LETTERS TO THE EDITOR

To the Editor:

By using the two-site heterogeneous surface model, Myers (1983) recently calculated the surface activity coefficients of ideal mixtures adsorbed on a heterogeneous surface. The calculated results show that the apparent surface activity coefficients are smaller than 1: i.e., there is negative deviation from Raoult's law. In addition, the calculations show the surface activity coefficient curves to be asymmetric, the result always found experimentally (Li and Gu, 1979; Everett and Podoll, 1981). Thus Myers (1983) concluded that the apparent nonidealities of the adsorbed layer may be due to the heterogeneity of the surface, not to nonidealities in the molecular interactions between unlike components of the adsorbed mixture. Unfortunately, Myers (1983) only calculated a single instance. Moreover, the total surface coverage in this instance was only about 0.8. When dealing with adsorption from solutions, the total surface coverage is usually 1.0.

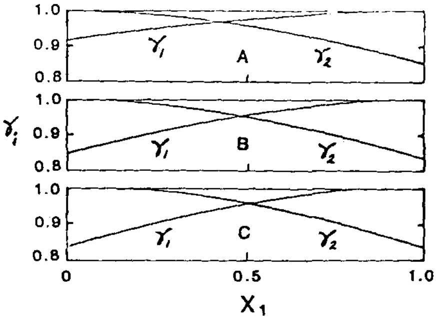

Figure 1. Theoretical surface activity coefficients: surface compositions of binary ideal mixture adsorbed on two-site heterogeneous surface model. (Refer to Table 1.)

Since the coverage is normally 1.0 in practical situations, it is important to calculate the theoretical surface activity coefficients at this coverage. Table 1 shows the values of parameters used in surface activity coefficients calculations. The first set of the data in Table 1 are those calculated by Myers (1983); the second and third sets of data were calculated by this author. To approach the condition of total surface coverage close to 1, I raised P from 10 to 1,000 (or, alternatively, raised all the Langmuir parameters C one hundred times), but kept the selectivities of the A and B surface unchanged. Under these conditions, the total surface coverages are greater than 0.99. Figure 1 shows that the apparent surface activity coefficient curves are very nearly symmetric when the total surface coverage is close to 1. Therefore, the asymmetric curves for the experimentally measured activity coefficients, are probably not due to the heterogeneity of the surface, but rather to nonidealities in the molecular interactions between the unlike components of the adsorbed mixture.

LITERATURE CITED

Everett, D.H., and R.T. Podoll, *J. Colloid Interface Sci.*, **82**, 14 (1981).

Li, P., and T. Gu, *Scientia Sinica*, **22**, 1384 (1979).

Myers, A.L., *AIChE J.*, **29**, 691 (1983).

TIREN GU
Dept. of Chemistry
Peking University
Peking, China

Reply:

Professor Gu raised the point that curves for activity coefficients become symmetric as the fractional coverage approaches unity. This is correct. However, the coverage does not in fact go to unity at saturation of the vapor. As shown on Figure 2 for adsorption of carbon dioxide on activated carbon (Reich, Ziegler and Rogers, 1980), the loading (10.8 mmol/g) at saturation (437 kPa) is less than the total capacity (13.2 mmol/g) predicted by the Toth equation (solid line). Condensation is at a fractional loading of about 0.8, which is the reason I chose that value for my paper. Fractional coverages near unity correspond to very high pressure, which is not attained by vapors because condensation occurs first. An analogous situation arises for a bulk liquid, for which the molar volume (or, to compare with adsorption, the reciprocal of the amount in a given volume) at saturation is greater than the limit at infinite pressure corresponding to the constant b in cubic equations of state.

As stated in my paper, large negative deviations from Raoult's law for mixtures adsorbed on heterogeneous, microporous solids, are *not* due to enhanced forces of attraction between unlike molecules. Sites of different energies have different selectivities, and the resultant segregation in composition is primarily responsible for the apparent negative deviations. In most cases, the curves for activity coefficients, at either constant pressure or at saturation where the fractional loading is about 0.8, are highly asymmetric.

TABLE 1. THEORETICAL SURFACE ACTIVITY COEFFICIENTS

C_1^A	C_2^A	C_1^B	C_2^B	$S_{1,2}^A$	$S_{1,2}^B$	P	Fig.	Ref.
2	0.2	0.3	0.1	10	3	10	1A	(1)
200	20	30	10	10	3	10	1B	This Work
2	0.2	0.3	0.1	10	3	1,000	1C	This Work

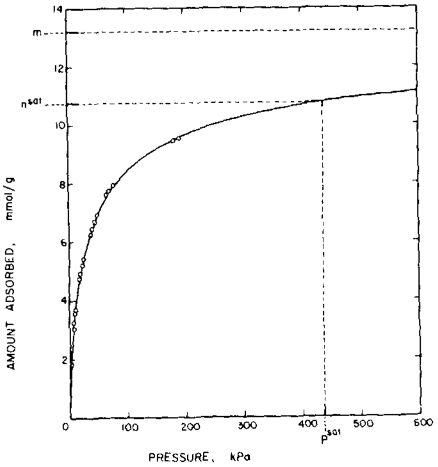

Figure 2. Absorption of carbon dioxide vapor on activated carbon at 212.7 K. Points are experimental data; solid line is Toth equation. *m* is total capacity at limit of infinite pressure.

LITERATURE CITED

Reich, R., W.T. Ziegler, and K.A. Rogers, "Adsorption of Methane, Ethane and Ethylene Gases and Their Binary and Ternary Mixtures and Carbon Dioxide on Activated Carbon at 212–301 K and Pressures to 35 atm," *Ind. Eng. Chem. Process Des. Dev.*, **19**, 336 (1980).

ALAN L. MYERS
Chemical Engineering Dept.
University of Pennsylvania
Philadelphia, PA 19104