



Correlation and Prediction of Adsorption from Liquid Mixtures on Solids by Use of G^E -Models

C. BERTI, P. ULBIG AND S. SCHULZ

Lehrstuhl für Thermodynamik, Universität Dortmund, Emil-Figge-Str. 70, D-44221 Dortmund, Germany

garcia@cata.spn.edu

Received August 14, 1998; Revised February 1, 1998; Accepted September 7, 1999

Abstract. A new approach to describe the adsorption behavior of liquid mixtures on solid surfaces by use of G^E -models is presented. In contrast to the classical formulation of adsorption equilibrium the adsorbed phase is considered to be a mixture containing the adsorbed species (adsorbate) and the adsorbent as additional component. By introducing the Gibbs excess energy G^{E*} for this *adsorbate-solid-solution* the free energy of adsorption is correlated with the respective activity coefficients of all involved components. This concept, in the following briefly called *ASST (adsorbate-solid-solution theory)*, thus leads to a thermodynamically consistent description of both the adsorption equilibrium and caloric properties.

For evaluation purposes the Wilson model was used to calculate the Gibbs excess free energy G^{E*} . First results show the good ability of ASST to correlate surface excess isotherms of different types and to predict their temperature dependence. Moreover, the concept enables the surface excess isotherm for a binary liquid mixture to be predicted if the parameters describing the interactions between adsorbent and the respective fluids have been estimated from different surface excess isotherms.

Keywords: liquid phase adsorption, adsorption equilibrium, adsorption isotherm theory

1. Introduction

Despite of numerous possible applications in the chemical industry liquid phase adsorption is only rarely considered to be an alternative process for the separation of liquid mixtures. One of the most obvious reasons is the lack of both experimental data and suitable models to predict the adsorption behavior of multicomponent mixtures the like of which they typically occur in separation processes. This applies particularly if the prediction is to include the solid, i.e. if a suitable solid has to be chosen for a given separation problem.

However, the selection of a suitable separation process during the basic engineering relies on corresponding possibilities to calculate equilibrium behavior of multicomponent mixtures in advance since a measurement of these properties is very time-consuming and cost-intensive. At this point group contribution

methods are widely used for a first design of classical separation processes like distillation or extraction. The success of these models suggests a similar approach for the calculation of adsorption processes.

However, a thermodynamic description of interfacial phenomena is far more difficult than the description of classical phase equilibria (e.g. VLE) since there is no two-dimensional, sharp phase boundary between an adsorbed phase and an uninfluenced bulk phase, but a three-dimensional transition region with a continuous change of the respective thermodynamic state variables (Heuchel et al., 1989; Schay, 1969). It is therefore not surprising that the thermodynamic description of interfacial phenomena is still subject of discussion (Heuchel et al., 1989; Everett, 1993).

Though the transition region may actually not be regarded as an autonomous phase, the concept of an adsorbed phase or surface phase—originally introduced

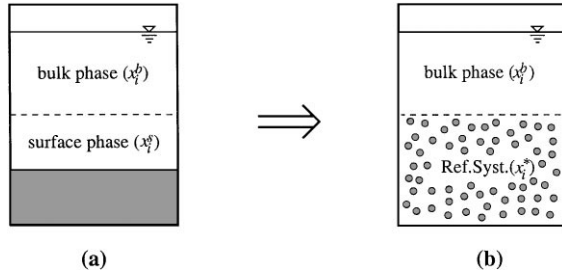


Figure 1. Definition of the reference system: (a) classical description, (b) reference system.

by Gibbs or Verschaffelt and Guggenheim (Ruthven, 1984; Everett, 1981)—is in principle the only possibility to formulate thermodynamic phase equilibrium conditions in the classical description of adsorption systems. This approach divides the total amount of fluid molecules n^o in two independent phases that are assumed to be homogeneous, the adsorbed or surface phase (s) with n^s moles of the liquid mixture and the uninfluenced bulk phase (b) (see Fig. 1(a)). By introducing activity coefficients for both phases, one obtains the well-known relation of phase equilibrium for each component i

$$x_i^b \gamma_i^b = x_i^s \gamma_i^s \exp\left(\frac{(g_i^{\text{ad}} - g_{oi}^{\text{ad}})}{RT \Gamma_{mi}^s}\right) \quad (1)$$

with g^{ad} being the free energy of immersion of the adsorbed solution and g_{oi}^{ad} the free energy of immersion of the pure adsorbed species i , respectively (Kaul and Sweed, 1983; Larinov and Myers, 1971; Minka and Myers, 1973). The corresponding activity coefficient in the surface phase has to be estimated from Eq. (1) by use of experimental data. The resulting functions $\gamma_i^s = f(x_i^s)$ show a complex variation with composition, e.g. extreme values, inflection points or non-monotonic behavior, thus questioning the physical meaning of these activity coefficients (Schay, 1969; Minka and Myers, 1973; Li et al., 1991). Moreover, for the pure component adsorption the respective activity coefficient equals 1 though the measurable enthalpy of immersion proves the existence of interactions between adsorbent and the pure liquid which actually are described by γ_i^s . Apart from Eq. (1) there is no independent relation between the activity coefficients in the surface phase and the free energy of immersion though both variables describe the same physical process, which suggests that γ_i^s and g^{ad} must be interrelated in some way (Schay, 1969).

These difficulties led to the formulation of a thermodynamically consistent framework that incorporates the adsorbent's properties by conceiving adsorption systems as a solution of the solid and the liquid adsorbates. This enables the influence of different structural groups of the adsorbent on the adsorption behavior to be estimated, thus forming a basis for a description of adsorption systems with a group contribution method that includes the adsorbent.

2. Theory

2.1. Model of Adsorption

In contrast to gas adsorption in liquid phase adsorption the total amount adsorbed Γ^s is not a meaningful variable to describe the process of adsorption since it is not directly measurable and depends on the extension of the surface phase. Therefore, the separation of liquid mixtures is generally described by the surface excess (Everett, 1993; Sircar et al., 1972)

$$\Gamma_i^e \equiv \Gamma_i^o (x_i^o - x_i^b) \quad (2)$$

$$= \Gamma^s (x_i^s - x_i^b) \quad (3)$$

The second relation which is easily derived by means of a mass balance enables the surface excess to be calculated if both the extension of the surface phase, i.e. the total amount adsorbed Γ^s , as well as the composition of the surface phase x_i^s are known. In Eqs. (2) and (3) the surface excess Γ^e and the total amount adsorbed Γ^s refer to a mass unit of adsorbent.

While the composition of the adsorbed phase may be calculated by use of general thermodynamic equilibrium relations, the calculation of the total amount adsorbed Γ^s has to be carried out based on an assumption concerning the extension or composition of the surface phase. It has to be stressed that these assumptions—commonly called *models of adsorption*—are specific for the respective adsorption system and should therefore clearly be distinguished from general thermodynamic relations (see, e.g., Everett, 1993).

