Adsorption 11: 229–234, 2005

Application of Excess Formalism to Multicomponent Liquid Adsorption Equilibria*

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Abstract. Thermodynamic equations for the description of multicomponent liquid adsorption equilibria on solids are often formulated in terms of absolute quantities instead of excess quantities. Considering the excess nature of liquid adsorption phenomena, the utilization of excess quantities seems to be more suitable for the analysis and prediction of multicomponent liquid adsorption. In this paper, a brief summary of four different possible applications of adsorption excess formalism is given. Calculations and experimental data are used to illustrate theoretical relations and to demonstrate their applicability.

Keywords: Excess formalism, thermodynamic prediction, adsorption isotherm, binary and ternary liquid mixtures, liquid/solid interface, liquid/air interface, activity coefficient, surface tension, calorimetric quantity

1. Introduction

The knowledge of multicomponent adsorption equilibria is essential for understanding and predicting many processes in the chemical industry, such as liquid/solid adsorption and separation, purification or flotation processes. Theory can help to reduce the number of necessary measurements of adsorption excesses for ternary or higher-order liquid mixtures. Up to now, the international standard of thermodynamic methods for predicting multicomponent adsorption on solids from binary data has been based on models applying absolute quantities (Larionov and Myers, 1971; Minka and Myers, 1973; Price and Danner, 1987; Myers et al., 1987; Price and Danner, 1988; Myers, 1991; Kalies et al., 2002).

Recently, however, we have shown that the utilization of excess quantities as a basis of the thermodynamic approach can simplify the prediction of multicomponent liquid adsorption from binary data. A fundamental equation was derived for the prediction of ternary or higher-order data from adsorption excess data for the constituent binary mixtures. An expression was obtained for the double Gibbs free excess energies, valid for the adsorption on liquid/air as well as liquid/solid interfaces (Kalies et al., 2004a). As different from previous models applying absolute quantities, the new approach is based exclusively on binary excess data and independent of assumptions for the Gibbs surface phase model. Qualitative and quantitative agreement between theory and experiment was obtained for different near-ideal and non-ideal ternary adsorption systems (Kalies et al., 2004b, 2004c). In addition, the application of excess formalism allows the calculation of immersion quantities (Kalies et al., 2005).

This paper presents, in a concise form, useful thermodynamic equations, formulated in terms of excess quantities, for describing multicomponent liquid adsorption. Four different fields of application are

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*Dedicated to Prof. Dr. Wolfgang Schirmer who died on April 16, 2005.

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shown:

1. the prediction of ternary adsorption excesses at the liquid/solid interface,
2. the calculation of ternary immersion quantities at the liquid/solid interface,
3. the prediction of ternary surface tensions at the liquid/air interface,
4. the calculation of ternary adsorption excesses at the liquid/air interface.

For each field of application, calculated data are illustrated in figures.

2. Theory and Application

2.1. Prediction of Ternary Adsorption at the Liquid/Solid Interface

Using the regular solution model of statistical thermodynamics for the excess formalism of adsorption, it can be shown that the double Gibbs free excess energy for a liquid mixture of n components can be predicted from its analogous binary quantities (Kalies et al., 2004a). The application of phenomenological thermodynamics results in (Kalies et al., 2004b):

$$\begin{aligned}\Phi^E_{123} &= \Phi^E_{12} + \Phi^E_{13} + \Phi^E_{23} \\ \Phi_{123} - \Phi^{id}_{123} &= \Phi_{12} - \Phi^{id}_{12} + \Phi_{13} - \Phi^{id}_{13} + \Phi_{23} - \Phi^{id}_{23}\end{aligned} \tag{1}$$

with Φ_{123} and Φ_{ij} being the specific free wetting energies of the adsorbent in the ternary or binary liquid mixtures (Bräuer et al., 2002; Kalies et al., 2004b). The quantities Φ_{123} and Φ_{ij} can be additively presented by their ideal parts Φ^{id}_{123} and Φ^{id}_{ij} and their excess parts Φ^E_{123} and Φ^E_{ij}.

Since the binary specific free wetting energies can be obtained from measured binary adsorption excesses and from the bulk activity coefficients of component j in the binary mixture, Eq. (1) can be used for predicting ternary specific free wetting energies and thus for predicting the ternary adsorption excesses Γ^σ_k, which are related to the mass of adsorbent (Kalies et al., 2004b). The excess parts of the binary and ternary specific free wetting energies can, for example, be described by Redlich-Kister polynomials.

