

# Understanding Adsorption of Nonideal Mixtures

The ability of porous materials to adsorb fluids selectively is the basis of many industrial applications, especially catalysis and the separation and purification of gases and liquids. Yet, the prediction of multicomponent equilibria is still one of the most challenging problems in the adsorption field. The main problem is a lack of accurate and consistent experimental data for testing theories, with almost no data available on enthalpy of adsorbed mixtures, says Alan Myers, professor emeritus of chemical engineering at the Univ. of Pennsylvania (Philadelphia).

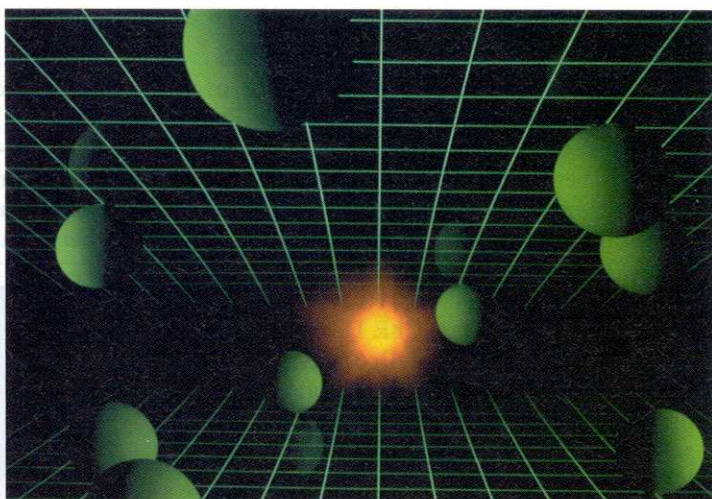
Myers and his colleague Flor Siperstein used a calorimeter that simultaneously measures mixture equilibria and heats of adsorption to study activity coefficients, excess free energies, and enthalpies of mixing in the adsorbed phase. The standard procedure for studying adsorption equilibrium is to measure loading at several temperatures; typically, three adsorption isotherms are measured at 30°C intervals so that system behavior is determined within a band of 60°C. Myers' volumetric-calorimetric method measures a single isotherm and the heat of adsorption, and the temperature dependence is provided by thermodynamic equations linked to the heat of adsorption.

Based on their studies of two types of zeolites (silicalite and NaX) and seven gas mixtures ( $\text{SF}_6/\text{CH}_4$ ,  $\text{C}_2\text{H}_6/\text{CH}_4$ ,  $\text{CO}_2/\text{C}_2\text{H}_6$ ,  $\text{CO}_2/\text{C}_3\text{H}_8$ ,  $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ ,  $\text{SF}_6/\text{C}_2\text{H}_6$ , and  $\text{CO}_2/\text{C}_2\text{H}_4$ ), Myers and Siperstein developed a three-constant model of binary adsorption in which the properties of the mixture are a function of the excess Gibbs free energy. The constants in the equation depend on the excess enthalpy, the excess entropy, and the excess reciprocal loading. This model, along with single-component isotherms and enthalpies, provides a complete thermodynamic description of mixture adsorption for type I isotherms without hysteresis loops, Myers explains.

More information about this work can be found in the May issue of *AIChE Journal*.

## Electrostatics Affect Protein Transport in Membranes

Ultrafiltration has traditionally been viewed as a purely size-based separation process. However, protein transport through semipermeable membranes is also strongly affected by electrostatic interactions. Numerous theoretical analyses of electrostatic effects on solute transport in membrane systems provide reasonable qualitative descriptions of experimental results, but quantitative comparisons between theory and data are limited, say Andrew Zydney, professor of chemical engineering at the Univ. of Delaware (Newark), and PhD student Douglas Burns.



Zydney and Burns have quantitatively compared predictions of available theoretical models with experimental data for protein transport under conditions with both attractive and repulsive electrostatic interactions. They studied the filtration of ovotransferrin in different KCl solutions through either standard 100,000 molecular weight cutoff polyethersulfone membranes or prototype 100,000 MW cutoff positively charged polyethersulfone membranes.

Existing hydrodynamic and partitioning models can provide a very good description of the effects of electrostatic interactions on the transport of a charged protein through a charged membrane in the presence of both repulsive and attractive interactions, Zydney explains. The models properly describe the effects of solution pH and ionic strength on protein transport through both membranes, and correctly predict the local maximum in the protein sieving coefficient at an intermediate ionic strength seen at pH 9.0, he adds. These theoretical insights are now being used in collaboration with researchers at Millipore and Genentech to develop new membrane processes for protein purification.

Additional information about this work can be found in the May issue of *AIChE Journal*.

## Packed-Bed Flow is Revealed

Although corrugated-sheet structured packings are widely used in distillation and related operations, their performance is still not fully understood. The development of more-detailed predictive models is hindered by lack of knowledge about the sources, nature, and extent of small-scale liquid maldistribution, says Zarko Olujic, of the Laboratory of Process Equipment at Delft Univ. of Technology (Delft, the Netherlands). He believes this obstacle could be overcome if one could see the liquid flow patterns inside the packed bed during operation — for example, by using a technique such as X-ray computed tomography.

Olujic, and Pierre Marchot and his coworkers at the Univ. of Liège (Liège, Belgium), studied the hydraulic performance of polypropylene packing in an air/water system