In the underlying relation for the most common models of adsorption of liquid mixtures like the pore filling model or monolayer model, Γ^s is given by (see, e.g., Messow et al., 1992)

$$\frac{1}{\Gamma^s} = \frac{x_1^s}{\Gamma_{m1}^s} + \frac{x_2^s}{\Gamma_{m2}^s} \quad (4)$$

By applying the pore filling model, the surface phase capacities Γ_{mi}^s may be assessed by the pore volume of the solid v_p and the molar volume of the respective fluid v_{oi} according to $\Gamma_{mi}^s = v_p/v_{oi}$.

As mentioned above, the calculation of the surface excess still requires the estimation of the composition of the surface phase by means of equilibrium relations. The formulation of these general thermodynamic relations based on the introduction of a Gibbs excess energy for a system containing both adsorbent and adsorbates is the main aim of this paper and will be dealt with in the following chapters.

2.2. Definition of the Reference System

The idea of incorporating the adsorbent as a component of the adsorbed phase has already been discussed in literature, inter alia by Kiselev, Bering and Tolmachev (Tolmachev, 1973a, 1973b; Tolmachev and Denisova, 1973a, 1973b). On the basis of the classical formulation of the phase equilibrium (Eq. (1)) a preliminary description of the enthalpy of adsorption by use of an excess enthalpy for an adsorbate-solid-solution has been developed (Friese et al., 1996). The fundamental equation for a system containing both adsorbent as well as the adsorbates may be formulated according to Ruthven (1984) and Rudzinski and Everett (1992)

$$dG^* = -S^*dT + V^*dp + \phi^*dm_0 + \sum_{i=1}^k \mu_i^*dn_i^* \quad (5)$$

where

$$\phi^* = \frac{\partial G^*}{\partial m_0} \quad (6)$$

is the change in the free Gibbs energy of the adsorbate-solid-mixture when a small mass of solid is added to the system. Thus, ϕ^* may be described as the chemical potential of the adsorbent in the presence of the adsorbate, containing the chemical potential of the pure, uninfluenced solid in the absence of the adsorbates (ϕ_0) and the free Gibbs energy of adsorption g^{ad} that takes into account the interactions between the adsorbent and the fluids:

$$\phi^* = \phi_0 + g^{ad} \quad (7)$$

Keeping the conception of an adsorbate solid mixture, one obtains the integrated form of Eq. (5) by keep-

ing the intensive variables constant

$$G^* = \phi^*m_0 + \sum_{i=1}^k \mu_i^*n_i^* \quad (8)$$

The differentiation of Eq. (8) and comparison with Eq. (5) yields the Gibbs-Duhem equation for the adsorbate solid mixture

$$m_0 d\phi^* = - \sum_{i=1}^k n_i^* d\mu_i^* \quad (9)$$

which in this form applies for constant temperature and pressure and corresponds to the Gibbs adsorption isotherm.

2.3. Gibbs Excess Energy

At this point a new approach for the description of the adsorbate-solid-solution shall be introduced by defining the Gibbs excess energy for the reference system, thus describing the interactions between the solid and the adsorbed liquid (Berti, 1997). By applying the customary definition of the Gibbs excess energy (Gmehling and Kolbe, 1992), one may formulate the free Gibbs energy in accordance with

$$G^* = \sum_{i=1}^k n_i^s g_{oi} + G_0 + G^{E*} \quad (10)$$

where g_{oi} is the molar free Gibbs energy of the component i and G_0 the free Gibbs energy of the pure, uninfluenced adsorbent, respectively. It has already been mentioned that many difficulties in the description of interfacial phenomena arise, among other things, from the fact that the surface phase may actually not be regarded as an autonomous phase since it only exists in the presence of a solid. Usually, the change in the energy of elements of both the solid and the liquid due to van der Waals interactions is attributed to the liquid by subtracting the free Gibbs energy of the uninfluenced solid, thus yielding an expression for the chemical potential of each liquid component i in the adsorbed phase. It is a natural consequence of these considerations that the chemical potential of each liquid of the adsorbate solid mixture corresponds to the chemical potential of the liquid in the surface phase, i.e.

$$\sum_{i=1}^k \mu_i^* n_i^s = \sum_{i=1}^k n_i^s g_{oi} + G^{Es} \quad (11)$$

However, in case of an adsorbate-solid-solution, the perturbations of the atoms of the solid due to interactions with the fluids do not need to be attributed to the liquid phase, but are already taken into consideration with the Gibbs excess energy G^{E*} . Thus, G^{E*} describes the interactions of a hypothetical mixture of all liquid adsorbates in the absence of the adsorbent.

With the Eqs. (7), (8), (10) and (11) and one finally obtains the relation between the free Gibbs energy of adsorption and the Gibbs excess energy of the adsorbate-solid-solution

$$G^{E*} = G^{ad} + G^{Es} \quad (12)$$

which indicates that G^{E*} contains both the solid-fluid-interactions (G^{ad}) as well as the interactions in a liquid mixture in the absence of the solid with the composition of the surface phase (G^{Es}). In case of the pure liquid adsorption the latter term equals zero, so that the Gibbs excess energy of the (binary) adsorbate-solid-solution corresponds to the free energy of adsorption, i.e. $G_{oi}^{E*} = G_{oi}^{ad}$.

2.4. Enthalpy of Immersion and Excess Enthalpy

The corresponding result may be obtained by an enthalpy balance for an immersion experiment which is in addition necessary to derive a relation between the excess enthalpy of the solid-adsorbate-mixture and the enthalpy of immersion. Considering an amount n^o of solution separate from an amount n_0 of the solid in the initial state, the immersion will result in the formation of an uninfluenced bulk phase with the composition x_i^b and the adsorbate-solid-mixture with the composition x_i^* (see Fig. 2). The molar fractions in the adsorbate-solid-solution x_i^* are closely connected with the molar weight of the adsorbent and will be dealt with in Chapter 2.6. Thus, the enthalpy balance for

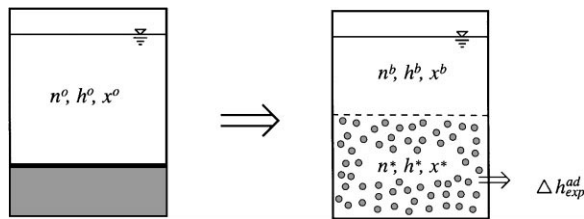


Figure 2. Enthalpy balance.

