Similarity of Ideal Adsorbed Solution and Potential Theories for Adsorption from a Bulk Phase onto a Solid Surface

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Both the Ideal Adsorbed Solution (IAS) theory originally proposed by Gibbs (1906) and adapted by Myers and Prausnitz (1965) for gas-phase adsorption and by Radke and Prausnitz (1972) for solution-phase adsorption, and the Potential theory (P) of Polanyi adapted to both gas- and liquid-phase adsorption by Manes and coworkers (1980) have been thought of as separate theories. In fact, both theories have not only been characterized differently, but are thought to have different limitations.

For liquid-phase adsorption the IAS model fits the data well for weakly adsorbing solute species (Radke and Prausnitz, 1972). For strongly adsorbing binary systems, however, the model-fit is poorer. For competitive adsorption of more than two components because of its mathematical complexity, the IAS Model has been modified to a much simpler calculation by DiGiano et al. (1978). Deviation from the theory is also observed when dissociation of the organic molecules occurs during multicomponent adsorption (Myers and Zolandz, 1980).

The wide scope, applicability and simplicity of the P-model has recently been reviewed by Manes (1980). As Manes and coworkers describe it, this model hypothesizes the existence of an adsorbed three dimensional phase instead of a two-dimensional surface proposed by the IAS theory. Gibbs in 1906 originally recognized the difficulty in defining the thermodynamic properties of the adsorbed layer and proposed the imaginary mathematical "surface phase" with abstract thermodynamic excess properties and characterized by spreading pressure π and molar surface area $\mathscr{A}$ (A_s/n) as the respective intensive and extensive variables. See Van Ness for an excellent, lucid account of this ideal-adsorption approach for gas-phase adsorption (Van Ness, 1969). The Gibbs adsorption isotherm is derived from the Gibbs-Duhem equation and the fundamental property relation for the two-dimensional surface phase:

$$-\mathscr{A} d\pi + \Sigma(x_i d\mu_i) = 0 \text{ (const } T) \tag{1}$$

Assuming that equilibrium holds between any species in the bulk and surface-adsorbed phase, i.e.,

$$\mu_i = \mu_i^b \tag{2}$$

and for any change of chemical potential

$$d\mu_i = d\mu_i^b \tag{3}$$

and

$$d\mu_i^b = RT\, d \ln f_i \text{ (const } T) \tag{4}$$

where the fugacity f_i could be represented by y_iP for an ideal-gas phase and by activity a_i (Raoult's Law) for an ideal-liquid phase. Substituting Eq. 4 into Eq. 3 and then into Eq. 1,

$$-\mathscr{A} d\pi + RT\, \Sigma(x_i\, d \ln f_i) = 0 \text{ (const } T) \tag{5}$$

For a single-component system Eq. 5 can be integrated from π to π_s as the equilibrium fugacity f_i varies from below saturation of the liquid of species i to saturation $f_{i,s}$ and realizing $x_i = 1$,

$$\mathscr{A}\Delta\pi = RT \ln f_{i,s}/f_i \text{ (const } T) \tag{6}$$

where $\Delta\pi = \pi_s - \pi$, with Eq. 6 having energy units (J mol^{-1}). Equation 6 is similar in form to the Manes representation of the Polanyi adsorption criterion (Manes, 1980), i.e.,

$$\epsilon \geq RT \ln f_{i,s}/f_i \text{ (const } T) \tag{7}$$

where ϵ is the "adsorption potential" of any molecule within the attractive force field of the solid (which is the sum of the attractive forces of all the contributing atoms of the solid) independent of the presence or absence or other molecules around it and represents the work required to remove a molecule to infinity from its location in the adsorption space. (Also see McBain, 1932.)

Combining Eq. 6 with the representation in Eq. 7, we get the link between the IAS-theory and the P-theory, i.e.,

$$\epsilon \geq \mathscr{A}\Delta\pi = -\mathscr{A}\Delta\sigma \tag{8}$$

This relation simply equates the "adsorption potential" with the work needed to change the spreading pressure from π to π_s or the interfacial tension from σ to σ_s (where $\pi_s - \pi = \sigma - \sigma_s$) at constant molar area, $\mathscr{A}$.

The main result of this note is that although both Eqs. 6 and 7 derive from completely different physical models, they are mathematically equivalent when expressed through the simple relation in Eq. 8. In fact, it is tempting to suggest nonuniqueness, i.e. that the ideal adsorption theory of Gibbs and the potential adsorption theory of Polanyi are one and the same theory. Their limitations should then, of course, be similar.

