ENERGETICS AND MECHANISM OF PHYSICAL SORPTION ON CARBONACEOUS SOLIDS: GRAFOIL FLEXIBLE CARBON

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Introduction

Physical adsorption of nitrogen at ca. 77.2 K is potentially a most facile and informative method for evaluation of surface area and porosity of solid materials. It has been shown that monolayer/multilayer adsorption is solely dictated by the initial sorption (Polyani) potential and the statistics of the filling of the liquid like monolayer-multilayer(s)[1]. Pendular rings will form in the accessible internal porosity and interstices between the powder particles in the mesoporous regime that are well described by the Young/Laplace and Kelvin relationships.

Experimental

Nuclear grade Grafoil[tm] (>99.5% graphite) with extremely low ash content and less than 50 ppm leachable chlorides, free of binders and resins. The sorption data were acquired using a Quantachrome [tm] volumetric Autosorb instrument. Equilibration was verified by allowing successively longer equilibration times that gave reproducible isotherm results in all but the highest pressure points (P>0,99 P(0). The sorption isotherm is presented in the classical format in Figure 1 for the 125 data points used in the present analyses.

Results and Discussion

The AutoShielding Potential (ASP) theory[1] has shown an exponential relationship related to the sorption potential {E = -RTln[P/P(0)]},

E=[E*]exp(-θ)   **Equation 1**

where

θ=fractional monolayer coverage=Γ/Γ(m)   Equation 2

with Γ expressed in the desired sorption units [cc(STP), mg/g, etc.]. The he first order rectilinear form

Γ=Γ(m){ln(E*/RT)-ln(E/RT)}   **Equation 3**

accurately defines sorption isotherms for numerous organic[2] and inorganic[3] substrates   Second order effects, due to chemical and/or structural heterogeneities are accommodated in the quadratic form:

Γ=Γ(m){ln(E*/RT)-ln(E/RT)-αln(E/RT))²} Equation 4

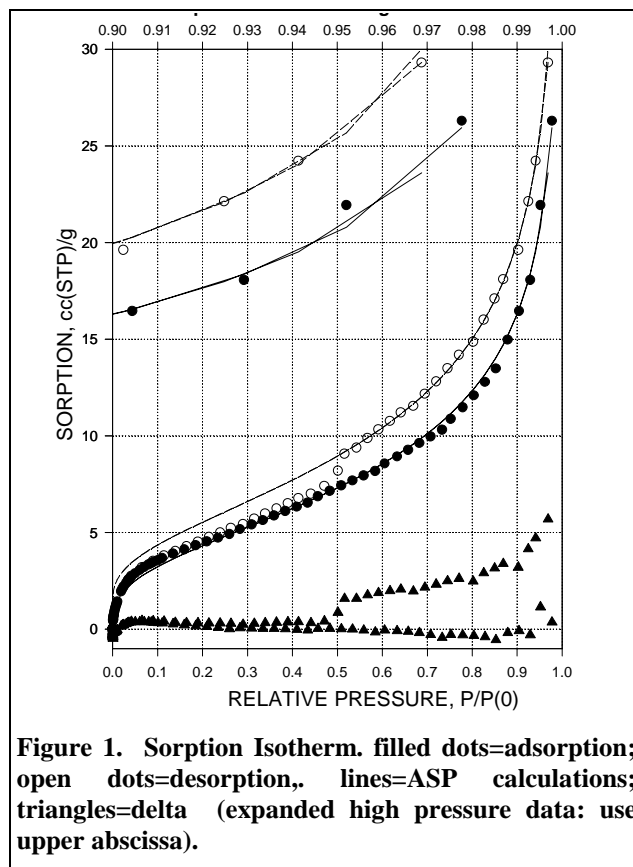These perturbations are present in the surface structure of

Figure 1. Sorption Isotherm. filled dots=adsorption; open dots=desorption,. lines=ASP calculations; triangles=delta (expanded high pressure data: use upper abscissa).

the pressed graphite flakes of Grafoil flexible sheets as noted in the ASP plots in Figure 2. The least squares regression fit is excellent for the entire range of sorption up to the 0.99P(0) rate effect limit mentioned above All of the sorption data is fitted well as compared to the very limited regimes of the BET and other existing theories. Relevant points: 1) there exists a cutoff (finite) energy below which there is no sorption; 2) the entire adsorption isotherm is fitted well with three adjustable parameters; 3) the hysteretic desorption data are also well defined in terms of three (different) adjustable parameters down to the closure of the hysteresis loop. These parameters (and the corresponding standard deviation variation of fit are given in Table 1. (r² = 1.00 for perfect fit to the experimental data). A SigmaPlot[tm] data processing package was used for graphics and statistical analyses where: ln(E*/RT)= b(0)/b(1), Γ(m)= b(1), α=b(2)/b(1).