the system yields

$$\begin{aligned} \Delta H_{exp}^{ad} &= H_{end} - H_{ini} \\ &= n^* h^* + n^b h^b - n^o h^o - n_0 h_0 \end{aligned} \quad (13)$$

where ΔH_{exp}^{ad} is the change in enthalpy on immersion observed experimentally and h the molar enthalpy of the respective phase. Except for h_0 which is the molar enthalpy of the pure, uninfluenced solid, h may be expressed in terms of the excess enthalpy (Gmehling and Kolbe, 1992)

$$h = \sum_{i=1}^k x_i h_{oi} + h^E \quad (14)$$

which then leads to a more detailed formulation of the enthalpy balance:

$$\begin{aligned} \Delta H_{exp}^{ad} &= n^* \sum_{i=1}^k x_i^* h_{oi} + n^* h^{E*} \\ &+ n^o \sum_{i=1}^k (x_i^b - x_i^o) h_{oi} - n^s \sum_{i=1}^k x_i^b h_{oi} \\ &+ n^o (h^{Eb} - h^{Eo}) - n^s h^{Eb} \end{aligned} \quad (15)$$

After some algebraic manipulations, one finally obtains the relation between the measurable enthalpy of immersion and the excess enthalpy of the adsorbate-solid-solution h^{E*}

$$\Delta H_{exp}^{ad} = n^* h^{E*} - n^s h^{Eb} + n^o (h^{Eb} - h^{Eo}) \quad (16)$$

The relation between the excess enthalpy of the adsorbate-solid-mixture and the true enthalpy of immersion may be derived from Eq. (16) by considering the borderline case $n^b \rightarrow 0$, i.e. a hypothetical immersion experiment in which the solid is wetted by a total amount of fluid n^s with the composition of the surface phase x_i^s . Since in this case there is not any mixing heat due to a change in composition of the liquid phase, the measurable change in enthalpy corresponds to the true enthalpy of immersion. From Eq. (16) it follows then with $\Delta h_{exp}^{ad} \equiv h^{ad}$ and $n^o = n^s$

$$H^{E*} = H^{ad} + H^{Es} \quad (17)$$

This relation corresponds to Eq. (12).

2.5. Phase Equilibria

The formulation of the conditions of phase equilibrium requires the choice of a standard chemical potential for the adsorbed phase. Usually, in the classical formulation the pure adsorbed species i at the same temperature as the adsorbed mixture is chosen to be the standard state (Larinov and Myers, 1971; Minka and Myers, 1973). From Eq. (9) one obtains for a pure component i

$$d\phi_{oi}^* = -\Gamma_{mi}^s d\mu_{oi}^* \quad (18)$$

An integration of this relation yields the standard chemical potential for the respective component i which is identical to the chemical potential μ_{oi}^* of the pure adsorbed component i in the same state as the adsorbed mixture:

$$\mu_{oi}^*(T, \phi^*) = \mu_{oi}^{o*}(T, \phi_{oi}^*) - \frac{\phi^* - \phi_{oi}^*}{\Gamma_{mi}^s} \quad (19)$$

where ϕ_{oi}^* refers to the chemical potential of the influenced solid in the presence of the pure liquid i . By introducing activity coefficients for the adsorbate-solid-solution γ_i^* , the expressions for the chemical potential of the liquid species i in the adsorbate-solid-mixture are obtained:

$$\mu_i^* = \mu_{oi}^* + RT \ln(\gamma_i^* x_i^*) \quad (20)$$

Now the formulation of the conditions of phase equilibrium is straightforward. By equating the chemical potentials of the fluid components in each phase

$$\mu_i^b = \mu_i^* \quad (21)$$

one finally obtains an equilibrium relation for the calculation of the mole fraction of each liquid in the adsorbate-solid-solution:

$$x_i^b \gamma_i^b = x_i^* \gamma_i^* \exp\left(-\frac{\phi^* - \phi_{oi}^*}{RT\Gamma_{mi}^s}\right) \quad (22)$$

The last equation is similar to the classical formulation of phase equilibrium (Eq. (1)); however, in the borderline case of the pure component adsorption, in Eq. (22) $x_i^* \rightarrow x_{oi}^*$ and thus $\gamma_i^* \neq 1$ while $x_i^s, \gamma_i^s \rightarrow 1$. Moreover, ϕ^* does not equal the free Gibbs energy of adsorption, even though the *change* in ϕ^* is equivalent to a change in the free Gibbs energy of adsorption at

$\phi_0 = \text{const.}$ Considering again the borderline case of the pure component adsorption at the same amount of uninfluenced solid as a reference state, Eq. (7) yields $\phi_{oi}^* = \phi_0 + g_{oi}^{\text{ad}}$. Thus, the change of the chemical potential of the influenced adsorbent in Eq. (22) is given by the Eqs. (7) and (12):

$$\phi^* - \phi_{oi}^* = \frac{1}{m_0} (G^{\text{E}*} - G^{\text{Es}} - G_{oi}^{\text{E}*}) \quad (23)$$

The Gibbs excess energy may be calculated from the respective activity coefficients according to

$$\frac{G^{\text{Es}}}{RT} = \sum_{i=1}^k n_i^s \ln \gamma_i(x_i^s) \quad (24)$$

$$\frac{G^{\text{E}*}}{RT} = \sum_{i=0}^k n_i^* \ln \gamma_i^* \quad (25)$$

Hence with a suitable model for the activity coefficients the relation of phase equilibrium (22) may be used to calculate the composition of the adsorbate-solid-solution. Note that $\gamma_i(x_i^s)$ is the activity coefficient of the component i in a hypothetical, autonomous phase that is uninfluenced by a solid and may not be confused with the activity coefficient γ_i^s in the surface phase in the classical formulation (Eq. (1)) which contains the perturbation of the atoms of the solid.

Equations (23)–(25) represent the connection between the activity coefficients of all components in the adsorbate-solid-solution and the free Gibbs energy of adsorption g^{ad} (for details see Berti (1997)). For the pure component adsorption, $\gamma_i(x_i^s) \rightarrow 1$ and $\gamma_i^* \rightarrow \gamma_{oi}^*$, where γ_{oi}^* is given by Eqs. (22) ($\phi^* \rightarrow \phi_{oi}^*$) and (27) (see below):

$$\gamma_{oi}^* = 1 + \frac{1}{\Gamma_{mi}^s M_0} \quad (26)$$

Obviously, in the borderline case of pure component adsorption, the activity coefficient of the respective fluid does not equal 1 but a fixed value that depends on the respective system of adsorbent and pure liquid, i.e. the respective binary adsorbate-solid-mixture.

