Isosteric Heat of Adsorption and the Vacancy Solution Model

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Vacancy Solution Model

The vacancy solution model (VSM) of Suwanayuen and Danner (1980a,b), especially as modified by Cochran et al. (1985a,b), has achieved considerable success in the correlation of easy-to-measure pure-component adsorption data and in the consequent prediction of hard-to-measure multicomponent adsorption equilibria. This paper explores the interrelation of the vacancy solution theory of pure-component adsorption with the isosteric heat of adsorption to gain new insights into the characteristics of the VSM and to suggest improvement in its application.

The VSM provides a relation between the variables that constitute a complete thermodynamic description of single-component gas adsorption, i.e., pressure, temperature, and amount absorbed. The extension to multicomponent systems is easier with the VSM than with other known multicomponent models because pure-component adsorption is already characterized as a binary solution of vacancies and gas molecules. Only parameters depicting lateral interactions between different molecular species cannot be determined from pure-component isotherms. For most cases these parameters were proven to be insignificant in the prediction of multicomponent equilibria (Suwanayuen and Danner, 1980b). Where the binary interaction parameters are significant, Cochran et al. showed how to determine them from theory and related pure-component parameters. Thus the success of the VSM in predicting multicomponent equilibria depends primarily on the accuracy of pure-component parameters. Cochran et al. also achieved a substantial improvement in the performance of the VSM by correlating the pure-component parameters with temperature. These temperature dependencies and their relation to the isosteric heat of adsorption are examined here.

All variations of the VSM picture pure-component adsorption as an equilibrium of vacancies and molecules in gas and adsorbate phases. The general VSM equation is

$$P = \left(\frac{n^{\infty}}{b}\right)\left(\frac{\theta}{1-\theta}\right)[f(\theta)] \tag{1}$$

where b is the Henry's law constant, n^{∞} is the adsorption capacity, i.e., the amount adsorbed at very high pressures, and θ is the fraction of the capacity that is occupied, n/n^{∞}. Species-designating subscripts, which appeared on b and n in earlier papers, are omitted here since this paper deals only with pure-component adsorption. The term $f(\theta)$, accounting for nonideality of the adsorbate mixture, is given as a general function of the vacancy activity coefficient by

$$f(\theta) = \left[\exp\left(-\int\frac{d\ln\gamma_v^s}{\theta}\right)\right]\left(\lim_{\theta\to 0}\exp\int\frac{d\ln\gamma_v^s}{\theta}\right) \tag{2}$$

Since the form of $f(\theta)$ depends on the definition of surface phase activity coefficients, the VSM has a built-in flexibility. Suwanayuen and Danner (1980a,b) utilized a Wilson-type activity coefficient equation to obtain a model designated W-VSM:

$$P = \left(\frac{n^{\infty}}{b}\right)\left(\frac{\theta}{1-\theta}\right)\left[\Lambda_{1v}\cdot\frac{1-(1-\Lambda_{v1})\theta}{\Lambda_{1v}+(1-\Lambda_{1v})\theta}\right] \cdot \exp\left[-\frac{\Lambda_{v1}(1-\Lambda_{v1})\theta}{1-(1-\Lambda_{v1})\theta} - \frac{(1-\Lambda_{1v})\theta}{\Lambda_{1v}+(1-\Lambda_{1v})\theta}\right] \tag{3}$$

Cochran et al. (1985a) utilized a Flory-Huggins type activity coefficient equation to obtain a model designated FH-VSM:

$$P = \left(\frac{n^{\infty}}{b}\right)\left(\frac{\theta}{1-\theta}\right)\exp\left(\frac{\alpha^2\theta}{1+\alpha\theta}\right) \tag{4}$$

For an ideal solution of vacancies and molecules, the nonideality term $f(\theta)$ equals unity and Eq. 1 reduces to the functional form

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of the Langmuir equation, in which all lateral interactions are neglected.