Figures 1–3 show ternary adsorption excesses predicted by Eq. (1). The predicted data are compared with consistent sets of experimental data (Minka and Myers, 1973; Kalies et al., 2004b). Qualitative and quantitative agreement between theory and experiment is obtained for the near-ideal n-hexane/n-octane/n-tetradecane ternary mixture on Carboxen 563 at 298 K as well as for the non-ideal cyclohexane/ethyl acetate/benzene ternary mixture on activated carbon at 303 K.

2.2. Calculation of Ternary Immersion Quantities at the Liquid/Solid Interface

Ternary adsorption excess isotherms at different temperatures as predicted by Eq. (1) can constitute the basis for the calculation of ternary immersion quantities such as immersion enthalpies or entropies.

The starting point for the calculation of caloric adsorption excess quantities is again an expression for the

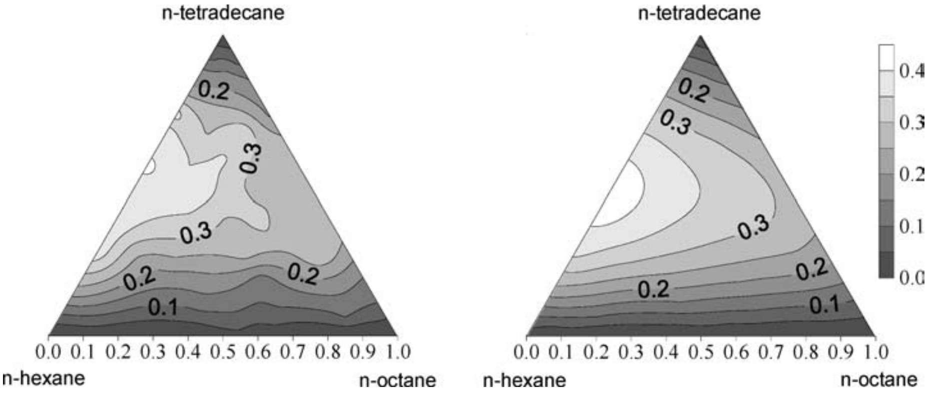

Figure 1. Comparison of the experimental (left-hand side) and predicted (right-hand side) adsorption (mmol/g) of n-tetradecane from the ternary n-hexane/n-octane/n-tetradecane mixture on Carboxen 563 at 298 K. Experimental data from Kalies et al. (2004b).

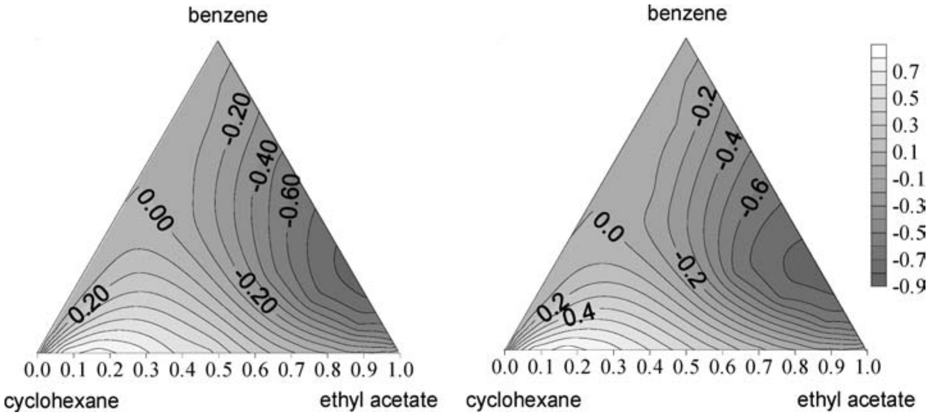

Figure 2. Comparison of the experimental (left-hand side) and predicted (right-hand side) adsorption excesses (mmol/g) of ethyl acetate from the ternary cyclohexane/ethyl acetate/benzene mixture on activated carbon at 303 K. Experimental data from Minka and Myers (1973).