2.6. Mole Fractions and Molar Weight

The formulation of mole fractions for the reference system has to include the solid, i.e. one has to assign a molar quantity n_0 to the solid. The introduction of a

molar weight M_0 for the adsorbent yields a convenient formulation of the mole fractions of the fluids (x_i^*) and the solid (x_0^*)

$$x_i^* = \frac{M_0 \Gamma_i^s}{1 + M_0 \sum_i \Gamma_i^s} \quad (27)$$

$$x_0^* = \frac{1}{1 + M_0 \sum_i \Gamma_i^s} \quad (28)$$

where $\Gamma_i^s = n_i^s/m_0$ is the molar quantity of the component i referring to a mass unit of the adsorbent. It has to be stressed that these definitions are only sensible for a system in equilibrium, i.e. for a system that contains more fluid molecules than necessary to cover all adsorption sites ($n^o > n^s$). Thus, the boundaries of the domain of definition are given by the borderline case of the pure component adsorption (i. e. $x_0^* \in]0, 1[$) for each component i in which $\Gamma_i^s \rightarrow \Gamma_{mi}^s$. The connection with the variables of the surface phase is given by

$$n^s = n^*(1 - x_0^*) \quad (29)$$

$$x_i^* = x_i^s(1 - x_0^*) \quad (30)$$

The definition of a molar weight for the solid is closely connected with its functional groups. The inner surface that is significant for adsorption is composed of different functional groups. Thus, the entire inner surface may be calculated from the van der Waals group surfaces Q_K :

$$A = am_0 = \sum_K v_K Q_K = v_0 \sum_K X_K^{(0)} Q_K \quad (31)$$

where v_K is the number of functional groups of type K in the solid, $X_K^{(0)}$ the corresponding fraction of all functional groups and v_0 the total number of all functional groups in the respective amount of the solid m_0 . As for amorphous solids, the functional groups may be regarded as molecules, i.e. $n_0 \equiv v_0/N_A$ is the respective molar quantity of the adsorbent. Thus, the molar weight of the solid is given by

$$M_0 \equiv \frac{m_0}{n_0} = \frac{N_A \sum X_K^{(0)} Q_K}{a} \quad (32)$$

For crystalline adsorbents like zeolites the definition of the unit cell as molecule yields a more detailed expression for the molar weight of the adsorbent. The total number v_0 of functional groups in the solid may then be expressed in terms of the number of functional

groups per unit cell $v_{0,uc}$ and the number of these unit cells in the solid N_{uc} :

$$v_0 = N_{uc} v_{0,uc} \quad (33)$$

Defining the molar quantity of the solid according to $n_0 \equiv N_{uc}/N_A$, the molar weight of the zeolite is given by

$$\begin{aligned} M_0 &= M_{uc} = v_{0,uc} \sum_K X_K^{(0)} M_K \\ &= \sum_K v_{K,uc} M_K \end{aligned} \quad (34)$$

where $v_{K,uc}$ is the number of all functional groups of type K in the unit cell. Considering the structural formula

$$M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot zH_2O \quad (35)$$

which applies to most zeolites (Breck, 1974; Smith, 1984), Eq. (34) yields

$$M_{uc} = x \left(\frac{M_{Kat}}{n} + M_{Al} + 2M_O \right) + y(M_{Si} + 2M_O) \quad (36)$$

2.7. G^{E*} -Model: Approach of Wilson

It has to be stressed that the relations derived in Chapters 2.3–2.5 are general thermodynamic relations that do not depend on specific models describing the nature of the interactions between the solid and the liquid components. The description of these interactions starts where an appropriate model for the calculation of the Gibbs excess energy of the adsorbate-solid-solution G^{E*} is chosen. This G^{E*} -model has to take into consideration the particular energy distribution of the respective adsorption system.

The concept of describing the adsorbate-solid-solution by use of the Gibbs excess energy offers an excellent basis to incorporate a group contribution methodology that takes into account the influence of different structural groups of the solid adsorbent with respect to adsorption. However, from the mathematical point of view, G^{E*} may in principle be calculated by application of any G^E -model that is suitable to describe solutions containing at least three components, as long as the model is not limited to small values of the excess enthalpy.

Since the aim of this paper is the investigation of the thermodynamic framework presented in the previous chapters the Wilson-model (Wilson, 1964) was chosen for the calculation of G^{E*} . The development of a G^{E*} -model based on group contributions that is applicable to describe the particular interactions of molecules in adsorption systems will be subject of future research. The Wilson model has originally been developed from statistical thermodynamics for the description of liquid systems. However, the underlying idea of treating the liquid as a solid by placing each molecule in a lattice with nearest neighbors suggests and justifies the application of this approach on heterogeneous systems such as the adsorption of liquids on solids.

Since in case of adsorption the borderline case is the pure liquid adsorption, i.e. a binary adsorbate-solid-solution, the respective boundary values according to Eq. (26) have to be incorporated in any G^E -model that is used to describe the adsorbate-solid solution. This is achieved by splitting the activity coefficient of the respective fluid into two parts:

$$\ln \gamma_i^* = \ln \gamma_{oi}^* + \ln \gamma_{GE,i}^* \quad (37)$$

where γ_{oi}^* is the boundary value and $\ln \gamma_{GE,i}^*$ a concentration dependent part of the activity coefficient that is given by the chosen G^E -model. $\ln \gamma_{GE,i}^*$ has to equal zero at the concentration border:

$$\ln \gamma_{GE,i}^* = \ln \gamma_{GE,i}^*(x_i^*) - \ln \gamma_{GE,i}^*(x_{oi}^*) \quad (38)$$

$\gamma_{GE,i}^*(x_{oi}^*)$ represents the activity coefficient of a binary adsorbate-solid-solution, i.e. the pure (adsorbed) liquid and the solid adsorbent. The introduction of a reference point does not have any effect on the qualitative variation of the activity coefficients with concentration but represents a simple normalization. For the adsorption of a pure component, the activity coefficient of the solid is directly given by the G^E -model. In case of the adsorption of a binary liquid mixture, i.e. a ternary adsorbate-solid-solution, the formulation of the Wilson-model yields

$$\ln \gamma_{GE,i}^* = -\ln \left(\sum_{j=0}^2 x_j^* \Lambda_{ij} \right) + 1 - \sum_{k=0}^2 \frac{x_k^* \Lambda_{ki}}{\sum_{j=0}^2 x_j^* \Lambda_{kj}} \quad (39)$$

where

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp(\lambda_{ij}/T) \quad (40)$$

The index 0 again refers to the solid component.

3. Calculation and First Results

3.1. Estimation of Parameters

The calculation of the surface excess requires the estimation of various parameters, such as the surface phase capacities Γ_{mi}^s , the activity coefficients of the bulk phase γ_i^b and the molar weight of the adsorbent M_0 .

With exception of the system *p*-xylene/*m*-xylene/ethylbenzene on KBaY all systems have been calculated taking into consideration the non-ideality of the bulk phase by use of the Wilson model. The respective parameters are listed in Table A.3. The surface phase capacities Γ_{mi}^s are taken from the respective publications or—if not available—assessed from the surface excess isotherm by a procedure described by Schay (1969).

