COMPARATIVE STUDIES OF GAS-PHASE AND LIQUID-PHASE ADSORPTION PROCESSES ON ACTIVE CARBONS

*M. Jaroniec and J. Choma**
Department of Chemistry, Kent State University, Kent, OH 44240, USA
**Institute of Chemistry, WAT, 00-908 Warsaw, Poland*

Introduction

Gas-solid adsorption measurements are commonly used to characterize the microporosity of active carbons [1]. For instance, nitrogen adsorption at 77.5 K is considered as a standard technique for evaluation of the specific surface area and the pore volume distribution of these solids. Although liquid-phase adsorption measurements, especially those involving dilute aqueous solutions, are also important for studying active carbons and related sorbents, they are seldom used for their characterization [2,3]. A major reason of this situation is a greater complexity of molecular interactions at the liquid-solid interface than in the case of the gas-solid interface as well as the lack of systematic comparative studies of adsorption phenomena at these interfaces.

It was shown in [2] that adsorption isotherms for benzene from dilute aqueous solutions on active carbons can be obtained from the gas-solid analogues, i.e., benzene vapor adsorption isotherms, by utilizing the so-called interfacial coefficient β defined as follows:

$$\beta = A_l / A_g \qquad (1)$$

where A_g and A_l denote the adsorption potentials for the gas-solid and liquid-solid systems, respectively. These potentials are defined as follows [2]:

$$A_g = RT \ln(p_o/p) \qquad (2)$$

$$A_l = RT \ln(c_o/c) \qquad (3)$$

where p and p_o are respectively the equilibrium and saturation vapor pressures, c_o and c are respectively the solute's solubility and its equilibrium concentration, T is the absolute temperature, and R is the universal gas constant. Equations (1)-(3) can be used to convert the pressure axis to the concentration axis and consequently to obtain the liquid-solid adsorption isotherms from the gas-solid ones. The value of β was found to be about 0.52 for active carbons studied [2].

The aim of the current work is to show the applicability of the α_s-plot method for analysis of the liquid/solid adsorption data. The main idea of this method bases on the comparison of the adsorption isotherm for a given porous solid with the standard isotherm measured on a reference nonporous material. At low pressures the comparative plot is not linear because the micropore filling process differs from the layer-by-layer adsorption that occurs on the reference solid. Also, a deviation from linearity is observed at the high pressures due to the capillary condensation that occurs in the mesopores. However, in the multilayer range (moderate pressures) the comparative plot is linear because the micropores are already filled and mechanisms of adsorption on the mesopore surface and the reference solid are identical. In this range the linear segment of the comparative plot can be represented by the following equation:

$$a = a_{mi} + s_{me}\alpha_s \qquad (4)$$

where a and a_{mi} denote respectively the total and maximum amounts adsorbed and α_s is the reduced standard adsorption for the reference solid [1]. As can be seen from eqn 4 the intercept of the linear segment of the comparative plot determines the maximum amount adsorbed in the micropores (a_{mi}), which can be converted to the micropore volume, whereas the slope of this plot is proportional to the monolayer capacity of the mesopore walls, which after multiplication by the adsorbate's molar area gives the external surface area of a given porous solid.

Experimental

Equilibrium adsorption isotherms were measured for four commercial active carbons: CAL, F-200, PCB (Calgon Carbon Co., Pittsburgh, PA, U.S.A.) and RIAA (Norit Co., Amersfoort, The Netherlands) at 293 K. Prior to making adsorption measurements the samples were outgassed under vacuum at 383K for 3 hours.

The liquid adsorption measurements were carried out for benzene from dilute aqueous solutions by using a conventional static method. The concentrations of benzene before and after adsorption were measured photometrically. Experimental procedure is described elsewhere [2].

The gas phase adsorption isotherms on the same carbons were determined gravimetrically [2]. For the α_s-plot analysis

of the gas-solid adsorption data the adsorption isotherm of benzene vapor measured on the SAO carbon black [4] was used as the reference isotherm. Also, this isotherm was converted to the liquid-solid one (see Fig. 1) by utilizing the concept of the interfacial coefficient β and subsequently used to analyze the liquid/solid systems by means of the α_s-plot.

