Wetting of Polymeric Adsorbents and Its Effect on Adsorption

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Several investigators (Van Vliet et al., 1980; Hasanain and Hines, 1981; Abe et al., 1983) have examined the use of nonfunctional macroreticular polymeric adsorbents for the removal or recovery of organic compounds from aqueous solutions. As these polymeric resins are hydrophobic and, furthermore, the extent of adsorption achieved in liquid phase is greater than that in vapor phase, pretreatment of these adsorbents to insure their complete wetting is commonly recommended. More recently, Rixey (1987) argued that, for purposes of recovering products from biochemical processes, use of these adsorbents without prewetting may be more desirable if such factors as selectivity and regenerability are considered.

To demonstrate the effect of wetting on the extent of adsorption of these adsorbents, adsorption isotherm data reported elsewhere (Rixey, 1987; Rixey and King, 1987, 1989) are reproduced in Figure 1. The results shown in Figure 1 were obtained by contacting Amberlite XAD-4 (a styrene divinylbenzene copolymer, manufactured by Rohm and Haas Co.), either prewetted or not, with aqueous solutions of acetic acid. The results obtained using prewetted adsorbents correspond to Curve A (wet case), while Curve B gives the results obtained using adsorbents without prewetting (nonwet case). Adsorbents without prewetting were said to be nonwet because of the fact that these adsorbent pellets, when placed in aqueous solutions of sufficiently dilute concentrations, were found to float at the liquid surface instead of settling down as found in the case of prewetted pellets.

When a pellet is placed into a liquid solution, whether it floats or sinks depends upon the total density of the pellet relative to the liquid density. The total density of a porous pellet is determined by its skeleton density, its porosity, and the extent of liquid penetration into the pore space of the pellet. The fact that a pellet is found to float (or sink) in a liquid solution does not necessarily imply that the pellet is nonwet (or totally wet). In fact, Rixey (1987) calculated that about 80% of the pores have to be wet in order for Amberlite XAD-4 pellets to sink in aqueous solutions and thereby raised the possibility of partial wetting which refers to the situation where liquid invasion of the pore space is not complete such that part of the pore space is occupied by liquid and the remainder occupied by the entrapped air.

The purpose of this note is threefold.

1. A simple experiment was devised and used to determine the extent of wetting of Amberlite XAD-4 with aqueous solutions of methanol, ethanol, and acetic acid at various concentrations.
2. We show that the so-called nonwet case discussed in the work of Rixey and King (1987, 1989) was really a case of partial wetting and that the isotherm data represented by curve B in Figure 1 are actually composite results of liquid-phase and vapor-phase adsorption isotherms.
3. We offer some general observations on modeling adsorption when adsorbents such as Amberlite XAD-4 are used without prewetting.

Experimental Determination of the Extent of Wetting

The experiment devised for measuring the extent of wetting is based on the following two observations:

1. The total amount of uptake by an adsorbent pellet from a solution is the sum of two contributions—adsorption and wetting (or pore filling).
2. Adsorption is a reversible process, while wetting is irreversible in the sense that once a pore is wetted by a liquid of low surface tension it remains wetted when the liquid of low surface tension is displaced through washing by another liquid of higher surface tension.

The second observation provides us a means of eliminating the adsorption contribution, while keeping the degree of wetting unchanged. Specifically, if we first contact a resin with an organic solution until equilibrium is reached and then wash it repeatedly with pure water, the amount of water that remains inside the resin after washing will be solely due to wetting, since

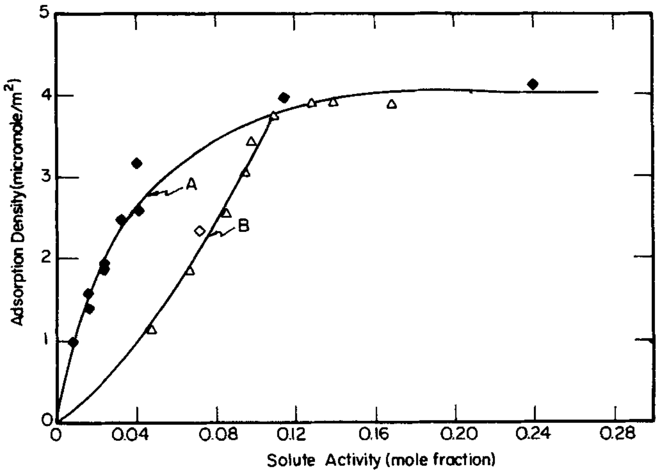

Figure 1. Adsorption isotherms of acetic acid on prewetted (*A*) and dry (*B*) Amberlite XAD-4 resins.
Data from Rixey (1987).

water is not adsorbed by the hydrophobic resin. This phenomenon quantitatively indicates the extent of wetting of the resin by the solution. (The nonadsorbability of water by XAD-4 is seen from the fact that when 1 g of the resin was suspended over water for a week, a negligibly small (a few milligrams) increase in the weight of the resin was observed.)