For the zeolites the molar weight has been estimated from the structural formula. Since there is no structural data available for silica gel or activated carbon in the respective publications, both the molar weight and the density of KBaY have been taken for these adsorbents. This is defensible since the value of the molar weight is somewhat arbitrary and does not influence the solution for the interaction parameters. All corresponding parameters are shown in the appendix (Table A.1).

3.2. Calculation Procedure

Starting point for the calculation of the surface excess $\Gamma_1^e = f(x_1^b)$ is the estimation of the bulk phase activity coefficients γ_i^b at the respective mole fraction x_i^b . Assuming known values for the Wilson parameters λ_{ij} of the adsorbate-solid-mixture, the activity coefficient γ_i^* as well as the mole fraction x_i^* of each fluid in the adsorbate-solid-solution have to be calculated simultaneously by iteration of Eqs. (22) and (39). The surface excess is then given by Eqs. (3), (4) and (30).

During optimization, i.e. estimation of the Wilson parameters λ_{ij} for the adsorbate-solid-solution from experimental data, the calculation procedure described above has to be carried out several times, thus improving the starting values for λ_{ij} iteratively by comparison of the calculated surface excess with the experimental values. All optimizations for the determination of the Wilson-parameters have been carried out by using the Simplex-algorithm of Nelder and Mead (1969) with the error function

$$\varepsilon = \frac{1}{N} \sum_{k=1}^N \left| \frac{\Gamma_{1,calc}^e - \Gamma_{1,exp}^e}{\Gamma_{1,exp}^e} \right| \quad (41)$$

Table 1. Correlated surface excess isotherms.

Adsorbent(0)	Fluid(1)	Fluid(2)	Source	ε (%)
Silica gel	Benzene	Cyclohexane	Valenzuela and Myers, 1989	2.7
NaY	Benzene	Heptane	Choi et al., 1994	1.1
Activ. carb.	Benzene	Ethanol	Valenzuela and Myers, 1989	6.4

Since enthalpies of immersion are not available for the examined systems, only surface excess data could be consulted to determine the interaction parameters. Future research will focus on the incorporation of both equilibrium and caloric data.

3.3. Correlation of Different Isotherms

The first aim is to examine the ability of ASST to correlate different types of surface excess isotherms. Table 1 and Figs. 3–5 show the results for the equilib-

rium data and the activity coefficients of the adsorbate-solid-solution. The Wilson-parameters for all correlated systems are shown in the appendix (Table A.4). All types of surface excess isotherms are represented well with only little deviations between correlation and experimental data which are in the order of the mean variation of the measured values.

The first system with benzene as preferably adsorbed component represent a surface excess isotherm of Type I in the classification of Schay (1969). The activity coefficients of the adsorbate-solid-solution show a monotonic behavior with an increase in the activity

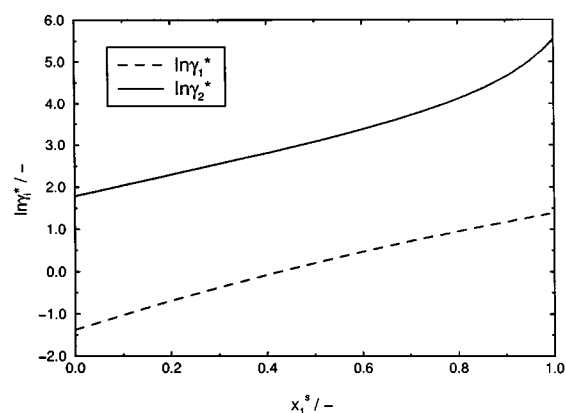
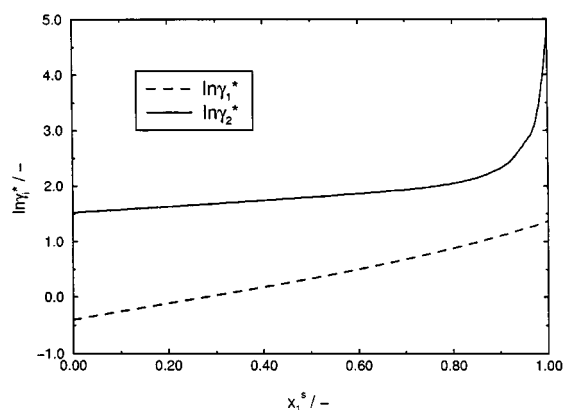
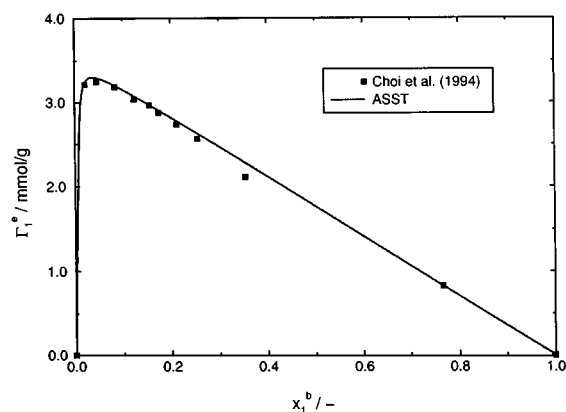
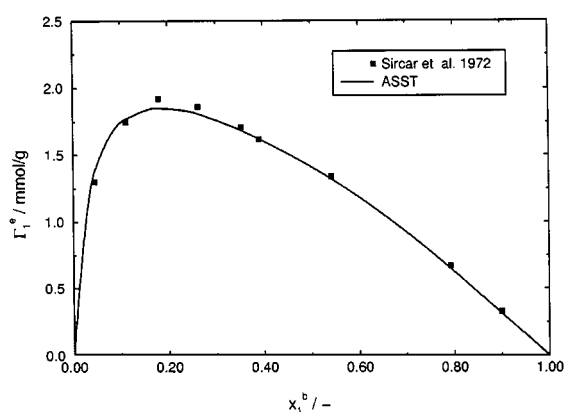


Figure 3. Benzene(1)/cyclohexane(2) on silica gel: excess isotherm and activity coefficients in the adsorbate-solid-solution.

Figure 4. Benzene(1)/heptane(2) on NaY: excess isotherm and activity coefficients in the adsorbate-solid-solution.