Isosteric Heat of Adsorption

In addition to describing phase equilibria, an adsorption model should reflect the energetics of adsorption processes. The temperature dependency of adsorption equilibria is linked theoretically to various heats of adsorption. The isosteric heat, q^{st}, is calculated from experimental isotherms at different temperatures, or it can be derived from any isotherm equation (Ross and Olivier, 1964). The isosteric heat determined from the FH-VSM, Eq. 4, is shown in Eq. 5.

$$-\frac{q^{st}}{R}=\left[\frac{\partial \ln P}{\partial(1/T)}\right]_n=-\left[\frac{\partial \ln b}{\partial(1/T)}\right]_n+\left[\frac{2\alpha\theta+\alpha^2\theta^2}{(1+\alpha\theta)^2}\right]\left[\frac{\partial\alpha}{\partial(1/T)}\right]_n + \left[-\frac{n}{n^\infty(n^\infty-n)}-\frac{\alpha^2\theta}{n^\infty(1+\alpha\theta)^2}\right]\left[\frac{\partial n^\infty}{\partial(1/T)}\right]_n \qquad (5)$$

The last term on the righthand side of Eq. 5 denotes the variation of adsorption capacity with temperature. The term $n^\infty - n$ appears in a denominator in the isosteric heat equations for all forms of the VSM. As the adsorption capacity is approached (e.g., at high pressure), $1/(n^\infty - n)$ goes to infinity. Thus, the derivative of adsorption capacity with respect to temperature, $[\partial n^\infty/\partial(1/T)]_n$, must vanish if the VSM is to have finite values of the isosteric heat of adsorption at high surface coverages. In other words, all forms of the VSM imply that the adsorption capacity is independent of temperature.

In their derivation of the VSM, Suwanayuen and Danner (1980a) defined the dividing surface such that partial molar areas of vacancies and molecules were both equal to a constant, which was taken to be the molar area of adsorbate at full coverage. Thus, the total number of entities (molecules and vacancies) in the vacancy solution does not change with coverage, which provides the necessary link between physically measurable quantities and the abstract vacancy solution properties. In the Gibbs definition of adsorption, total area is a property of the solid and thus is independent of temperature, pressure, and composition. Therefore, inherent in the derivation of the VSM is the constancy of the extent of the surface phase (i.e., adsorption capacity).

The findings of Cochran et al. (1985a), who allowed the adsorption capacity to vary with temperature by introducing an empirical relation between adsorption capacity and temperature, support the above argument. In 14 out of 18 cases their regressions resulted in adsorption capacities independent of temperature. They attributed some of this to insufficient data at high coverages to adequately define this temperature dependence of n^∞, and we agree. However, in other instances the data appeared to warrant a temperature dependence (see Figure 3 in their paper for a conventional isotherm plot for propane adsorbed on activated carbon, Nuxit-Al), while the model regressions found none. We believe the lack of temperature dependence observed in the regressions can be attributed to the nature of the FH-VSM as described earlier.

A plot of the amount adsorbed vs. the reciprocal of the pressure, in which the extrapolation to very large pressures goes to a finite limit, is shown in Figure 1 for the same propane-activated carbon data. The lines on this graph represent Suwanayuen and Danner's fit of these data with the parameters of their original W-VSM, including a temperature-independent n^∞. Clearly, the data at all four temperatures are fit within experimental error. This indication of the temperature independence of n^∞ confirms our theory and the findings from the FH-VSM regressions.

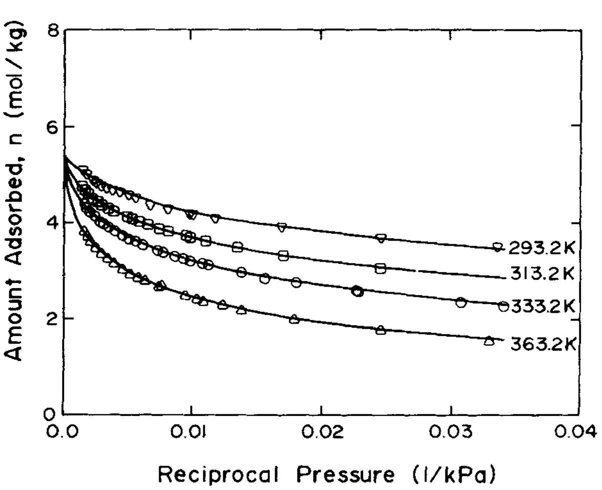

Figure 1. Reciprocal pressure plot for the determination of adsorption capacity.
Data from Szepesy and Illes (1963a,b)

