

# ESTIMATION OF MESOPOROUS STRUCTURE OF CARBON MATERIALS BY MACROMOLECULAR POROSIMETRIC METHOD

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## INTRODUCTION

Conventional methods of the study of pore structure, i.e. the techniques of capillary condensation and mercury porosimetry, require sophisticated equipment and are followed by a series of other disadvantages and limitations (see, for example, [1, 2]). Liquid - phase adsorption methods are usually characterized as simple and quick techniques accessible in any laboratory. Continued studies of adsorption of such polymers from solutions on porous solids have shown that the accessibility of polymers to the internal surface of pores is determined by the relationship between polymer molecular size and pore size [3, 4]. Thus, wide porous silicagel actually does not adsorb polystyrene from tetrachloromethane [3]. In polymer dilute solutions, flexible-chain macromolecules take a form of random coil. Such a form is caused by intramolecular free rotation and mobility of segments as well as by interaction between segments themselves and between segments and solvent molecules. By applying advanced experimental methods to polymer solutions (light scattering, viscosity and diffusion measurements), it is possible to calculate the dimensions of these coils. When polymer interacts strongly with the adsorbent surface, macromolecular coils may spread out by creating the adsorbed monolayer where macromolecules are oriented parallel to the surface. In this work we present the results of a study on adsorption of spreading dextrans and polyethylene glycols of different molecular weights with narrow molecular weight distributions from dilute solutions by carbon materials undertaken to evaluate the parameters of pore structure of these solids.

## EXPERIMENTAL

Three samples of carbon sorbents were used for the adsorption experiments: Sample CS-1 prepared by pyrolytic treatment of phenolic resin-silica gel composite with subsequent leaching the silica matrix

by NaOH  $d = 20$  nm and  $A = 550$  m<sup>2</sup>/g [5], Sample CS-2 obtained according to zinc chloride activation from a plant stock ( $d = 5$  nm and  $A = 870$  m<sup>2</sup>/g) [6] and Sample CS-3 prepared by graphitization of fural carbon black [3]. Prior of the study all adsorbents were dried at 150°C in vacuum oven for 4 hours. Dextrans (DX) (Pharmacia, Sweden) and polyethylene glycols (PEG) (Schuchardt, FRG) were used in this study. Each of the samples has a narrow distribution of molecular weight. We used DX with average molecular weight from 20000 to 500000 and PEG from 300 to 40000. Triply distilled water was used as a solvent. The adsorbed amounts were measured at 25°C by a conventional manner [5]. Normally the adsorption cell (20 ml) was filled with 0.2 g of dried adsorbent and then 4 ml of polymer solution was added. The cells were sealed and the mixture was stirred for 8 hours. After adsorption process, the concentrations in polymer solutions were analyzed with an interferometer

## RESULTS AND DISCUSSION

Figure 1 shows the adsorption isotherms of PEG and DX on carbon from water solutions in terms of amount adsorbed per unit surface area. In the case of PEG's with  $M_w = 6000$  and  $15000$  adsorption isotherms pass through maximums in the region of equilibrium concentration  $c = 5-7$  mg/g. The isotherm maximum is shifted into higher concentration for PEG with  $M_w = 300$ . This indicates that PEG with  $M_w = 300$  has a smaller adsorption energy. The monolayer capacity  $a_m$ , i.e. the amount of PEG required for coating the adsorbent surface with a monolayer of PEG macromolecules stretched out along the surface, as estimated from molecule size, would be about 0.5 mg/m<sup>2</sup>. This value is practically independent of PEG molecular weight. The  $a_m$  values for PEG correspond approximately to maximum adsorption values (Figure 1). Apparently, during the PEG adsorption on carbon black surface from water solutions, the adsorbed layers are similar to the