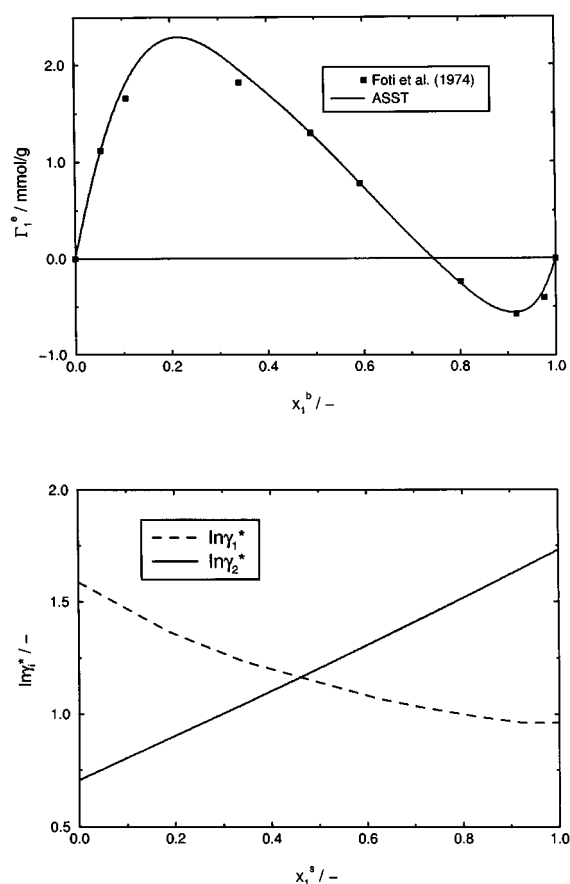


Figure 5. Benzene(1)/ethanol(2) on activated carbon: excess isotherm and activity coefficients in the adsorbate-solid-solution.

coefficient of cyclohexane on a value at infinite dilution which is typically observed for liquid mixtures.

Similar results are obtained for the system benzene(1)/heptane(2) on NaY (see Fig. 4). Surface excess isotherms of this type are represented particularly well by ASST. In comparison to the first system the gradient of the activity coefficient of the second component is relatively small for high concentrations of benzene in the surface phase x_1^s .

This corresponds to the linear part of the surface excess isotherm which indicates an almost exclusive presence of the preferably adsorbed component in the surface phase (Schay, 1969), thus pointing out an almost constant composition of this phase.

Finally, with the system benzene(1)/ethanol(2) on activated carbon, an adsorption azeotrop could be correlated with a satisfying mean deviation as well (Fig. 5). As expected, the activity coefficients show a more symmetric variation with composition due to a change of the preferable adsorbed component.

3.4. Prediction of Isotherms at Different Temperatures

To examine the ability of ASST to predict surface excess isotherms at different temperatures, the system benzene(1)/cyclohexane(2) on silica gel (Valenzuela and Myers, 1989) was chosen. With the Wilson-parameters determined at 273.15 K the surface excess isotherms were predicted at 303.15 K (mean deviation: 3.0%) and 333.15 K (mean deviation: 4.1%), respectively.

The results are shown in Fig. 6. The order of magnitude of the maximum as well as its shifting towards higher concentrations is represented well at both temperatures. The change of the surface excess with temperature results from both a change of the activity coefficients in the adsorbate-solid-solution as well as a change of the surface phase capacities with temperature.

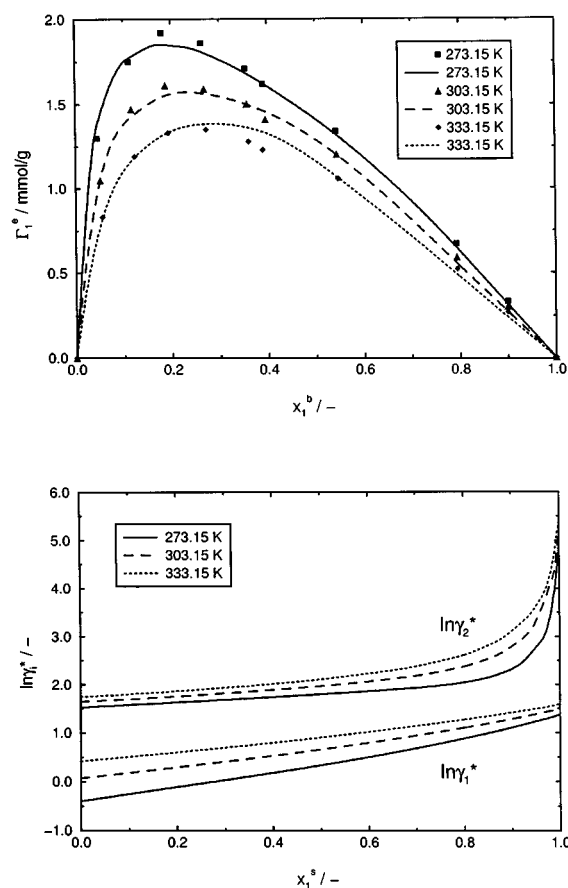


Figure 6. Benzene(1)/cyclohexane(2) on silica gel: excess isotherm and activity coefficients at different temperatures. Symbols refer to experimental data (Sircar et al., 1972), lines refer to correlated (solid line) or predicted (dashed and dotted lines) values.

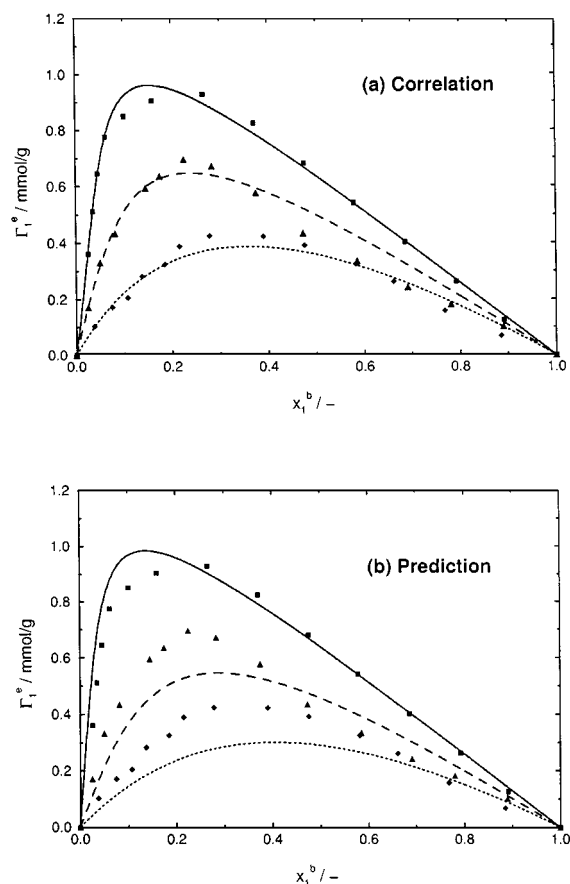


Figure 7. Correlated and predicted excess isotherms for different liquid mixtures on KBaY. Symbols refer to experimental data (Li et al., 1991); lines refer to the correlation or prediction with ASST: —■— *p*-xylene(1)/*m*-xylene (2), --▲-- ethylbenzene(1)/*m*-xylene(2), ···◆··· *p*-xylene(1)/ethylbenzene(2).