specific free wetting energy Φ. The following relations are given for the specific immersion entropy (Kalies et al., 2005):

$$\Delta_w s_{sp} = -\left[\frac{\partial\left(\Phi_{123} - \Phi_{1^*}\right)}{\partial T}\right]_{P,x_2^\alpha,x_3^\alpha} + \Delta_w s_{sp,1*} \quad (2)$$

and the specific immersion enthalpy

$$\Delta_w h_{sp} = \left(\frac{\partial\left[\left(\Phi_{123} - \Phi_{1^*}\right)/T\right]}{\partial\left(1/T\right)}\right)_{P,x_2^\alpha,x_3^\alpha} + \Delta_w h_{sp,1^*} \quad (3)$$

$\Delta_w h_{sp,1^*}$ being the immersion enthalpy of the pure first component to be measured calorimetrically. The differential term of Eq. (3) can be calculated from the ternary adsorption isotherms at different temperatures. Thus, the caloric data of ternary mixtures can be calculated from the adsorption-equilibrium data at different temperatures if the immersion enthalpy is known for one pure component of the mixture.

The right-hand side of Fig. 4 shows the immersion enthalpies of the ternary *n*-hexane/*n*-octane/*n*-hexadecane mixture on TA 95 activated carbon, calculated by Eq. (3). The enthalpies show continuous behavior inside the Gibbs triangle and correspond to the experimental enthalpies of pure *n*-alkanes on TA 95. The pictures show that phenomenological thermodynamics allows the estimation of the immersion quantities of mixtures, which otherwise would require time-consuming measurements (Kalies et al., 2005).

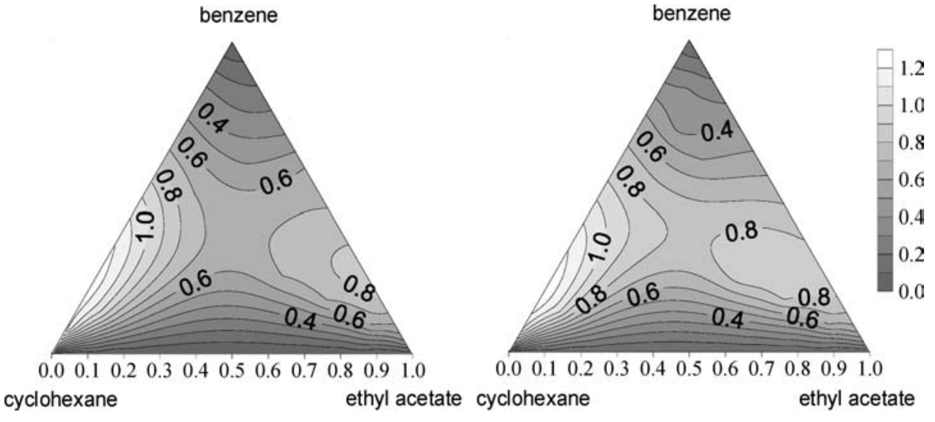

Figure 3. Comparison of the experimental (left-hand side) and predicted (right-hand side) adsorption excesses (mmol/g) of benzene from the ternary cyclohexane/ethyl acetate/benzene mixture on activated carbon at 303 K. Experimental data from Minka and Myers (1973).