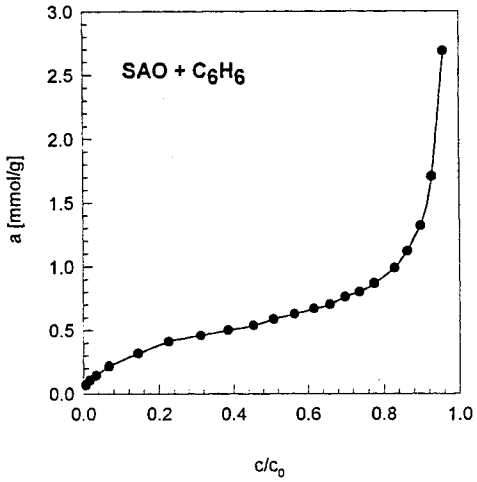

Figure 1. Standard adsorption of benzene from dilute aqueous solutions on the SAO carbon black at 293 K.

Results and Discussion

The standard adsorption isotherm shown in Fig. 1 was used to construct the α_s-plots for the liquid-solid adsorption systems. Shown in Fig. 2 are two α_s-plots for the CAL and RIAA carbons. Analogous plots were obtained for the remaining carbons. The values of the intercept and slope of the α_s-plots were used to calculate the micropore adsorption capacity a_{mi} (in mmol/g) and the mesopore surface area S_{me} (in m^2/g) for the active carbons studied (see Table 1). For the purpose of comparison the corresponding values of a_{mi} and S_{me} evaluated by the α_s-plot analysis of the gas-solid adsorption isotherms are also given in Table 1.

Table 1. Comparison of the micropore volumes and the mesopore surface areas obtained by the α_s-plot analysis of the gas-solid and liquid-solid adsorption isotherms of benzene.

Carbon	Gas adsorption		Liquid adsorption	
	a_{mi}	S_{me}	a_{mi}	S_{me}
CAL	3.96	110	3.90	130
F-200	3.68	60	3.52	100
PCB	5.04	50	4.47	80
RIAA	6.74	80	5.36	150

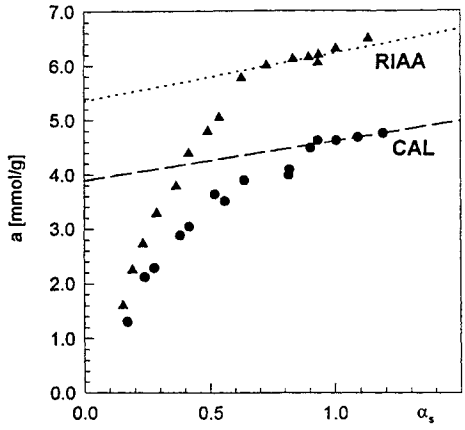

Figure 2. The α_s-plots for the CAL and RIAA active carbons obtained for adsorption isotherms of benzene from dilute aqueous solutions at 293 K.

As can be seen from Table 1 the values of the micropore adsorption capacity and the mesopore surface area obtained from the gas-solid and liquid-solid adsorption isotherms are similar. The observed differences between these values can be smaller if the experimental standard adsorption isotherm of benzene from dilute aqueous solutions on the reference carbon is available. Note that this isotherm was calculated from the corresponding gas-solid one. In addition, the agreement between the gas-solid and liquid-solid parameters can be improved if the adsorption isotherms from solutions contain more points at higher concentrations in order to extend the linear segment of the α_s-plot.

Conclusions

It was shown the α_s-plot analysis of adsorption isotherms for benzene from dilute aqueous solutions leads to similar values of the micropore adsorption capacity and the mesopore surface area. It appears that adsorption data for benzene from dilute aqueous solutions are suitable for characterization of microporous carbons because they provide analogous information as the corresponding vapor adsorption isotherms.

References

1. Jaroniec, M. and Choma, J., *Chemistry and Physics of Carbon*, **22**, 197 (1989).
2. Choma, J., Burakiewicz-Mortka, W., Jaroniec, M. and Gilpin, R.K., *Langmuir*, **9**, 2555 (1993).
3. Heuchel, M. and Jaroniec, M., *Langmuir*, **11**, 1297 (1995).
4. Choma, J. and Jaroniec, M., *Polish J. Chem.*, **71**, 380 (1997).