The second term on the righthand side of Eq. 5 represents the variation of nonidealities with temperature for the FH-VSM. Cochran et al. related α to temperature through the adsorption capacity as shown in Eq. 6:

$$\alpha = mn^\infty - 1 \qquad (6)$$

Using Eq. 6 with constant adsorption capacities implies that α, too, is independent of temperature. For this case only the first term remains on the righthand side of Eq. 5. Thus the isosteric heat equation for the FH-VSM reduces to a constant that is the limiting isosteric heat at zero coverage:

$$-\frac{q^{st}}{R}=-\left[\frac{\partial \ln b}{\partial(1/T)}\right]_n=\lim_{n\to 0}-\frac{q^{st}}{R} \qquad (7)$$

Thus, according to the FH-VSM the isosteric heat of adsorption is independent of surface coverage, θ.

A qualitative rationalization may be instructive. In the VSM, all lateral interactions are lumped in the activity coefficient equation. The definition of adsorbate activity coefficients determines the types of nonidealities that are included. The Flory-Huggins activity coefficient equation includes only configurational contributions to nonideality by excess entropy; interactions (enthalpic contributions) are omitted. Thus, in the FH-VSM all lateral interactions are neglected.

In contrast the Wilson activity coefficient equation includes interactions (while neglecting excess entropy); thus it can accommodate a variation of isosteric heat with coverage as shown in Eq. 8:

$$-\frac{q^{st}}{R}=-\left[\frac{\partial \ln b}{\partial(1/T)}\right]_n+\frac{2\theta\Lambda_{1v}+(1-\Lambda_{1v})\theta^2}{\Lambda_{1v}[\Lambda_{1v}+(1-\Lambda_{1v})\theta]^2}\cdot\left[\frac{\partial\Lambda_{1v}}{\partial(1/T)}\right]_n + \frac{\theta\Lambda_{v1}[2-(1-\Lambda_{v1})\theta]}{[1-(1-\Lambda_{v1})\theta]^2}\cdot\left[\frac{\partial\Lambda_{v1}}{\partial(1/T)}\right]_n \qquad (8)$$

Figure 2 shows isosteric heat of adsorption vs coverage for CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, and CO_2 on activated carbon Nuxit-Al (Szepesy and Illes, 1963a,b). Figure 3 shows isosteric heat of adsorption vs. coverage for O_2, N_2, and CO on molecular sieve 10X (Nolan et al., 1981).

The original data were used to calculate experimental isosteric heats, which are shown as solid curves in Figures 2 and 3. The absissas of these figures are normalized using adsorption capacity values given by Suwanayuen and Danner (1980a). The solid lines end at coverages where the data are no longer sufficient to allow calculation of the heat of adsorption. Corresponding curves for butane on Nuxit-Al are not shown because the isotherms of butane have very steep initial slopes followed by sharp knee-bends at intermediate pressures. Thus it was not possible to calculate experimental isosteric heats within reasonable accuracy for butane, especially at low surface coverages.

The dashed horizontal lines in Figures 2 and 3 are the constant isosteric heats according to the FH-VSM fits of Cochran et al. (1985a). The parameter values given by Suwanayuen and Danner (1980a) for the Wilson form of the VSM were used with Eq. 3 to generate isosteres, the slopes of which are the isosteric heats, shown as dotted curves in the figures.

Results

In every instance the constant q^{st}/R for the FH-VSM reasonably represents a mean value of the data for Nuxit-Al adsorbent