The experiment was done on XAD-4 at room temperature, and the organics used were acetic acid, methanol, and ethanol. The procedures and the results are discussed in the following.

We first ran the experiment with pure organics. The measurement is basically a four-step process: i) soak the dry resin in the organics; ii) wash it with distilled water; iii) remove the interstitial water by centrifugation; and iv) determine the amount of water that remains with the resin by weighing. We found that, in all three cases (acetic acid, methanol, and ethanol), the amount of water that is retained by the resin is about 0.926 g/g of resin (subsequently "per gram of resin" is always implied but not spelled out when we talk about the amount of water retained by the resin). At room temperature, the surface tension of acetic acid is 29×10^{-3} N/m and those of methanol and ethanol are about 22×10^{-3} N/m. Since the amount of water that is retained by the resin remains constant as the surface tension of the wetting liquid changes from 22×10^{-3} to 29×10^{-3} N/m, it is reasonable to assume that 0.926 g of water is the maximum amount of water that can be retained and represents the maximum degree of wetting or complete wetting.

When the dry resin was put in contact with pure water, the amount of water which remained after centrifugation was found to be 0.091 g. We shall assume that this 0.091 g of water was the residue water adhered to the external surface, which was not removed by centrifugation. As a relative measure of the degree of wetting, we define "volume fraction of wetting" such that 0.926 g of water retained by the resin corresponds to 100% fraction of wetting and 0.091 g to 0% fraction of wetting. Thus, if the amount of water that is retained by the resin after centrifugation is w grams, then the fraction of wetting is calculated as (w-0.091)/(0.926-0.091).

For solutions of various organic concentrations, the procedure is essentially the same as that for pure organics except that now the concentration of the solution is also monitored during the adsorption part of an experimental run. By adjusting the initial concentration and the solution/resin ratio, we were able to observe the change of the degree of wetting with the initial and the final (equilibrium) concentrations of the solution. We found that the degree of wetting does not depend on the initial concentration, but on the final concentration. This suggests that wetting and adsorption take place at a similar rate and may be interdependent.

The complete results are shown in Figure 2 where the fraction of wetting is plotted against the equilibrium concentration of the solution for the three organics considered.

To gain better insight into the wetting behavior of a resin we plotted the fraction of wetting vs. the surface tension of the equilibrium solution, Figure 3. The closeness of the three wetting curves in Figure 3 suggests that the ability of a solution to wet XAD-4 is determined mainly by its surface tension. The slight horizontal shifts between the wetting curves are probably due to differences in contact angles in these three cases. According to Ottewill and Vincent (1972) who measured the contact angles of aqueous solutions of methanol and ethanol on polystyrene surfaces, at the same surface tension a methanol solution makes a slightly larger contact angle than the corresponding ethanol solution. Although the resin we used is a copolymer of styrene and divinylbenzene, it may be reasonable to assume that the relation between the contact angles of methanol and ethanol solutions on the resin is similar to that on polystyrene. Since the capillary force responsible for wetting is proportional to the cosine of the contact angle, larger contact angle would result in lower degree of wetting, which qualitatively explains the horizontal shift between the wetting curves for methanol and ethanol solutions. Measurement of contact angles for acetic acid solutions is not available, but a similar explanation is expected for the shift between the wetting curve for acetic acid solution and that for ethanol solution in Figure 3.

