

Thermodynamically Consistent Equilibrium Adsorption Isotherms for Mixtures of Different-Size Molecules

Elias I. Franses,* Faisal A. Siddiqui, Dong June Ahn,[†]
Chien-Hsiang Chang,[‡] and Nien-Hwa Linda Wang

School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907-1283

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Simple and general differential criteria are derived for testing equilibrium adsorption isotherms for consistency with the laws of thermodynamics. The generalized Langmuir isotherm (L-model) for binary solutes of different sizes or adsorption capacities fails the test, as previously noted. A consistent isotherm is derived for the first time, by using the framework of the ideal adsorbed solution (IAS) theory of Myers and Prausnitz (*AIChE J.* **1965**, *11*, 121). The scaled particle theory isotherms for circular disks are shown to be thermodynamically consistent and to lead to almost identical predictions as an IAS model based on a modified Langmuir isotherm. All models with ideal mixing in the adsorbed solution predict that at high coverages the larger molecules (those with smaller adsorption capacity) are substantially depleted from the surface for steric and entropic reasons. With increasing concentration, the models predict selectivity reversals in cases where the larger molecules are not much more surface active than the smaller molecules.

1. Introduction

Binary and multicomponent adsorption at air/water, oil/water, gas/solid, and liquid/solid interfaces is an important practical problem in foams, emulsions, detergency, catalysis, and certain separation methods.¹⁻⁷ One normally determines the adsorption equilibria of the individual components and then describes the adsorption of the mixtures.⁸⁻²⁴ The Langmuir equilibrium isotherm is the simplest and most popular among the adsorption isotherms, for noninteracting molecules on a lattice. Improvements include modified forms of the Langmuir isotherm, the Frumkin isotherm, and others.²⁴⁻²⁷ The simplest isotherm for mixtures is a generalization of the

single-component isotherm, without introducing additional mixing parameters. This is the point of reference for introducing intermolecular adsorbate-adsorbate interactions in classical thermodynamic or in molecular thermodynamic theories.

A set of adsorption equations are the generalized Langmuir isotherms (see section 2.2.1), which are still cited in recent books and monographs and are still used by researchers in adsorption, chromatography, and other areas.^{3,21-23,28,29} These equations have been reported, however, by various authors, to be thermodynamically inconsistent if the molecular sizes or adsorption capacities of the components are different.^{15,30,31} This has given the impetus for developing improved isotherms, such as the scaled-particle theory isotherm²⁵ or the ideal adsorbed solution theory.⁸

In this article, we develop (i) simple and quite general criteria for testing isotherms for necessary conditions for thermodynamic consistency and (ii) guidelines for developing thermodynamically consistent isotherms. We derive the thermodynamically rigorous form of the Langmuir isotherm for mixtures of different-size molecules, using the ideas of the ideal adsorbed solution model of Myers and Prausnitz.⁸ The predictions of the consistent and the inconsistent Langmuir isotherms for mixtures differ substantially, both quantitatively and qualitatively. Differences between the consistent form and experimental data may still exist, of course, if there are significant adsorption features or intermolecular interactions which are not incorporated in the model.

Using the same approach, we also prove that the Scaled-Particle Theory (SPT) isotherms of hard disks are indeed thermodynamically consistent and essentially equivalent to the ideal adsorbed solution model of a modified version of the Langmuir isotherm. These models account explicitly for steric effects of adsorbed molecules in dense packings at high area coverages.²⁵

2. Theory

2.1. General Criteria. For a dilute solution of two components 1 and 2 and a solvent, the Gibbs adsorption

[†] Present address: Department of Chemical Engineering, Korea University, Seoul 136-701, Korea.

[‡] Present address: Chemical Engineering Department, National Cheng Kung University, Tainan, Taiwan 701, The Republic of China.

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