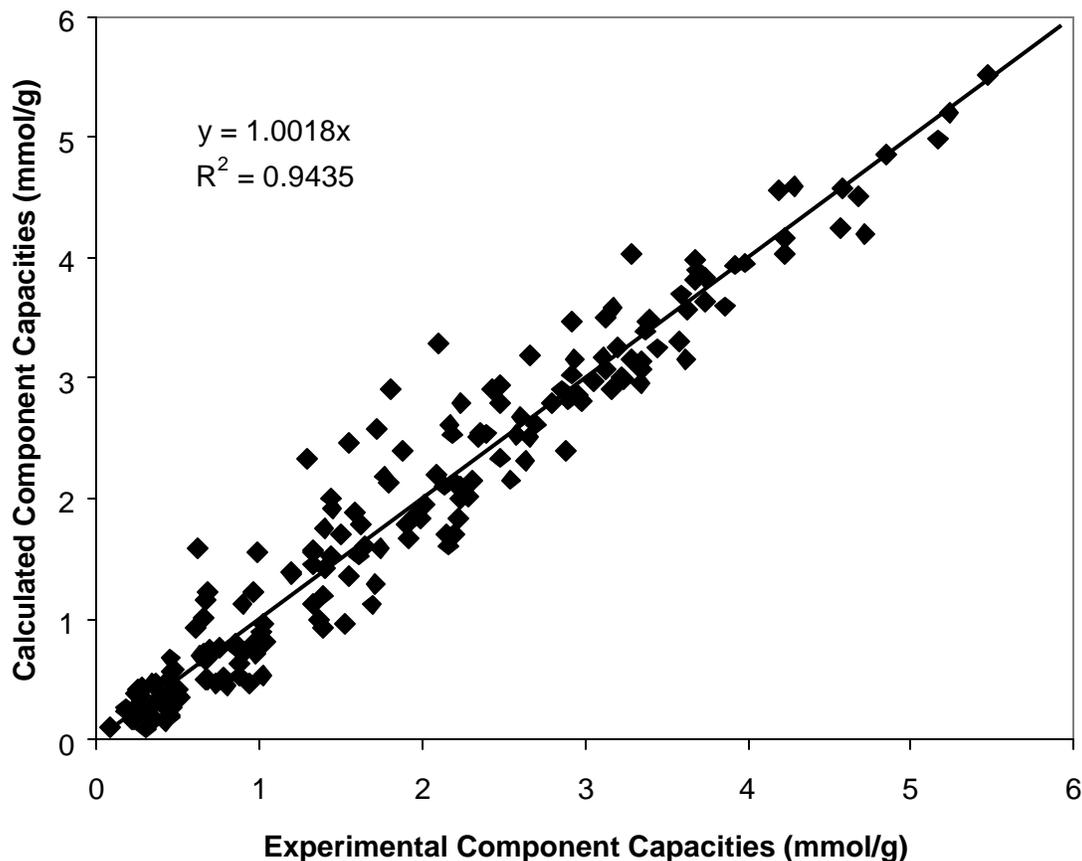


Figure. 1. Comparison of calculated and experimental capacities of 186 components of binary adsorbed mixtures using the IAST-D/R-Bering1-IAS combination of equations and options. The linear least squares slope (forced zero intercept) and squared correlation coefficient quantify average accuracy and precision, respectively.

Figure 1 shows a comparison of component capacities for both components of the 93 binary mixtures calculated by the IAST-Bering1-IAS combination model with experimental values. The largest positive deviations were obtained with carbon tetrachloride and isopropanol. Deviations include both experimental and model errors.

Conclusions

We conclude from this study that the best model for calculating equilibrium molar distributions of components of adsorbed binary mixtures of organic compounds using known single-component Dubinin/Radushkevich isotherm parameters is the Ideal Adsorbed Solution Theory. An analytical solution (Equation 13) for the necessary isotherm integrations (Equation 12) avoids the problem of no Henry's Law limit. The error function (erf) in this solution can be calculated by a series expansion. This IAST-D/R model can be extended to multiple components; however, an iterative solution (easily done by computer) is required.

A second equation is needed with the IAST-D/R to calculate total and component adsorbed capacities. The best ones were found to be the Lewis (Equation 7) and the Bering1 (Equation 2) with the Ideal Adsorbed Solution assumption, $p_{si}^o = x_i p_{sati}^o$, for single-vapor isotherm contributions and for mixed adsorption potential contributions, respectively.

The IAST-D/R-Bering1-IAS combination seems to be easier to apply than the IAST-D/R-Lewis-IAS, requiring fewer D/R equation calculations. After determining mole fractions x_i of adsorbed mixture components by equating spreading pressures (Equation 13) of components and requiring that $\sum x_i = 1$, one can calculate component i molar capacity (e.g., mol/g) by the Bering1-IAS combination:

$$n_i = \frac{x_i W_o}{\sum x_j V_{mj}^o} \exp \left[-\frac{R^2 T^2 \left\{ \frac{\sum x_j \ln(x_j p_{sati}^o / p_j)}{\sum x_j \beta_j} \right\}^2}{E_o^2} \right] \quad (18)$$

where the summation index j includes i , p_j is a component j pressure (or concentration) in the vapor phase in equilibrium with the adsorbed mixture, $p_{\text{sat}j}^o$ is a vapor pressure (or concentration) that would be in equilibrium with the bulk pure single component j at the same temperature T , V_{mj}^o is a pure component liquid molar volume, β_j is a pure component affinity coefficient, E_o is the reference (benzene) adsorption energy of the activated carbon, and W_o is its micropore volume. The corresponding Lewis-IAST equation is:

$$n_i = x_i n_T = x_i \left[\sum_j \frac{x_j}{\frac{W_o}{V_{\text{mj}}^o} \exp \left[- \left\{ \frac{R T}{\beta_j E_o} \ln \left(\frac{x_j p_{\text{sat}j}^o}{p_j} \right) \right\}^2 \right]} \right]^{-1} \quad (19)$$

where j again includes i .

The results in Table 3 indicate that the Lewis and Molar Proportionality equations should not be used to calculate molar distributions from total molar adsorbed capacities. They are, however, useful for calculating total and component molar adsorbed capacities from molar distributions obtained experimentally or from separate calculations (Tables 2 and 4).

The IAST is successful for mixtures of compounds with similar adsorption isotherms, e.g., Type I for organic compounds on activated carbon. Mixed Langmuir or Langmuir-Freundlich models may also give good results, but lack the predictive capability of the D/R equation. When component isotherms are dissimilar, The IAST may be less successful.

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