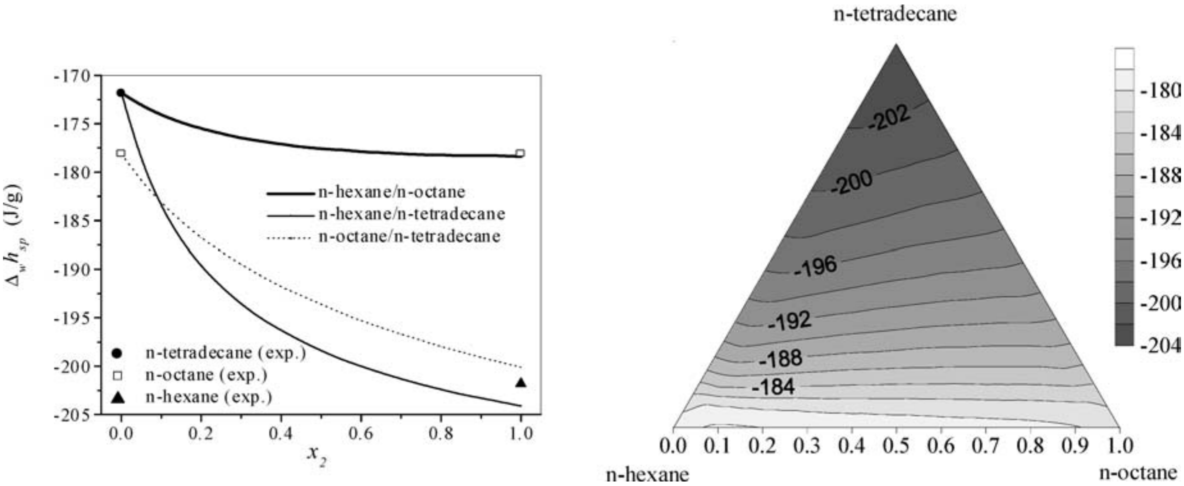

Figure 4. Calorimetrically measured immersion enthalpies $\Delta_w h_{sp}$ (J/g) of pure n-alkanes on TA 95 and calculated binary (left-hand side) and ternary (right-hand side) immersion enthalpies $\Delta_w h_{sp}$ (J/g) of the ternary n-hexane/n-octane/n-tetradecane mixture on TA 95 at 293 K.

2.3. *Prediction of Ternary Surface Tensions at the Liquid/Air Interface*

The following equation can be used for predicting ternary surface tensions σ_{123} at the liquid/air interface from binary ones σ_{ij} (Kalies et al., 2004c):

$$\begin{aligned}&\sigma_{123}^E = \sigma_{12}^E + \sigma_{13}^E + \sigma_{23}^E\\&\sigma_{123} - \sigma_{123}^{id} = \sigma_{12} - \sigma_{12}^{id} + \sigma_{13} - \sigma_{13}^{id} + \sigma_{23} - \sigma_{23}^{id}\end{aligned} \tag{4}$$

The quantities σ_{123} and σ_{ij} can be presented additively by their ideal parts σ_{123}^{id} and σ_{ij}^{id} and their excess parts σ_{123}^E and σ_{ij}^E. The excess parts of the binary and ternary surface tensions can, for example, be described by mathematical functions or by thermodynamic models such as Li's expressions (Li et al., 2000; Li and Wang, 2001).

In Fig. 5, the experimental surface tensions of the ternary n-hexane/n-octane/n-tetradecane mixture (experimental data from Siskova and Hampl (1984)) are compared with those predicted by Eq. (4). A simple Redlich-Kister polynomial was used to describe the excess part of surface tension. The experimental and predicted surfaces are similar in the Gibbs ternary triangle. The accuracy of prediction is comparable to that of other thermodynamic models published so fare. For near-ideal mixtures, theory is in quantitative agreement with the experimental data, but it needs to be improved for predictions concerning aqueous mixtures (Kalies et al., 2004c).

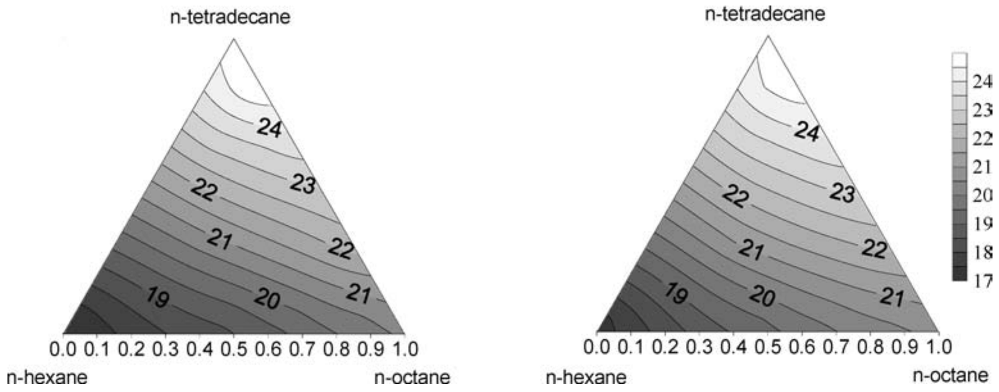

Figure 5. Comparison of the experimental (left-hand side) and predicted (right-hand side) surface tensions (mN/m) of the ternary n-hexane/n-octane/n-tetradecane mixture at 303 K. Experimental data from Siskova and Hampl (1984).

