Vacancy Solution Theory of Adsorption Revisited

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The vacancy solution theory, originally proposed two decades ago (Suwanayuen and Danner, 1980a,b; Cochran et al., 1985), offers a unified representation of single, as well as multicomponent, isotherms within the same framework. However, it has been criticized by Talu and Myers (1988) as being erroneous, based on inconsistent binary selectivity predictions in the Henry's law limit (except when the saturation capacities for both components are the same), and it has received relatively little attention. Despite this, no effort has been made at correcting this deficiency and identifying the root cause. In this article we revisit this model and reformulate it in a thermodynamically consistent way that leads to the multisite Langmuir model of Nitta et al. (1984), which has been shown to satisfy the consistency criteria of binary adsorption (Rao and Sircar, 1999).

The vacancy solution theory considers the adsorbed phase as a nonideal mixture of adsorbed molecules and unoccupied adsorption sites termed vacancies. In the original theory the usual phase equilibrium relations

$$\mu_i^a = \mu_i^g,\ \mu_v^a = \mu_v^g \tag{1}$$

are used, together with the Lucassen-Reynders (1972) equation of state and the Wilson's or Flory-Huggins activity coefficient model for the adsorbed (surface) phase, where μ_i, μ_v are the chemical potentials of adsorptive species i and of the vacancy, respectively, and the superscripts a and g correspond to the adsorbed and gaseous phases, respectively. It may be argued that a key source of error in the vacancy solution theory is the incorrect disposition of vacancies during an adsorption event. This is because Eq. 1 assumes that the adsorption of a molecule of species i and desorption of a vacancy are mutually uncorrelated and independent. In reality the addition of a molecule to the adsorbed phase results in removal of vacancies from this phase, contradicting the assumption that these are independent events. Indeed, if a vacancy solution model is also adopted for the bulk phase, then it may be assumed that vacancies are simultaneously transferred in the opposite direction as molecules are exchanged between the bulk and adsorbed phases. Alternately, if the existence of vacancies as independent entities is not recognized for the bulk phase, vacancies must be considered as being consumed on addition of a molecule to the adsorbed phase. In either case it may be shown that the relationship for thermodynamic equilibrium is one akin to that of a mass-action law, in place of Eq. 1. We consider the latter alternative, for which vacancies are explicitly recognized as an entity only in the adsorbed phase.

Theory

We represent the adsorption of any species i in terms of the transformation

$$A_i(g) + \nu_i v(a) \Leftrightarrow A_i(a) \tag{2}$$

where ν_i represents the number of vacancies consumed on adsorption of a molecule of i. The condition of equilibrium is now given by

$$\frac{d(\Delta G)}{dn_i} = \mu_i^a - \nu_i\,\mu_v^a - \mu_i^g = 0 \tag{3}$$

Upon expressing the chemical potentials in terms of activities, we obtain the familiar mass-action law

$$\frac{a_i^a}{\left(a_v^a\right)^{\nu_i}\phi_i^g y_i P} = -\,e^{-\Delta G_i^0/RT} \tag{4}$$

in which a_i^a and a_v^a are the activities of the adsorbate and vacancies, respectively. Here, the standard state for the adsorbed molecules of species i is taken as that of complete coverage with no vacancies (for which $a_i^{oa} = 1$), and for the vacancy as the completely bare adsorbent with no adsorbate (for which $a_v^{oa} = 1$). For the gas phase, it is the pure adsorptive i in the ideal gas state at $P = 1$ atm. Further, ϕ_i^g is a fugacity coefficient and ΔG_i^o is a standard excess free energy, following

$$\Delta G_i^o = \mu_i^{oa} - \nu_i\,\mu_v^{oa} - \mu_i^{og} \tag{5}$$

Equation 4 can also be written as

$$\frac{\gamma_i^a X_i^a}{\left(\gamma_v^a X_v^a\right)^{\nu_i}} = \phi_i^g y_i P e^{-\Delta G_i^o/RT} \tag{6}$$