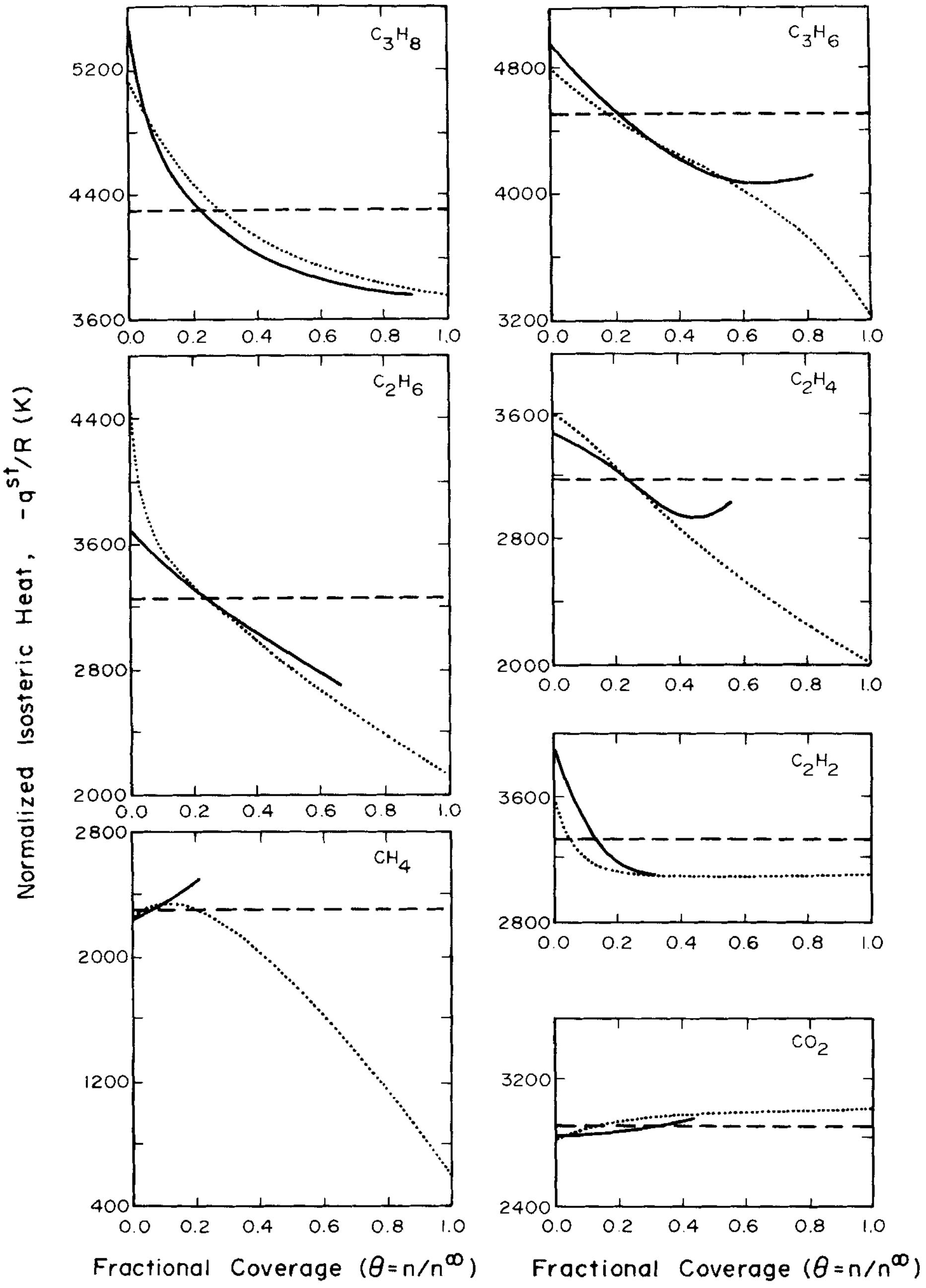

Figure 2. Isosteric heats of adsorption on Nuxit-Al.

Data from Szepesy and Illes (1963a,b).