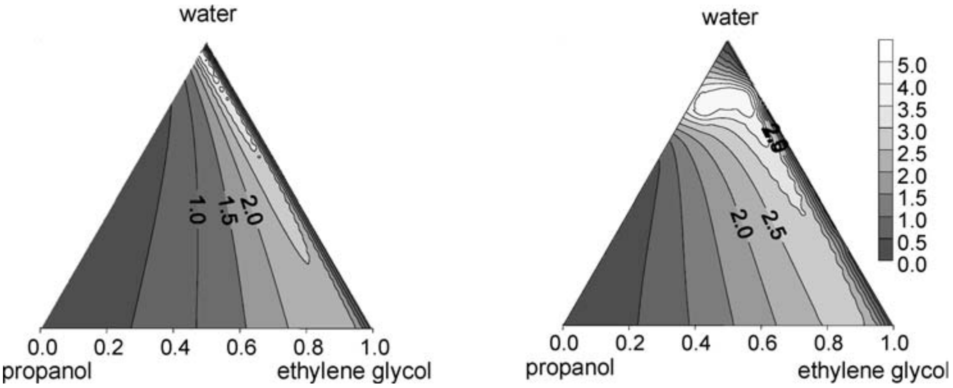

Figure 6. Calculated ideal (left side) and real (right side) adsorption $\Gamma_i^\sigma = f(x_1, x_2, x_3)$ (μmol/m^2) of *n*-propanol from the ternary *n*-propanol/ethylene glycol/water mixture at 293 K.

2.4. Calculation of Ternary Adsorption Excesses at the Liquid/Air Interface

The following thermodynamic equations as derived in Kalies et al. (2002) can be used for the calculation of adsorption excesses $\hat{\Gamma}_k^\sigma$, which are related to the surface of the liquid mixture, from predicted ternary surface-tension data:

$$\hat{\Gamma}_2^\sigma = \frac{A_2 R_{331}^\alpha - A_3 R_{321}^\alpha}{R_{231}^\alpha R_{321}^\alpha - R_{221}^\alpha R_{331}^\alpha}, \tag{5}$$

$$\hat{\Gamma}_3^\sigma = \frac{A_3 R_{221}^\alpha - A_2 R_{231}^\alpha}{R_{231}^\alpha R_{321}^\alpha - R_{221}^\alpha R_{331}^\alpha}. \tag{6}$$

A_2 and A_3 are abbreviations for the derivation of the ternary surface tension to the mole fractions x_2 and x_3. The symbols R_{k21}^α and R_{k31}^α for $k = 2, 3$ denote the coefficients of real fluid corrections and can be calculated from known mole fractions and activity coefficients of the liquid mixture.

Figure 6 gives an example of ternary adsorption excesses at the liquid/air interface as calculated from experimental surface tensions. The ideal and real adsorption excesses of *n*-propanol from the ternary *n*-propanol/ethylene glycole/water mixture are shown (Kalies et al., 2002). Ideal excesses are calculated without considering activity coefficients. In either case, *n*-propanol is preferentially adsorbed over the whole concentration range, i.e. *n*-propanol shows a tendency to get to the surface. A high separation factor can be found, confirming the well-known fact that *n*-propanol behaves in a similar way as a surface-active agent. Thus it becomes evident that thermodynamic treatment can yield reliable information about adsorption behavior even if direct experimental data are not available.

3. Conclusions

A brief summary of four different possible applications of adsorption excess formalism is given. The approach is thermodynamically rigorous and relatively simple. The calculation examples given in this paper indicate that the excess formalism of adsorption represents a natural way of describing and predicting multicomponent adsorption equilibria at the liquid/solid and liquid/air interfaces.

Nomenclature

Formula sign

G	Gibbs free energy, J/mol
$\Delta_w h_{sp}$	specific immersion enthalpy, J/mol
P	pressure, Pa
$\Delta_w s_{sp}$	specific immersion entropy, J/(mol K)
T	temperature, K
x_k^α	mole fraction of component k in adsorption equilibrium
Γ_k^σ	adsorption excess of component k, related to the mass of solid, mmol/g
$\hat{\Gamma}_k^\sigma$	adsorption excess of component k, related to the surface of the liquid mixture, μmol/m^2
Φ	specific free wetting energy, J/g
σ	surface tension at the liquid/air interface, J/m^2