where γ_i^a and γ_v^a are activity coefficients for adsorbate and vacancies, respectively. We may now express the mole fractions X_i^a in terms of the amounts adsorbed by

$$X_i^a = \frac{n_i}{n_t}, \quad i = 1, \ldots, N, v \tag{7}$$

where n_i is the adsorbed amount of species i, and

$$n_T = n_v + \sum_{j=1}^{N} n_j \tag{8}$$

is the total amount of adsorbate (n_i) and vacancies (n_v). A balance over the vacancy species yields

$$n_{v\infty} = n_v + \sum_{j=1}^{N} \nu_j n_j \tag{9}$$

which combines with Eqs. 7 and 8 to provide

$$X_i^a = \frac{n_i}{\left[n_{v\infty} - \sum_{j=1}^{N} \left(\nu_j - 1 \right) n_j \right]} \tag{10}$$

$$X_v^a = \frac{\left[n_{v\infty} - \sum_{j=1}^{N} \nu_j n_j \right]}{\left[n_{v\infty} - \sum_{j=1}^{N} \left(\nu_j - 1 \right) n_j \right]} \tag{11}$$

Here $n_{v\infty}$ is the maximum vacancy concentration. Following Cochran et al. (1985), the Flory-Huggins model may be utilized for the activity coefficients in terms of X_i^a, in the form

$$\ln \left(\gamma_i^a \right) = 1 - \ln \left[\sum_{j=1}^{N+v} \frac{X_j^a}{\left(1 + \alpha_{ij} \right)} \right] - \left[\sum_{j=1}^{N+v} \left(\frac{X_j^a}{\left(1 + \alpha_{ij} \right)} \right) \right]^{-1}, \quad i = 1, \ldots, N, v \tag{12}$$

where the constants α_{kj} are the Flory-Huggins parameters representing the k-j interaction, and satisfy

$$\alpha_{jj} = 0 \tag{13}$$

$$\alpha_{jk} + 1 = \left(\alpha_{ji} + 1 \right) \left(\alpha_{ik} + 1 \right) \tag{14}$$

$$\alpha_{kj} + 1 = \left(\alpha_{jk} + 1 \right)^{-1} \tag{15}$$

for $i, j, k = 1, 2, \ldots, N, v$. This is a particularly convenient choice of activity coefficient model because the Flory-Huggins parameter $(1 + \alpha_{iv})$ represents the ratio of molecular area to vacancy area, and is directly related to the site occupancy ν_i. By virtue of Eqs. 13–15, the set of parameters α_{iv}, $j = 1, 2, \ldots, N$ completely specifies the activity coefficient model. It is possible to relate the equilibrium constant $e^{-\Delta G_i^o/RT}$ in Eq. 7 to the Henry's Law coefficient by considering the limit $X_i^a \rightarrow 0$ and $X_v^a \rightarrow 1$ for $P \rightarrow 0$. In this limit Eq. 12 yields

$$\frac{\gamma_i^a}{\gamma_v^a} = (1 + \alpha_{iv}) e^{-\alpha_{iv}} \tag{16}$$

so that Eq. 6 simplifies to

$$X_i^a = \frac{y_i P e^{\alpha_{iv}} e^{-\Delta G_i^o/RT}}{(1 + \alpha_{iv})}, \quad i = 1, \ldots, N \tag{17}$$

From Eq. 17, it is apparent that in the Henry's Law limit

$$n_i = n_{v\infty} X_i^a = \frac{n_{v\infty} e^{\alpha_{iv}} e^{-\Delta G_i^o/RT}}{(1 + \alpha_{iv})} y_i P \tag{18}$$