It is also interesting to note that the shape of the wetting curve is very similar to that of the mercury-injection curve in mercury porosimetry (where the relative volume of mercury injected into a macroporous medium is plotted against the applied pressure). Percolation theory has been used to explain the shape of the mercury-injection curve. By analogy, an explanation for the

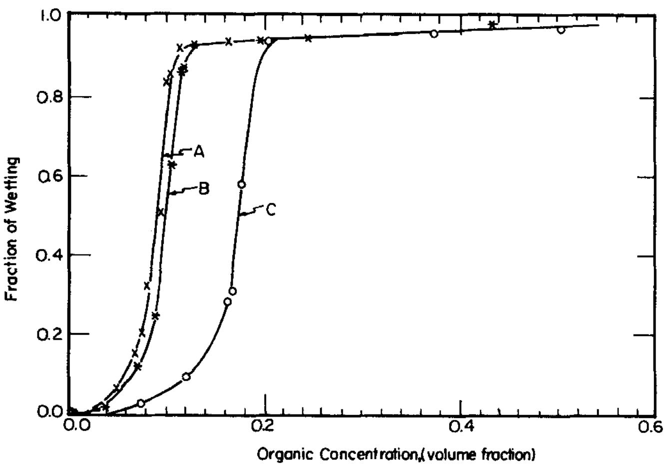

Figure 2. Equilibrium fraction of wetting as a function of adsorbate concentration of aqueous solutions.
Curve A, ethanol; Curve B, acetic acid; and Curve C, methanol.

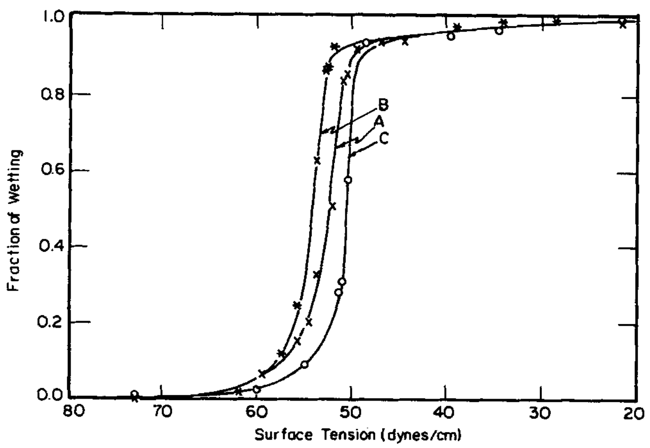

Figure 3. Equilibrium fraction of wetting as a function of surface tension of wetting liquid.

Curve A, ethanol-H_2O; Curve B, acetic acid-H_2O; and Curve C, methanol-H_2O.

shape of the wetting curve probably can be offered but is not pursued here.

Estimation of Apparent Adsorption Isotherms

From the results on wetting of XAD-4 pellets, one may infer that the adsorption isotherm data obtained from using hydrophobic adsorbents without prewetting result from both liquid- and vapor-phase adsorptions, or

$$q = q_\ell f_a + q_v(1 - f_a) \tag{1}$$

where q is the amount of adsorption of an adsorbent without prewetting (the so-called nonwet or apparent adsorption) in equilibrium with a solution of concentration c, and f_a is the fraction of wetting based on surface area as opposed to volume, which, as will be shown later on, is related to the volume fraction of wetting given earlier through the pore-size distribution. q_ℓ is the amount of adsorption with completely-wetted pellets (namely, liquid-phase adsorption), and q_v is the amount of adsorption in vapor phase. q_v is the value in equilibrium with a vapor mixture which, in turn, is in equilibrium with the liquid solution of concentration c. Thus, from the knowledge of the respective liquid- and vapor-phase isotherms and the wetting and pore-size distribution data, the apparent isotherm such as that given by Curve B of Figure 1 can be readily estimated.

As an example, we demonstrate the estimation of Curve B of Figure 1. For this estimation, the liquid-phase adsorption isotherm is given by Curve A of Figure 1 and the wetting (i.e., volume fraction of wetting) data by Curve B of Figure 2. To calculate the area fraction of wetting from the volume fraction of wetting, use is made of the pore area and volume distributions of XAD-4 measured by Albright (1989). The data of Albright enable us to construct a relationship between the cumulative volume (expressed as a fraction of the total pore volume) of all pores from 20 Å in diameter up to a certain size and the corresponding cumulative pore area (expressed as a fraction of the total pore area). This relationship is shown in Figure 4. We then assume that the relationship between the area and volume fractions of wetting is the same as that given in Figure 4. In other words, we assume that, in a solution of certain concentration, all pores of the resin from 20 Å up to a certain size are wetted and the remainder unwetted. This assumption is reasonable since, according to the cylindrical pore model which was used to obtain the pore area and volume distributions, smaller pores result in larger capillary pressure and are thus wetted more easily.