Abbreviation

A_2	abbreviation for $(\partial\sigma^{123}/\partial x_2^\alpha)_{T,P,x_3^\alpha}$
A_3	abbreviation for $(\partial\sigma^{123}/\partial x_3^\alpha)_{T,P,x_2^\alpha}$
R_{k21}^α, R_{k31}^α	coefficients of real fluid corrections, $k =$ 2,3 (Kalies et al., 2002)

Upper index

σ	adsorption excess
E	mixture excess
α	adsorption equilibrium

Lower Index

$123\ldots n$	multicomponent mixture
ij	binary mixture
$1, 2, 3, k$	the corresponding component in liquid mixture
i, j	the corresponding component in binary liquid mixture; $i = 1, 2,\ j = 2, 3; i \neq j$
1^*	pure first component

Acknowledgments

The financial support for this project by Deutsche Forschungsgemeinschaft (DFG, Ka 1540/1-3, Ka 1560/2-1) and the Saxon State Ministry for Science and Art is gratefully acknowledged.

References

Bräuer, P., M. Heuchel, and M. Jaroniec, "Thermodynamic Description of Interfaces", in M. Dekker (Ed.), *Encyclopedia of Surface and Colloid Science*, New York, pp. 5326–5343, 2002.

Kalies, G., P. Bräuer, and F. Rouquérol, "Prediction of Ternary Liquid Adsorption on Solids from Binary Data," *J. Colloid Interface Sci.*, **229**, 407–417 (2000).

Kalies, G., P. Bräuer, and U. Messow, "Prediction of Multicomponent Liquid Adsorption Using Excess Quantities, I. Statistical Thermodynamic Derivation of the Basic Equation of Excess Formalism," *J. Colloid Interface Sci.*, **275**(1), 90–96 (2004a).

Kalies, G., P. Bräuer, and U. Messow, "Prediction of Multicomponent Liquid Adsorption Using Excess Quantities, II. Calculations for the Liquid/Solid Interface," *J. Colloid Interface Sci.*, **275**(2), 410–418 (2004b).

Kalies, G., P. Bräuer, M. Kudra, and U. Messow, "Prediction of Multicomponent Liquid Adsorption Using Excess Quantities, III. Calculations for the Liquid/Air Interface," *J. Colloid Interface Sci.*, **275**(2), 419–427 (2004c).

Kalies, G., R. Rockmann, and R. Denoyel, "Calculation of Immersion Enthalpy Data from Adsorption Excess Isotherms," *J. Colloid Interface Sci.*, **282**(2), 327–334 (2005).

Kalies, G., P. Bräuer, A. Schmidt, and U. Messow, "Calculation and Prediction of Adsorption Excesses on the Ternary Liquid Mixture/Air Interface from Surface Tension Measurements," *J. Colloid Interface Sci.*, **247**, 1–11 (2002).

Larionov, O.G. and A.L. Myers, "Thermodynamics of Adsorption from Nonideal Solutions of Nonelectrolytes," *Chem. Eng. Sci.*, **26**, 1025–1030 (1971).

Li, C., W. Wang, and Z. Wang, "A Surface Tension Model for Liquid Mixtures Based on the Wilson Equation," *Fluid Phase Equilibria*, **175**, 185–196 (2000).

Li, C. and W. Wang, "A Surface Tension Model for Liquid Mixtures Based on NPTL Equation," *Chin. J. Chem. Eng.*, **9**(1), 45–50 (2001).

Minka, C. and A.L. Myers, "Adsorption from Ternary Liquid Mixtures on Solids," *AIChE J.*, **19**(3), 453–459 (1973).

Myers, A. L., P. E. Price, and R. P. Danner, "Letters to the Editor," *AIChE J.*, **33**, 1757 (1987).

Myers, A.L., "Equation for Equilibrium Adsorption from Liquid Mixtures", in A.B. Mersmann and S.E. Scholl (Eds.), *Fundamentals of Adsorption*, United Engineering Trustees, Inc., pp. 609–618, 1991.

Price, P.E. and R.P. Danner, "Prediction of Multicomponent Liquid Adsorption Equilibria," *AIChE J.* **33**, 551–557 (1987).

Price, P.E. and R.P. Danner, "Extension and Evaluation of the Minka and Myers Theory of Liquid Adsorption," *Ind. Eng. Chem. Res.* **27**(3), 506–512 (1988).

Siskova, M. and P. Hampl, "Surface Tensions of Ternary *Systems*," *Collection Czechoslovak Chem. Commun.*, **49**, 903–910 (1984).