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ADSORPTION ISOTHERMS OF CHLOROFORM ON MACROPOROUS COPOLYMERS DETERMINED BY INVERSE GAS CHROMATOGRAPHY

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Abstract

The inverse gas chromatography (IGC) under finite surface coverage conditions was used for the determination of adsorption isotherms of chloroform on macroporous crosslinked poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate), PGME and copolymer modified with ethylene diamine, EDA, PGME-en. The specific surface areas of initial and modified copolymer samples calculated from IGC data are in fair agreement with those determined by the BET method from the low-temperature nitrogen adsorption isotherms.

Introduction

Nowadays, most adsorption methods for cleaning, extracting and concentrating pollutants from gaseous environmental samples utilize macroporous polymeric adsorbents [1,2]. Among them, macroporous hydrophilic copolymer adsorbents based on glycidyl methacrylate, GMA, produced by radical suspension copolymerization in the shape of regular beads of required size and porosity are particularly attractive, due to possibility of chemical modification of epoxy groups [3]. In this paper, the adsorption isotherms determined from chromatographic peaks of chloroform obtained by inverse gas chromatography (IGC) under finite surface coverage were used for estimation of the surface area of macroporous poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate), PGME and copolymer modified with ethylene diamine, EDA, PGME-en. The specific surface areas of initial and modified copolymer samples were compared with values determined by the BET method from the low-temperature nitrogen adsorption isotherms (77 K).

Experimental

Macroporous crosslinked poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate), PGME, was synthesized by a radical suspension copolymerization, described elsewhere [4]. After reaction, the copolymer particles were washed with water and ethanol, kept in ethanol for 12 h, and dried in vacuum at 40 °C. The samples were purified by extraction in a Soxhlet apparatus with ethanol, and modified with tenfold excess of ethylene diamine, in toluene at 70 °C for 7h. The modified copolymer was labeled as PGME-en (the additional label -en designates modification

with ethylene diamine). The sorption properties of copolymer samples were examined using a Hewlett-Packard 5890II gas chromatograph, with a flame ionization detector (FID) maintained at 250 °C, the injector at 220 °C. Varian Star 4.5 software was applied to collect the data. Dry nitrogen was used as a carrier gas, at a flow rate in the range 24-28 cm³ min⁻¹. Methane was used for determination of the dead volume. A stainless steel column (50 cm long, 2.2 mm I.D.) was cleaned with both polar (C₂H₅OH) and nonpolar (C₆H₁₄) solvent, than packed with initial and modified copolymer sample (fraction with particle size of 150-500 μm). After each packing, the column was conditioned overnight in a stream of nitrogen (flow rate 5 cm³ min⁻¹) at 363 K. The appropriate amounts of analytical grade chloroform were injected in the column. Relevant IGC results from the retention data collected were calculated by a Mathcad program developed for the purpose.

Results and Discussion

The fronts of all peaks obtained by IGC were vertical and sharp suggesting that the predominant factor governing the bandwidth was isotherm curvature, typical for finite coverage conditions. Peak deformation due to high concentration of the injected organic compound was the basis for the determination of the gas adsorption isotherms on PGME and PGME-en. The adsorption isotherms for the chloroform on PGME and copolymer modified with ethylene diamine, PGME-en were obtained in the range 333-363 K, as described in the literature [5]. From the $\alpha(p)$ -(p) data, the adsorption isotherms were drawn (Fig. 1) and the related parameters were evaluated.

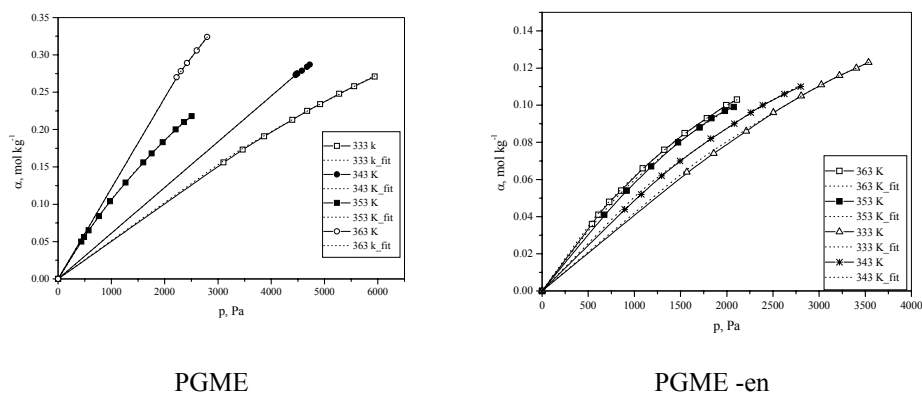


Figure 1. Adsorption isotherms of chloroform on PGME and PGME-en at indicated temperatures (dotted line represent BET fits).

The specific surface areas of the copolymer samples calculated from the IGC data, with values determined by the BET method from the low-temperature nitrogen adsorption isotherms (77 K) are shown in Table 1. The specific surface area for chloroform calculated from IGC data for PGME and PGME-en are in fair agreement with those determined by the BET method from the low-temperature nitrogen

adsorption isotherms. The accuracy of the IGC determination of the specific surface areas depends on the used adsorbate, porous structure of the material, as well as the adsorbate-adsorbent interactions.

Table 1. Specific surface areas, S_a , of PGME and PGME-en samples calculated from IGC data (temperature range 333-363 K) and from low-temperature nitrogen isotherms (77 K).

Adsorbate	$S_a, m^2/g$	
	PGME	PGME-en
CHCl ₃	30.8	47.4
N ₂	27.6	48.6

Conclusion

The adsorption isotherms of chloroform on PGME and PGME-en were determined by inverse gas chromatography (IGC) under finite surface coverage. The values of the specific areas for chloroform calculated from IGC data are in fair agreement with those determined by the BET method from the low-temperature nitrogen adsorption isotherms.

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