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SORPTION CHARACTERISTICS OF HYDROXYETHYL METHACRYLATE GELS

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SUMMARY

The determination of the specific surface area by the thermal desorption method is described. New macroporous hydrophilic materials (Uniflex) based on hydroxyalkyl methacrylate copolymers were used as adsorbents. The heats of adsorption were determined from elution data at different temperatures and the reproducibility of the measurements was verified. The values thus obtained contribute to the characterization of polymeric macroporous materials used in gas and gel chromatography.

INTRODUCTION

The determination of the specific surface area by the thermal desorption method was first described by NELSON AND EGGERTSEN¹. The specific surface area of the adsorbent can be determined from the amount of the adsorbate needed for the formation of a monomolecular layer on the surface under investigation. The adsorption from the gaseous mixture adsorbate-inert gas proceeds at the temperature of liquid nitrogen, and change in the composition of the gaseous mixture caused by the adsorption is detected with a catharometer. The desorption that occurs at a certain elevated temperature leads again to a concentration change in the gaseous phase, which can be followed readily by means of a detector.

The main condition for the correctness of the method based on a single point in the adsorption isotherm consists in choosing a partial pressure of the adsorbate that will lead to the formation of a monomolecular layer on the surface of the adsorbent. The use of a low-temperature adsorption at -189° and a relative pressure of the adsorbate of 0.2 fulfils this requirement for the majority of adsorbents.

An important role is also played by the choice of the adsorbate. The sorption of compounds that associate with the formation of hydrogen bonds on non-specific adsorbents (hydrophobic polymers of the Porapak type², graphitized carbon black³, etc.) gives rise to multilayer agglomerates of adsorbed molecules, which distort the experimental results. The formation of multilayer centres can also be assumed for interactions of adsorbents that are characterized by a markedly energetically heterogeneous surface (zeolites) with polarizable molecules. The influence of this phenomenon can be eliminated by using nitrogen or argon as the adsorbate.

To obtain reliable results, the varying amount of gas passing through the catharometer during the measurement must be taken into account. During the low-tem-

perature adsorption from a flow of the gaseous mixture, not only the composition of this mixture but also its volume rate vary, the latter owing to thermal contractions. A suitable experimental arrangement makes it possible to reduce the sensitivity of the catharometer to the changes in the flow-rate of the mixture being analyzed. However, even such an arrangement does not provide for reliability in the results of measurements of specific surfaces less than $0.5 \text{ m}^2/\text{g}$.

JOHNSON AND BARALL⁴ used the thermal desorption method for the determination of the specific surfaces of polymer sorbents of the Porapak type. This paper summarizes the results of measurements of the specific surfaces of hydroxyethyl methacrylate gels, which are used for the same purposes. These gels can be prepared in a number of modifications with different specific surfaces and capable of interactions of an adsorption character. The interactions exhibit a certain specificity that is dependent on the character of the adsorbate.

Interactions in the adsorbent-adsorbate system are expressed by heats of adsorption obtained either by a direct calorimetric measurement or by calculations based on the isotherms. For temperatures above 25° , the gas chromatographic method can be used advantageously; the heats of adsorption are obtained from the graph of the dependence of the corrected retention data on temperature^{5,6}. The chromatographic heats of adsorption for various compounds have been published earlier^{7,8}, and their dependence on the temperature range under investigation allowed the characterization of the interaction in the system⁹. The favourable results obtained earlier⁹ prove the suitability of the method applied.

The heats of adsorption for carbon dioxide, ethylene and propane given in this paper were calculated from the elution chromatographic data.

EXPERIMENTAL

Apparatus

Measurements of the specific surfaces of macroporous hydrophilic polymers were carried out in a sorptiometer constructed in the Institute of Physical Chemistry, Czechoslovak Academy of Sciences. The apparatus used was suggested by GRUBNER¹⁰; the results of a check on its operating properties were published by PATZELOVÁ¹¹. The elution chromatographic data were obtained with an apparatus made in the Institute of Instrumental Analytical Chemistry, Czechoslovak Academy of Sciences, Brno; the apparatus was equipped with a thermal conductivity detector and two parallel columns⁹.

Adsorbents

Hydrophilic macroporous gels (Uniflex) were prepared by suspension-precipitation copolymerization of 2-hydroxyethyl methacrylate and ethylene dimethacrylate in an aqueous dispersion in the presence of solvents¹². After the suspension had been thoroughly washed with water and methanol, the copolymeric products were extracted with methanol in a Soxhlet apparatus, dried *in vacuo* at 80° and fractionated on sieves. The specific surface areas were measured on fractions with a particle diameter of $100\text{--}200 \mu\text{m}$.

Adsorbate

The gaseous mixture used consisted of 15.3 % (v/v) of bulb nitrogen and 84.7 %

(v/v) of electrolytic hydrogen (both obtained from Moravian Chemical Works, Ostrava); its composition was determined chromatographically.