Finally, given the above result, is was probably not fortuitous, that, after severe criticism of the suggested three-dimensional adsorbed phase, Polanyi in 1928 explicitly modified his compressed film theory by making the film *two-dimensional* (McBain, 1932). Gibbs would probably not have been surprised.

NOTATIONS

a_i = activity of component i
$\mathscr{A}$ = molar surface area of sorbent, cm^2 mol^{-1}
A_s = surface area of sorbent, cm^2
f_i = fugacity of component i, Pa
$f_{i,s}$ = saturation fugacity of component i, Pa
n = number of moles adsorbed, mol
P = total pressure, Pa
$\mathscr{R}$ = gas constant, J · °K^{-1} · mol^{-1}
T = temperature, °K
x_i = mole fraction of component i in adsorbate
y_i = mole fraction of component i in gas phase

Greek Letters

ϵ = adsorption potential, J · mol^{-1}
μ_i = chemical potential of component i in the sorbed phase J · mol^{-1}
μ_i^b = chemical potential of component i in the bulk phase, J · mol^{-1}

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On the Temperature Dependence of ASOG Parameters for VLE Calculations

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A simple and efficient method for generating vapor-liquid equilibrium (VLE) values for mixtures where data are lacking is always in demand because VLE data are essential in distillation design calculations. One of the frequently used methods is the analytical-solution-of-groups (ASOG) method. All molecules are considered to be consisting of a number of functional groups. The nonideal behavior of a component in a mixture, expressed in terms of activity coefficient, is due to the differences in molecular size (configurational contribution) and in intermolecular forces originating from the different functional groups (group-interaction contribution). Therefore, the ASOG method involves the reduction of activity coefficients, obtained from experimentally determined VLE values, into a number of binary group interaction parameters. Successful application of these parameters in the prediction of VLE values at various isobaric/isothermal conditions requires that their temperature dependence be properly represented. Otherwise, poor results are obtained.

The logarithm of the activity coefficient of component i in a mixture is expressed by the sum of $\ln\gamma_i^S$, the size contribution which depends on the number of size groups in the molecules of the mixture, and $\ln\gamma_i^G$, the contribution due to the interaction of the functional groups of the molecule with those in the mixture. Furthermore, the size term is treated by means of the Flory-Huggins theory for athermal mixtures of unequal-sized molecules. Hence

$$\ln\gamma_i = \ln\gamma_i^S + \ln\gamma_i^G \tag{1}$$

and

$$\ln\gamma_i^S = 1 - \frac{\nu_i}{\sum\limits_j \nu_j x_j} + \ln\frac{\nu_i}{\sum\limits_j \nu_j x_j} \tag{2}$$

In Eq. 2, ν_j and x_j refer to the number of non-hydrogen atoms in molecule j and the liquid mole fraction of component j, respectively. The summation, $\sum\limits_j$, extends over all components, including component i. In addition,

$$\ln\gamma_i^G = \sum_k \nu_{ki}(\ln\Gamma_k - \ln\Gamma_k^{(i)}) \tag{3}$$

where ν_{ki} is the total number of non-hydrogen atoms in all the functional groups of kind k in a molecule of component i, and Γ_k and $\Gamma_k^{(i)}$ are the activity coefficients of the group k in the mixture and in the standard state (pure component i), respectively. The summation, $\sum\limits_k$, extends over all functional groups of the mixture. The quantity, Γ_k, is given by the Wilson equation

$$\ln\Gamma_k = -\ln\sum_l X_l a_{kl} + 1 - \sum_l \frac{X_l a_{lk}}{\sum\limits_m X_m a_{lm}} \tag{4}$$

where a_{kl} and a_{lk} are the group-interaction parameters, characteristic of the groups k and l, but $a_{kl} \neq a_{lk}$. The summations, $\sum\limits_l$ and $\sum\limits_m$, extend over all the functional groups. The group fraction of group l, X_l, is given by

$$X_l = \frac{\sum\limits_j x_j \nu_{lj}}{\sum\limits_j x_j \sum\limits_k \nu_{kj}} \tag{5}$$

The parameters a_{kl} and a_{lk} are obtained from VLE values and are temperature dependent.

Derr and Deal (1969) plotted the logarithm of the parameters a_{kl} and a_{lk} versus temperature to indicate their temperature dependence and suggested that although these parameters "tend to vary quite regularly with temperature it is hazardous to extrapolate them over large temperature ranges." To illustrate

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