Table 1. Least Squares Regression Parameters for Grafoil ASP Sorption Functions; Nitrogen at 77.2 K.

ADSORPTION		DESORPTION	
b[0]	5.9316	b[0]	7.3505
b[1]	3.6037	b[1]	4.1331
b[2]	0.4416	b[2]	0.6480
r^2	0.9973	r^2	0.9991

The nature of the desorption hysteresis is further defined by the Δ curve (with respect to the adsorption curve) and the related cutoff at pressures corresponding to pores ca. 2 nm in size. If one knows *a priori* the surface area and the sorption potential for the first molecule there is really only one adjustable parameter, α, which is related to the distribution of heterogeneities (fractal nature) of the mesoporous surface(s). A complete independent know-ledge of this substrate would define this parameter also. Until alternate verification is found we will use the physisorption isotherms as diagnostic tools and the ASP parameters to define the data accurately for statistical and thermochemical analyses.

For clarity these parameter are used to approximate the experimental sorption isotherms (Figure 1) where the lines approximate the data points in each case within experimental error. Expanded data plots (>0.9P(0)) show that the trend is continuous to ca 0,99 P(0), well into the mesopore regime.

Figure 2. ASP Plot for Nitrogen on Grafoil at 77 K. filled=adsorption, open=desorption,   lines=regression fit to data, triangles=delta.

Conclusions

- The ASP procedure for analyzing physical sorption of nitrogen by Grafoil is productive and informative.
- The statistical analyses provides excellent descriptions of the data with a minimum of adjustable parameters (.far superior to any other concept or theory available to this author (ELF) at this writing).
- The results indicate little or no micropores (<2 nm)
- A nonlinear second order effect is noted for the inherent mesoporosity
- Adsorption experiments are consistent with a second order perturbation due to the specific mesopore (>2 nm) geometry, probably slit like in nature .
- Desorption hysteresis reveals some mesoporosity (>2nm) accessible through limited (restricted) orifices.
- One must be aware that sorption near the saturation pressure is slow[4] and achievement of equilibration must be verified.
- Modeling of sorption processes must be consistent with the intensive and extensive thermodynamic terms provided by the ASP treatment of the sorption processes.
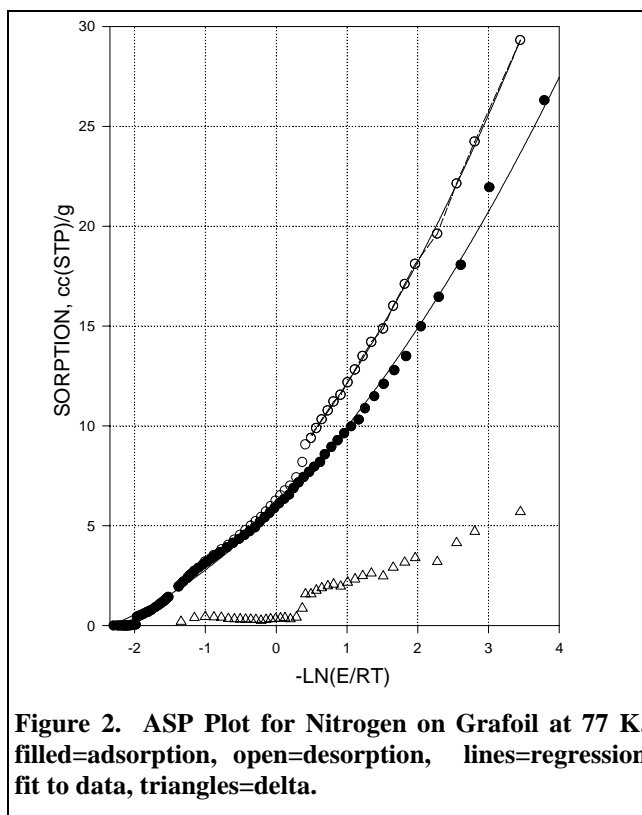
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