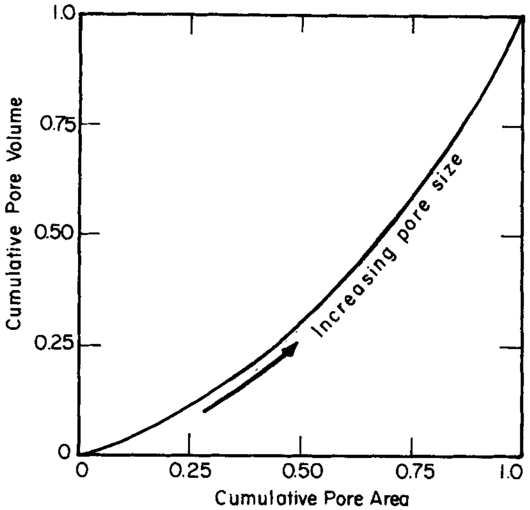

Figure 4. Relationship between the cumulative pore volume and area of XAD-4.

Constructed from data of Albright (1989).

The last piece of information that remains to be given in order to calculate q from Eq. 1 is the vapor-phase adsorption isotherm. Since experimental data on adsorption of acetic acid vapor on XAD-4 were not available, we estimated q_v from similar data (vapor-phase adsorption of benzene, toluene, *p*-xylene, and cyclohexane by XAD-4) reported by Noll et al. (1987) and the application of the potential theory. According to the potential theory, for a specific adsorbent, there exists a unique relationship (or characteristics curve) between the amount of adsorption (in volume of adsorbate in saturated liquid state per unit mass of adsorbent) and the adsorption potential, ϵ, defined as $(RT/\bar{V}_A) \ln (p_s/p)$, where R is the gas law constant, T, the absolute temperature, p_s the vapor pressure of the adsorbate at T, and p the partial pressure of the adsorbate. $\bar{V}_A$ is the molar volume of the adsorbate in the adsorbed state which may be approximated as the saturated liquid molar volume. When the results of Noll et al. are plotted on this basis as shown in Figure 5, the resulting characteristic curve can be used to determine q_v. In this connection, the adsorption potential and the solute activity νx, where ν is the activity coefficient and x the mole fraction of the adsorbate in the solution used as the abscissa of Figure 1 are related by the expression

$$\epsilon = \frac{RT}{\bar{V}_A} \ln \frac{p_s}{p} = \frac{RT}{\bar{V}_A} \ln \frac{1}{\nu x} \tag{2}$$

and the amount of adsorption in volume of saturated liquid per gram of adsorbent and the adsorption density can be readily related to one another by the density of the adsorbate and the specific surface area of the adsorbent.

The results of the estimation are shown in Figure 6, where Curves A and B are the same as those in Figure 1, Curve C is the

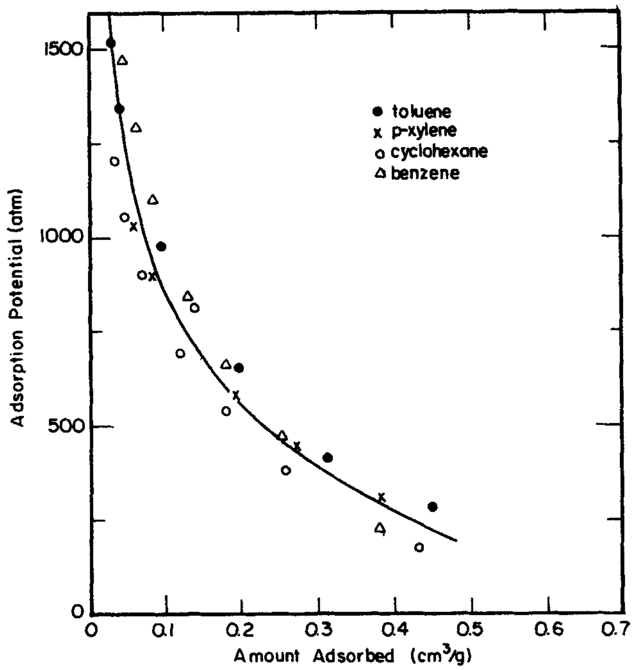

Figure 5. Adsorption characteristic curve of Amberlite XAD-4.