dence monomolecular layer of plane - oriented and densely packed PEG molecules at all values of Mw. There is a coincidence of adsorption isotherms for PEG (Mw = 20000) and DX (Mw = 20000) which has to be emphasized. Some of this isotherms exhibit a clear maximum as well. A shift of the position of isotherm maximum to lower equilibrium concentrations with increasing of polymer Mw can be observed for certain isotherms. Figure 2. presents the plot of maximum adsorption value (amount adsorbed) vs. molecular weight, Mw for polymers PEG and DX on CS-1, CS-2 and CS-3.. An increase in maximum adsorption values for PEG on praphitized carbon black with increasing Mw may be explained with the monolayer adsorption model as compacting process of adsorbed macromolecules layer caused by reducing space per Van der Waals distances between the adsorbed molecules in polymer monolayer film. The branch of curve 3 corresponds to a decrease in the pore internal surface area accessible to macromolecules adsorption. The lowering branch is determined by the dependence of adsorption on internal surface of pores accessible by macromolecule of a given molecular weight and it is accompany by a fall in the maximum adsorption value with the further increase in molecular weight. It should be emphasized that the maximum position and the form of the dependences of maximum adsorption value on Mw are determined generally by the pore structure parameters. The maximum adsorption value are equal to 125 mg/g for CS-1 which corresponds to Mw = 32000 and 480 mg/g for Cs-2 which corresponds to Mw = 8000 , respectively. A hydrodynamic diameter of a macromolecule in solution, D, can be determined with the use of Flory-Fox equation [7]

$$D = ([\eta] M / \Phi)^{1/3} = (k M w^{1+a} / \Phi) \quad (2)$$

where  $[\eta]$  is the intrinsic viscosity, Mw is the molecular weight of polymer and  $\Phi$  represents Flory parameter. The assumed correlation between mocromolecule coil sizes and pore diameters allows to calculate a cumulative dependence of the accessible pore volume, V, vs. d. For the cylindrical pore model an equation of the type

$$V = 0.25 \times 10^{-3} d A \quad (3)$$

was used in the calculation, where d and A were expressed in nm and m<sup>2</sup>/g, respectively.

### CONCLUSION

The study of polymer adsorption allowed to suggest a new tool for characterization of porous solids.

Water-soluble polymer adsorption can be applied for the evaluation of porous structure parameters of hydrophobic sorbents

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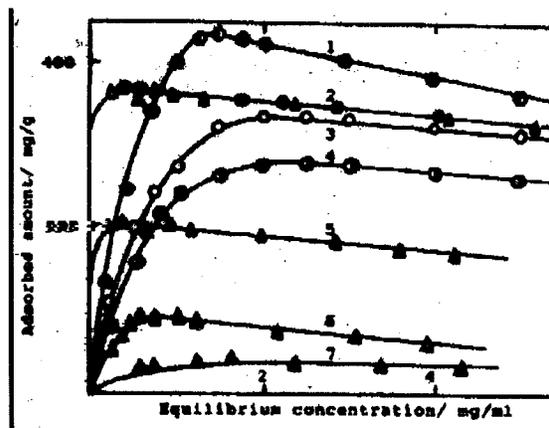


Figure 1 - Adsorption isotherms on CS-2. PEG 6000 (1), PEG 20000 and DX 20000 (triangles) (2), PEG 1000 (3), PEG 300 (4), DX 40000 (5), DX 110000 (6), DX 500000 (7).

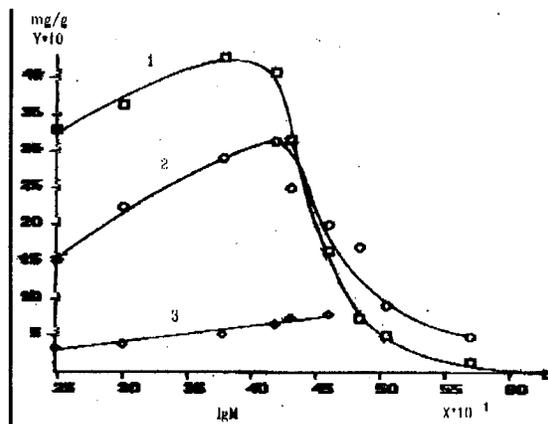


Figure 2 - Maxima adsorption values vs. log Mw for PEG and DX on CS-2 (1), CS-1 (2) and CS-3 (3).