In this limit we may also write

$$n_i = K_i \frac{y_i P}{RT} \tag{19}$$

where K_i is a Henry's Law coefficient. Equations 18 and 19 yield

$$K_i = \frac{RT n_{\nu\infty} e^{\alpha_{iv}} e^{-\Delta G_i^o/RT}}{(1 + \alpha_{iv})} \tag{20}$$

which combines with Eq. 6 to provide, in terms of the Henry's Law coefficients,

$$\frac{\gamma_i^a X_i^a}{\left(\gamma_v^a X_v^a \right)^{\nu_i}} = \frac{(1 + \alpha_{iv}) e^{-\alpha_{iv}} K_i}{n_{v\infty} RT} \phi_i^g y_i P, \quad i = 1, \ldots, N \tag{21}$$

that together with Eqs. 12–15 provides the modified vacancy solution model based on the Flory-Huggins activity coefficients.

In the above formulation it may be recognized that both the parameters ν_i and $(1 + \alpha_{iv})$ represent the number of vacancies occupied by an adsorbate molecule, and must be equal. Thus, thermodynamic consistency requires that

$$\nu_i = (1 + \alpha_{iv}) \tag{22}$$

It is now possible to simplify the above model by defining the surface coverage for species i

$$\theta_i = \frac{n_i \nu_i}{n_{v\infty}} \tag{23}$$

which combines with Eqs. 10 and 11 to provide

$$X_i^a = \frac{\theta_i}{\nu_i D} \tag{24}$$

$$X_v^a = \frac{\left(1 - \sum_{j=1}^{N} \theta_j\right)}{D} \tag{25}$$

where

$$D = 1 - \sum_{j=1}^{N} \theta_j(\nu_j - 1)/\nu_j = 1 + \sum_{j=1}^{N} \alpha_{vj}\theta_j \tag{26}$$

In Eq. 26 we have utilized Eqs. 22 and 15 with $k = v$. The Flory-Huggins activity coefficient model in Eq. 12 then provides

$$\ln(\gamma_i^a) = 1 - (1 + \alpha_{iv})D + \ln[(1 + \alpha_{iv})D] \tag{27}$$

$$\ln(\gamma_v^a) = 1 - D + \ln(D) \tag{28}$$

It is now a matter of algebraic detail to substitute Eqs. 22–28 into Eq. 21 to finally obtain

$$\frac{\theta_i}{\left(1 - \sum_{j=1}^{N} \theta_j\right)^{\nu_i}} = \frac{\nu_i K_i}{n_{v\infty} RT} \phi_i^g y_i P \tag{29}$$

which is precisely the multisite Langmuir model of Nitta et al. (1984). The thermodynamic consistency of this equation has already been verified (Rao and Sircar, 1999), thereby confirming the consistency of our approach to the vacancy solution theory.

Discussion

It is evident that a key flaw in the existing vacancy solution theory lies in the incorrect treatment of vacancies in the surface equation of state. Instead, if the mass-action principle is correctly utilized, a thermodynamically consistent formulation is readily obtained. Clearly, the statistical mechanical arguments of Nitta et al. (1984) are the same as those behind the Flory-Huggins model, so that, when the latter is used for the surface phase, the multisite Langmuir isotherm is recovered. It should be noted that the occupancy parameter ν_i can, in general, vary with temperature, pressure, and coverage, as dictated by the activity coefficient model used. For the Flory-Huggins model in Eq. 12, the underlying athermal assumption implies that α_{iv} and, hence, ν_i (Eq. 22) is constant. Other activity coefficient models can also be utilized to obtain alternate isotherms, but the parameters in the models used must be consistent with the stoichiometry of Eq. 2. This is an essential requirement to ensure thermodynamic consistency of the final multicomponent isotherm, and it is precisely its violation that resulted in the deficiency of the earlier vacancy solution theory which corresponds to the choice of $\nu_i = 1$ regardless of the activity coefficient model parameters. The present formulation thus opens the door to a variety of new single and multicomponent isotherm models based on a consistent and suitable choice of adsorbed-phase activity coefficient model.

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