3.5. Prediction of Isotherms

If the interaction parameters have a physical meaning it should be possible to predict surface excess isotherms by estimating the Wilson-parameters from different isotherms. Figure 7(a) and Table 2 show the correlation of three binary mixtures on KBaY investigated by Li et al. (1991). The corresponding Wilson-Parameters for the three correlated systems are shown in Table A.4 in the appendix.

To predict the adsorption equilibrium for one of the three systems from the two different ones the parameters for the interactions between the adsorbed molecules have to be neglected ($\lambda_{12} = \lambda_{21} = 0$) since it is not possible to determine these variables from other binary adsorption systems unless one applies a group

Table 2. Adsorption on KBaY: Correlation.

Fluid(1)	Fluid(2)	ε (%)
<i>p</i> -xylene	<i>m</i> -xylene	3.2
Ethylbenzene	<i>m</i> -xylene	11.1
<i>p</i> -xylene	Ethylbenzene	11.3

Table 3. Adsorption on KBaY: Prediction.

Fluid(1)	Fluid(2)	ε (%)
<i>p</i> -xylene	<i>m</i> -xylene	12.4
Ethylbenzene	<i>m</i> -xylene	21.0
<i>p</i> -xylene	Ethylbenzene	27.6

contribution methodology. The remaining four parameters describing the interactions between the liquids and the adsorbent may then be estimated from the two different adsorption systems.

The results for all three predictions are shown in Table 3 and Fig. 7(b). The corresponding Wilson-Parameters for the three systems are shown in Table A.5 in the appendix. The system *p*-xylene(1)/*m*-xylene shows an excellent agreement with the experimental data. Better results may be expected by taking into consideration the interactions between the adsorbed species which requires the application of a group contribution model for the calculation of G^{E*} . However, again both the order of the maxima of the isotherms as well as their shifting towards higher concentrations are represented satisfactorily for all three of the isotherms.

4. Conclusion

A new theory for the description of the adsorption behavior of liquid mixtures on solid surfaces has been developed. Both correlations as well as predictions of surface excess isotherms at different temperatures are presented. The prediction of surface excess isotherms of binary liquid mixtures from other binary adsorption data proves the physical meaning of the Wilson interaction parameters. The activity coefficients of the adsorbate-solid-solution show a monotonic variation with composition revealing first regularities; however, at present it is not yet possible to give a complete physical interpretation for these variables. Future research will focus on the development of a G^{E*} -model based on group contributions to include both the interactions between the adsorbed fluids as well as the composition of the adsorbent in the prediction.

Appendix

Table A.1. Surface phase capacities and molar weights of the correlated systems.

Solid(0)	M_a (g/mol)	ρ (g/mol)	Fluid(1)	Γ_{m1} (mol/g)	Fluid(2)	Γ_{m2} (mol/g)
Silicagel	106.6	1.25	Benzene	273.15 K: 3.18 303.15 K: 2.73 333.15 K: 2.41	Cyclohexane	2.61 2.24 1.98
NaY	93.86	1.25	Benzene	3.54	Heptane	2.15
Act. carbon	106.6	1.25	Benzene	6.0	Ethanol	9.15
KBaY	106.6	1.25	<i>p</i> -xylol	1.32	<i>m</i> -xylene	0.84
KBaY	106.6	1.25	<i>p</i> -xylene	1.32	Ethylbenzene	1.13
KBaY	106.6	1.25	Ethylbenzene	1.13	<i>m</i> -xylene	0.84

Table A.2. Molar volumina (Regen et al., 1987).

Component	v_{oi} (cm ³ /mol)	Component	v_{oi} (cm ³ /mol)
Benzene	89.36	<i>p</i> -xylene	123.92
Cyclohexane	108.8	<i>m</i> -xylene	123.49
Ethanol	58.60	Ethylbenzene	122.49

Table A.3. Wilson parameters for liquid mixtures (Gmehling and Kolbe, 1992).

System	λ_{12} (K)	λ_{21} (K)
Benzene(1)/cyclohexane(2)	63.14	70.56
Benzene(1)/heptane(2)	103.2	75.92
Benzene(1)/ethanol(2)	104.3	704.5

Table A.4. Fitted Wilson parameters for the adsorbate-solid-solution.

Fig.	System			λ_{01} (K)	λ_{10} (K)	λ_{02} (K)	λ_{20} (K)	λ_{12} (K)	λ_{21} (K)	ε (%)
	Adsorbent(0)	Fluid(1)	Fluid(2)							
3	Silicagel	Benzene	Cyclohexane	−280	−1176	−9	3039	−1632	1245	2.7
4	NaY	Benzene	Heptane	−721	−267	−393	673	38	1483	1.1
5	Act. carbon	Benzene	Ethanol	−531	−91	−500	184	1497	496	6.4
7a	KBaY	<i>p</i> -xylene	<i>m</i> -xylene	−945	114	−979	32	900	1353	3.2
7a	KBaY	<i>p</i> -xyene	Ethylbenzene	−945	114	−943	−708	−101	3090	11.3
7a	KBaY	Ethylbenzene	<i>m</i> -xylene	−1187	235	−1212	−15	175	21.6	11.1

Table A.5. Wilson parameters for the adsorbat-solid-solution. Parameters in parenthesis are not fitted; bold lines refer to predicted systems (Fig. 7(b)).

System		λ_{01} (K)	λ_{10} (K)	λ_{02} (K)	λ_{20} (K)	ε (%)
Fluid(1)	Fluid(2)					
<i>p</i>-xylene	<i>m</i>-xylene	(−1218)	(204)	(−1263)	(−139)	12.4
<i>p</i> -xylene	Ethylbenzene	−1218	204	(−1264)	(1437)	11.4
Ethylbenzene	<i>m</i> -xylene	−1264	1437	−1263	−139	12.2
<i>p</i> -xylene	<i>m</i> -xylene	−1239	1016	(−1263)	(−139)	3.7
<i>p</i>-xylene	Ethylbenzene	(−1239)	(1016)	(−1264)	(1437)	27.6
Ethylbenzene	<i>m</i> -xylene	−1264	1437	−1263	−139	12.2
<i>p</i> -xylene	<i>m</i> -xylene	−1538	−6545	−1600	−687	4.2
<i>p</i> -xylene	Ethylbenzene	(−1538)	(−6545)	−1576	718	11.5
Ethylbenzene	<i>m</i>-xylene	(−1576)	(718)	(−1600)	(−687)	21.0