Constructed from data of Noll et al. (1987).

estimated vapor-phase adsorption isotherm, and the open circles represent the estimated apparent adsorption isotherm. As one can see, a remarkable agreement exists between the measured (Curve B) and the estimated apparent adsorption isotherms. This agreement leads us to conclude that the assumptions we made (e.g., those involved in applying the potential theory and in relating the area and volume fractions of wetting) are justified and that the apparent (or nonwet) adsorption isotherm is indeed a composite of vapor- and liquid-phase adsorption isotherms.

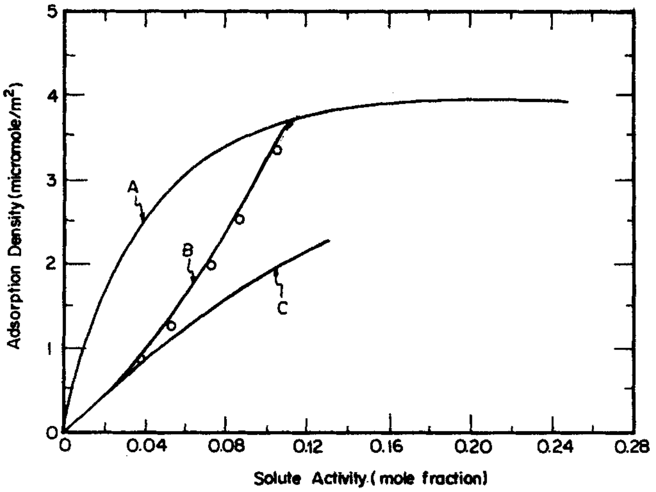

Figure 6. Comparison between estimated and measured adsorption isotherms of acetic acid on Amberlite XAD-4.

Curve A, measured liquid-phase isotherm; Curve B, measured apparent adsorption isotherm; Curve C, estimated vapor-phase isotherm; and open circles, estimated apparent adsorption isotherm.

Adsorption Processes Using Hydrophobic Adsorbents

The problem of describing adsorption (gas- or liquid-phase) processes, to a large degree, is solved, and models for adsorption processes abound in the literature. The results of these studies, however, cannot be applied directly to the case of partially-wet resins. Instead, one must consider the uptake of adsorbates in the wetted and nonwetted region separately. The adsorption rate of the former is controlled by both the liquid-phase adsorption equilibrium and the various rate parameters (such as the external mass transfer coefficients and the intraparticle diffusion coefficients). The vapor-phase adsorption rate depends upon the relevant equilibrium and rate information, as well as the volatility of the adsorbate. It is also necessary to bear in mind that the fraction of wetted pore space is time-dependent as well as the surface tension (therefore, the concentration of adsorbates) of the solution to which the adsorbent pellet is subject. The results shown in Figure 3 represent the value of f at equilibrium and, therefore, only represent the upper limit of f to be used in estimating adsorption rates.

In addition to the data on the change of the extent of wetting with time, another piece of information necessary for a rigorous description of adsorption rates of hydrophobic adsorbents is the distribution of the wetted and nonwetted regions within a given pellet. For example, if they are distributed uniformly throughout a pellet, vapor- and liquid-phase adsorption may be considered to take place simultaneously, and the concentration of solution to which the pellet is exposed determines directly the partial pressure of the adsorbates in the pore space of the nonwetted region. On the other hand, if there is a nonrandom distribution of these two regions, diffusion of adsorbates in the pore space of the wetted region and that in the nonwetted region are more likely to occur sequentially. Given the complexities of the problem, it is doubtful that a simple model consisting of two or three parameters can be devised to describe the adsorption process in general. The problem, however, becomes greatly simplified if either the wetted or nonwetted region is dominant. For example, aqueous solutions of acetic acid, with acid concentrations less than 2 wt. % do not wet XAD-4 resins to any significant degree. The uptake of acetic acid is, therefore, largely by vapor-phase adsorption. This may explain the success of Rixey and King in using one-phase fixed-bed adsorption model in fitting their experimental data (Rixey and King, 1989).

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Notation

f = (volume) fraction of wetting
f_a = area fraction of wetting
p = partial pressure
p_s = saturated vapor pressure
q = amount of apparent adsorption
q_l = amount of adsorption in equilibrium with a liquid phase
q_v = amount of adsorption in equilibrium with a vapor phase

R = gas law constant
T = absolute temperature
$\bar{V}_A$ = saturated liquid molar volume
x = mole fraction
ϵ = adsorption potential
ν = activity coefficient

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