

# Adsorbent Surface Area Determination by Measurement of Adsorption from Liquid Mixtures

BY

S. SIRCAR, AIR PRODUCTS AND CHEMICALS, INC  
ALLENTOWN, PA 18105

## Abstract

Various problems in estimating the surface area of adsorbents from binary liquid adsorption isotherms are discussed. Knowledge of adsorbate selectivity and adsorbent heterogeneity are required for the surface area measurement.

Estimation of surface areas of solid adsorbents from the equilibrium isotherms for adsorption of binary liquid mixtures has attracted considerable attention [1,2]. The principle is based on the assumption that the adsorption from the binary liquid mixture is confined to a monolayer and the specific amounts of each component adsorbed ( $n_1, n_2$ ) can be estimated from the experimentally measured binary Gibbs surface excess isotherm ( $n_1^e$ ) of component 1 [4].

$$n_1^e = n_1 x_2 - n_2 x_1 \quad (1)$$

where  $x_1$  is the mole fraction of the  $i$ th species in the equilibrium bulk liquid phase. The specific surface area ( $A$ ) can then be calculated by  $A = \sum n_i a_i$ , where  $a_i$  is the molar surface area of the  $i$ th species.

Schay and Nagy [1] proposed a technique to obtain  $n_1$  by observing that many "U" shaped surface excess isotherms, where one component (say #1) of the binary liquid mixture is selectively adsorbed at all compositions, exhibit an apparent linear section in the region of  $x_1 \rightarrow 1$  as shown by Figure 1. The isotherm in that region can be expressed by

$$n_1^e = b x_2 \quad (2)$$

where negative  $b$  is the limiting slope of the isotherm at  $x_1 \rightarrow 1$ . These authors assumed by comparing Eqs. 1 and 2 that  $n_1 = b$  and  $n_2 = 0$  in the linear region. Thus  $A$  can be estimated. Although this procedure has been used [1-3] with some success, the method is strictly correct only when the selectivity of adsorption for component 1 ( $S = n_1 x_2 / n_2 x_1$ ) is infinite in the linear region. Otherwise, a serious error can be made in the estimation of  $A$  as discussed in the following.

We will restrict our study to the simple case of equal adsorbate sizes ( $a_1 = a$ ) and ideal bulk liquid mixtures. The expression for  $n_1^e$  for this case is [4]:

$$n_1^e = \frac{m x_1 x_2 (S-1)}{S x_1 + x_2} \quad (3)$$

$m$  is the monolayer capacity.  $A$  is then equal to  $ma$ . Component 1 is selectively adsorbed when

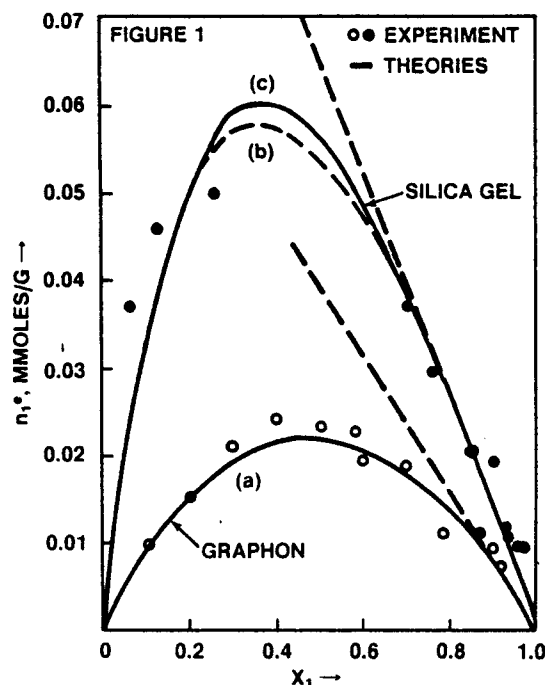


Figure 1.

$S > 1$ . Adsorption thermodynamics gives [4]:

$$S = \exp \left[ \frac{A}{mRT} (\sigma_2^0 - \sigma_1^0) \right] \quad (4)$$

where  $R$  is the gas constant and  $T$  is the system temperature.  $\sigma_1^0$  is the surface tension of pure liquid 1 at the liquid-solid interface. Thermodynamics also gives [4]

$$\frac{A}{RT} (\sigma_2^0 - \sigma_1^0) = \int_0^1 \frac{n_1^e}{x_1 x_2} dx_1 \quad (5)$$

Eqn. (5) shows that  $\frac{A}{RT} (\sigma_2^0 - \sigma_1^0)$  can be estimated from the  $n_1^e(x_1)$  data. Thus, there is only one adjustable parameter,  $m$ , in Eqn. (3). The limiting slope of the isotherm given by Eqn. (3) is

$$-b = -m \left[ \frac{S-1}{S} \right] \quad (6)$$

Eqn. (6) clearly demonstrates that  $b = m$  only when  $S \rightarrow \infty$ . Otherwise,  $m > b$  and the Schay and Nagy procedure will give an  $A$  lower than the real surface area of the adsorbent. The error can be very large if  $S$  is small.