— data, ----- FH-VSM, ... W-VSM

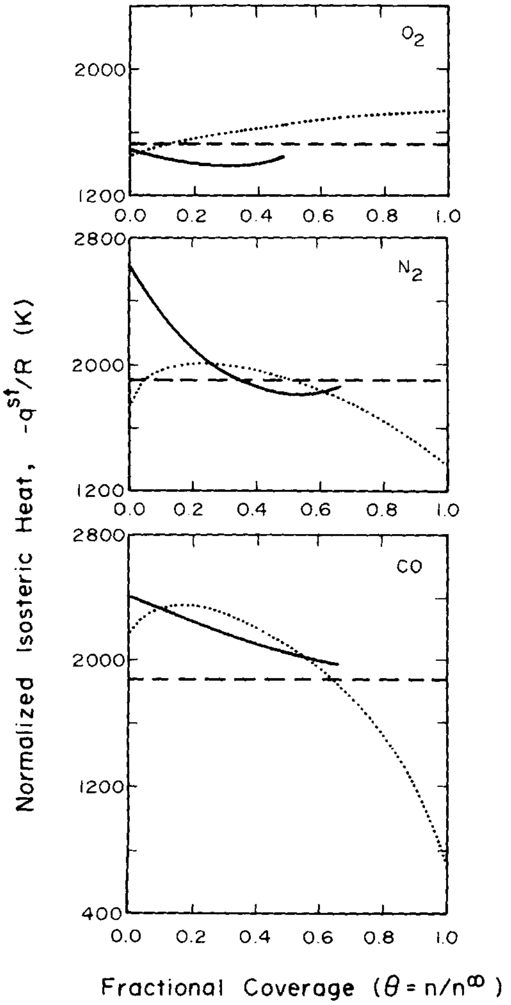

Figure 3. Isosteric heats of adsorption on zeolite 10X.
Data from Nolan et al. (1981)
— data, ----- FH-VSM, ... W-VSM

shown in Figure 2. Thus, within its power to match isosteric heats of adsorption, the FH-VSM does a physically reasonable job. The Wilson form of the VSM follows the experimental data with reasonable accuracy in most cases, although dramatic departures sometimes occur near or beyond the limits of the supporting data.

The experimental isosteric heats of adsorption of O_2, N_2, and CO on zeolite 10X are compared to model predictions in Figure 3. The Flory-Huggins predictions displayed essentially the same character as in Figure 2. The Wilson form of the VSM does not follow the experimental isosteric heat curves as closely as for Nuxit-Al. No more definite statements can be made because of uncertainty in the experimental values. As with the larger molecules on Nuxit-Al, the experimental isotherms for these systems rise steeply and bend sharply.

The isosteric heat of adsorption usually varies with surface coverage. The relation between isosteric heat and coverage somewhat explains the surface structure (Ross and Olivier, 1964). For homogeneous surfaces, as coverage increases lateral interactions increase; thus, isosteric heat of adsorption increases. Vertical interactions do not depend on coverage and are determined from limiting isosteric heat at zero coverage. For heterogenous surfaces, high-energy patches are filled preferentially as adsorption proceeds, causing vertical interactions to decrease as coverage increases. On the other hand, lateral interactions on all patches increase with coverage. Thus, the isosteric heat vs. surface coverage relation cannot be determined *a prior* for heterogenous surfaces. However, a decreasing isosteric heat with increasing surface coverage usually indicates a heterogenous surface. Constant isosteric heat would theoretically mean either a homogenous surface with no lateral interactions, or a heterogenous surface where the change in lateral interactions exactly cancels the change in vertical interactions.

Figures 2 and 3 show the experimental heats of adsorption to vary by only 10–20% from the constant values obtained by FH-VSM correlations. This explains why the FH-VSM usually yields statistically well-defined parameters in regressions. The fact that the FH-VSM implies n^{∞} independent of temperature explains why the regressions have so often shown this result. Thus, for cases where greater rigor is unnecessary, the demonstrated effectiveness of the FH-VSM can be understood.

When the isosteric heat of adsorption varies so strongly with coverage that the constancy assumption cannot be tolerated, the versatility of the Wilson form of the VSM can be invoked. One should be cautious, however, about extrapolating the W-VSM beyond the range of the supporting data because predicted and experimental isosteric heats, while not showing large deviations, may diverge strongly.

This study has shown that adsorption capacities are more likely to be independent of temperature than the data seem to suggest. An alternate graphical technique is suggested for improved accuracy in the assessment of temperature dependence and the estimation of values of adsorption capacity. The fact that the relationships of the FH-VSM and the W-VSM to isosteric heat of adsorption have been defined now, offers encouragement for more effective use of the VSM and ultimately should allow generalization of parameters over ranges of adsorbates and finally adsorbents.

Notation

b = Henry's law constant, mol/kg · kPa
$f(\theta)$ = nonideality function in isotherm equation
m = temperature-independent constant in Flory-Huggins equation linking α and n^{∞}, kg/mol
n = amount adsorbed, mol/kg
n^{∞} = adsorption capacity, i.e., limiting amount adsorbed at very high pressures, mol/kg
P = gas pressure, kPa
q^{st} = isosteric heat of adsorption, J/mol
R = universal gas constant = 8.31 J/mol · K
T = absolute temperature, K

Greek letters

α = nonideality parameter in Flory-Huggins form of VSM
γ_v^s = activity coefficient of vacancy in adsorbed phase
θ = fractional coverage = n/n^{∞}
Λ_{1v}, Λ_{v1} = nonideality parameters in Wilson form of VSM

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