Nomenclature

a	Specific surface of adsorbent (m ² /kg)
A	Total surface of adsorbent (m ²)
G	Gibbs energy (J)
g	Molar Gibbs energy (J/mol)
G^E	Gibbs excess energy (J)
g^{ad}	Specific Gibbs energy of adsorption (J/kg)
H	Enthalpy (J)
H^E	Excess enthalpy (J)
H^{ad}	Enthalpy of adsorption (J)
$\Delta H_{\text{exp}}^{\text{ad}}$	Experimental enthalpy of adsorption (J)
$\Delta h_{\text{exp}}^{\text{ad}}$	Specific experimental enthalpy of adsorption (J/kg)
h	Molar enthalpy (J/mol)
m	Mass (kg)
M_0	Molar weight of the adsorbent (kg/mol)
n	Molar quantity (mol)
N_A	Avogadro constant (1/mol)
N_{uc}	Number of unit cells
p	Pressure (Pa)
Q	v. d. Waals Group surfaces (m ²)
R	Gas constant (J/(mol K))
S	Entropy (J/(mol K))
T	Temperature (K)
V	Volume (m ³)
v	Molar volume (m ³ /mol)
x	Molar fraction (—)
x_{oi}^*	Molar fraction of the pure adsorbed component i in the adsorbate-solid-solution (—)
X	Fraction of a functional group (—)

Greek Letters

γ	Activity coefficient (—)
μ	Chemical potential (J/mol)
ϕ_0	Chemical potential of the pure solid (J/kg)
ϕ^*	Chemical potential of the wetted solid (J/kg)
ϕ_{oi}^*	Chemical potential of the wetted solid, at adsorption of the pure component i (J/kg)
Γ	Specific molar quantity (mol/g adsorbent) (mol/g)
Γ^s	Total specific amount adsorbed (mol/g)
Γ_i^e	Specific surface excess (mol/g)
Γ_{mi}^s	Specific surface phase capacity of component i (mol/g)

Subscripts

1, 2, i	Component 1, 2 or i
oi	Pure component i or pure adsorbed component i

0	Adsorbent
exp	Experimentally
K	Group of type K
uc	Unit cell

Superscripts

(0)	Adsorbent
b	Bulk phase
s	Surface phase
o	Total amount (of fluid/before wetting)
*	Adsorbate-solid-solution
ad	Adsorption
E	Excess quantity
e	Surface excess quantity

References

- Berti, C., Diploma thesis, Institute for Thermodynamics, Universität Dortmund, 1997.
- Breck, D.W., *Zeolite Molecular Sieves*, John Wiley & Sons, New York, 1974.
- Choi, J.-W., K.-Y. Choi, and B.-H. Ha, "Liquid-Phase Adsorption of a Benzene + Heptane Mixtures on NaHY Zeolites," *J. Chem. Eng. Data*, **39**, 27 (1994).
- Everett, D.H., "Thermodynamics of Interfacial Phenomena," *Pure Appl. Chem.*, **53**, 2181 (1981).
- Everett, D.H., "Thermodynamics of Interfaces: An Appreciation of the Work of Geza Schay," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **71**, 205 (1993).
- Friese, T., P. Ulbig, and S. Schulz, "Development of a Universal Group Contribution Model for Single-Component and Multicomponent Adsorption of Liquids on Various Adsorbents (UGCMA)," *Ind. Eng. Chem. Res.*, **35**, S. 2032–2038 (1996).
- Gmehling, J. and B. Kolbe, *Thermodynamik*, VCH Verlagsgesellschaft mbH, Weinheim, 1992.
- Heuchel, M., P. Bräuer, U. Messow, and M. Jaroniec, "Phenomenological Thermodynamics of Adsorption from Binary Non-electrolytic Liquid Mixtures on Solid Surfaces," *Chemica Scripta*, **29**, 353 (1989).
- Kaul, B.K. and N.H. Sweed, "Adsorption Equilibrium Data and Model Needs," *Fundamentals of Adsorption, Proceedings of the Engineering Foundation Conference*, Schlo Ellmau, Bayern, p. 249, 1983.
- Larinov, O.G. and A.L. Myers, "Thermodynamics of Adsorption from Nonideal Solutions of Nonelectrolytes," *Chem. Eng. Sci.*, **26**, 1025 (1971).
- Li, M.-H., H.-C. Hslao, and S.-M. Yih, "Adsorption Equilibria of Xylene Isomers on a KBa-Y Zeolite," *J. Chem. Eng. Data*, **36**, 244 (1991).
- Messow, U., P. Bräuer, M. Heuchel, and M. Pysz, "Zur experimentellen Überprüfung der Vorhersage von Gleichgewichtsdigrammen bei der Adsorption binärer flüssiger Mischungen in porösen Festkörpern," *Chem. Tech.*, **44**, 56 (1992).
- Minka, C. and A.L. Myers, "Adsorption from Ternary Liquid Mixtures on Solids," *AIChE Journal*, **19**, 453 (1973).
- Nelder, J.A. and R. Mead, *Computer J.*, **7**, 303–313 (1969).

- Regen, O., R. Altmann, and J. Schneider, *Chemisch-technische Stoffwerte—eine Datensammlung*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1987.
- Rudzinski, W. and D.H. Everett, *Adsorption of Gases on Heterogeneous Surfaces*, Academic Press, London, 1992.
- Ruthven, D.M., *Principles of Adsorption and Adsorption Processes*, John Wiley & Sons, Inc., 1984.
- Schay, G., "Adsorption of Solutions of Nonelectrolytes," *Surface and Colloid Science*, Vol. 2, E. Matijevic (Ed.), p. 155, Wiley-Interscience, New York, 1969.
- Sircar, S., J. Novosad, and A.L. Myers, "Adsorption from Liquid Mixtures on Solids: Thermodynamics of Excess Properties and Their Temperature Coefficients," *Ind. Eng. Chem. Fundam.*, **11**, 249 (1972).
- Smith, J.V., "Definition of a Zeolite," *Zeolites*, **4**, 309 (1984).
- Tolmachev, A.M., "Thermodynamics of Sorption. I. General Equilibrium Conditions in the Adsorbate (Mixed)-Sorbent System," *Russ. J. Phys. Chem.*, **47**, 1478 (1973a).
- Tolmachev, A.M., "Thermodynamics of Sorption. Chemical Potentials of the Components and Certain Characteristics of the Sorption Phase with Limited Capacity," *Russ. J. Phys. Chem.*, **47**, 1478 (1973b).
- Tolmachev, A.M. and L.V. Denisova, "Thermodynamics of Sorption. II. Stoichiometry of the Sorption of Individual Substances and of Their Mixtures," *Russ. J. Phys. Chem.*, **47**, 1480 (1973a).
- Tolmachev, A.M. and L.V. Denisova, "Thermodynamics of Sorption. III. Stoichiometry in the Ideal Sorption of Pure Substances and Calculation of the Equilibrium Characteristics of the Sorption of a Mixture from Individual Isotherms," *Russ. J. Phys. Chem.*, **47**, 10 (1973b).
- Valenzuela, D.P. and A.L. Myers, *Adsorption Equilibrium Data Handbook*, 1989.
- Wilson, G.M., "Vapour Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing," *J. Am. Chem. Soc.*, **86**, 127–131 (1964).