This is demonstrated by the data for adsorption of bromobenzene (1) + chlorobenzene (2) on graphon at 0°C [5], shown in Figure 1. Bromobenzene is selectively adsorbed by the graphon. The adsorbates have nearly equal sizes ( $a_1 = 202.4$ ,  $a_2 = 200.5$  m<sup>2</sup>/mmole) and the liquid mixture is ideal. Eqn. (3)-(5) describe the data very well (curve a). The parameters for the system are:  $m = 0.42$  mmol/g,  $\frac{A}{RT} (\sigma_2^0 - \sigma_1^0) = 0.089$  mmol/g,  $S = 1.24$  and  $b = 0.075$  mmol/g. The limiting slope is about 5.3 times smaller than the real  $m$  value due to the low selectivity for component 1. Consequently,  $A$  calculated by the Schay and Nagy method is much smaller (15.6 m<sup>2</sup>/g) than the BET area (84 m<sup>2</sup>/g) for the graphon [5] while the area obtained by using the monolayer capacity extracted from Equation (3) is identical (84 m<sup>2</sup>/g) to the BET area.

Eqn. (3) is, however, derived for an energetically homogeneous adsorbent and it can give a wrong value for  $m$  when applied to a heterogeneous adsorbent. This is shown by the data (Figure 1) for adsorption of the same binary liquid mixture on silica gel at 20°C [6]. Chlorobenzene (component 1) is selectively adsorbed on the gel. Eqns. (3)-(5) can describe the data adequately (curve b) with  $m = 0.22$  mmol/g,  $\frac{A}{RT} (\sigma_2^0 - \sigma_1^0) = 0.233$  mmol/g and  $S = 3.0$ . The corresponding  $A$  is only 43.7 m<sup>2</sup>/g while the real BET area for the gel is 420 m<sup>2</sup>/g [6]. The Schay and Nagy method yields a still lower ( $b = 0.13$  mmol/g) value (26.7 m<sup>2</sup>/g) of  $A$ .

The reason for this is that the gel surface is energetically heterogeneous. The heterogeneity can be described by a simplified model [7] which assumes that the adsorbent surface consists of a distribution of homogeneous patches and the overall surface excess isotherm can be obtained by the

integration of the surface excess contributions of each patch. Each patch is defined by a characteristic selectivity parameter, Eqn. (4), and the local homogeneous isotherm, Eqn. (3). The selectivity probability density function  $[\lambda(S)]$  is given by a gamma function in

$$S [\lambda(S) = \frac{\alpha^{n+1}}{n!} S^n e^{-\alpha S}]. \quad \alpha \text{ and } n \text{ (integer)}$$

are constants. The model gives the following expression for  $n_1^e(x_1)$

$$n_1^e = m[x_2 - \theta e^\theta E_{n+1}(\theta)] \quad (7)$$

$$\theta = \frac{\beta n}{S^*} \cdot \frac{x_2}{x_1} \quad (8)$$

$$\beta = \frac{\exp \left[ \sum \frac{1}{n} - 0.577 \right]}{n} \quad (9)$$

$S^*$  is the overall selectivity for the adsorbent which is defined by Eqn. (4). There are two parameters in the model viz  $m$  and  $n$ .  $n$  determines the degree of heterogeneity which decreases as  $n$  increases.  $n \rightarrow \infty$  corresponds to a homogeneous adsorbent.

Eqns. (7)-(9) can describe the isotherm data on the gel very well (curve c) with  $m = 2.08$  mmol/g,  $n = 9$ , and  $S^* = 1.12$ . The corresponding  $A$  is 420 m<sup>2</sup>/g which is identical with the BET area for the gel. The analysis shows the importance of adsorbent heterogeneity in evaluating  $A$ . The limiting slope for Eqn. (7) is

$$-b = -m \left[ 1 - \frac{\beta}{S^*} \right] \quad (10)$$

$\beta$  is equal to unity for a homogeneous adsorbent ( $n \rightarrow \infty$ ) and its value increases as  $n$  decreases. Thus Eqn. (10) shows that the difference between  $b$  and  $m$  increases as the surface heterogeneity increases. The Schay and Nagy method will give a lower value of  $A$  for a heterogeneous adsorbent than that for a homogeneous solid unless  $S^*$  is infinity or very large. It may be concluded that no simple method exists for estimating  $A$  from liquid adsorption isotherm data. The entire isotherm should be fitted by a model which takes into account of the adsorbent heterogeneity in order to obtain  $m$  or  $A$ .

## References

- [1] Schay, G., and Nagy, L., J. Chem. Phys. **58**, 149 (1961).
- [2] Schay, G., and Nagy, L., J. Coll. Interface Sci., **38**, 302 (1973).
- [3] Conford, P. V., Kipling, J. J. and Wright, E. H. M., Trans. Faraday Soc., **58** (1962).
- [4] Sircar, S. and Myers, A. L., J. Phys. Chem. **74**, 2828 (1970).
- [5] Everett, D. H. and Podoll, R. T., J. Coll. Interface Sci., **82**, 14 (1981).
- [6] Li, P. and Gu, T., Scientia Sinica, **22**, 1384 (1979).
- [7] Sircar, S., JCS Faraday Trans. I, **79**, 2085 (1983).