RESULTS AND DISCUSSION

Copolymerization of the monovinyl and divinyl monomers in the presence of solvents gives rise to three-dimensional gels with permanent porosity. The pore size distribution and the specific surface area are functions of the reaction conditions, particularly of the concentration and type of the cross-linking monomer and of the components of the solvent system. An appropriate choice of the stabilizer for the suspension enables particles with a perfectly spherical shape and a very narrow size distribution to be obtained.

Compared with the B.E.T. method, the results attain a relative accuracy of $\pm 3\%$ while observing the above requirements; this accuracy seems satisfactory for the majority of cases⁹. An advantage of the thermal desorption method is its experimental simplicity and rapidity. It is therefore particularly suitable for measurements on large series of samples, *e.g.*, when determining the effect of after-treatments of the adsorbents on the determination of the specific surface area of the products obtained. If this method is applied to the investigation of macromolecular porous compounds, it enables the effect of the reaction conditions used during polymerization on their final structure to be followed.

The character of the structure can be seen from the electron micrograph of the cross-section of a gel bead (Uniflex 300) in the dry state (Fig. 1). The heterogeneity

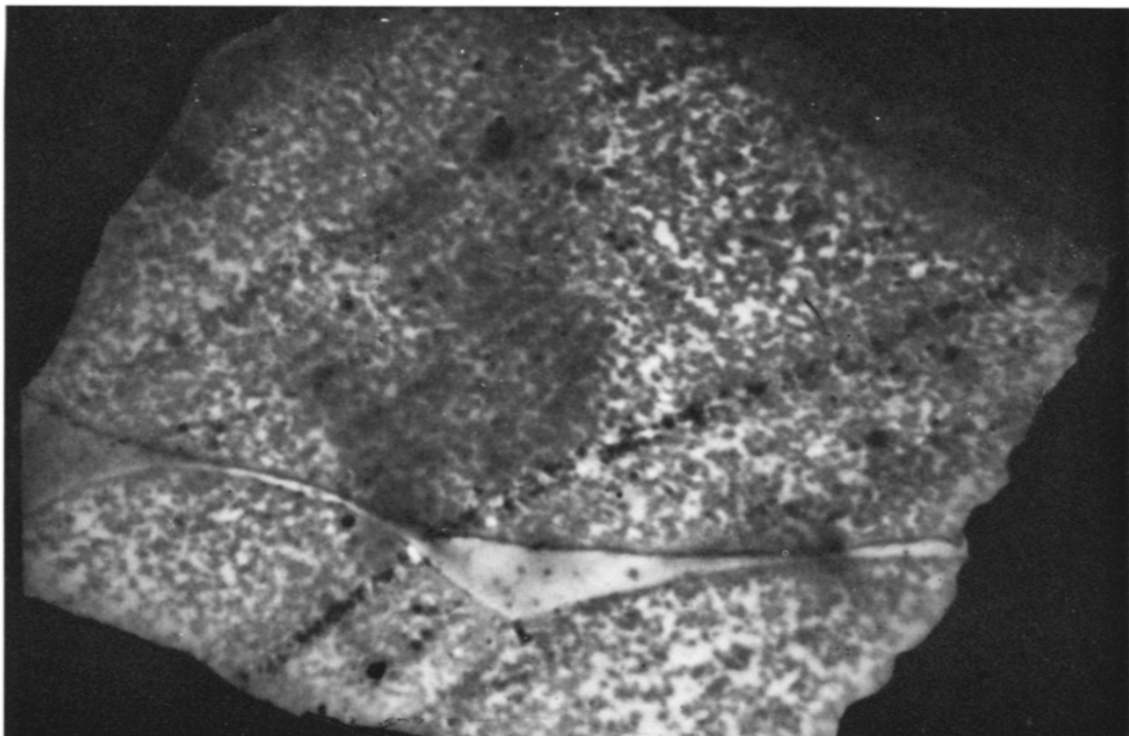


Fig. 1. Electron micrograph of Uniflex 300.

of the gel remains the same throughout the cross-section, and the pores communicate with each other, so that the gel has the structure of a genuine sponge.

The results of the measurements of the specific surfaces of hydroxyethyl methacrylate gels are summarized in Table I. The figures following the name of the gel give the value of the exclusion limit¹³ of the molecular weight in thousands, if defined dextran fractions were used as the testing standard in the gel chromatographic analysis carried out on these materials. As assumed, the specific surface area attains a maximum with increasing exclusion limit, as the number of pores and apparently also the articulation of their surfaces decrease with increasing pore size. A deviation was observed for Uniflex 40 gel, for which the mechanism of the formation of the internal surface is different. In this instance, the solvent system does not contain any polymer precipitant and the separation of phases occurs only after the critical density of cross-links has been reached. In other instances the polymerization proceeds by a heterogeneous mechanism after attaining a low degree of conversion (3-5%).

The shapes of the adsorption and desorption curves representing the course of sorption (Fig. 2) do not exhibit any pronounced broadening, in either the ascending or descending part. The completion of the sorption process is defined unambiguously by a return to the zero line. The relative reproducibility of the measurements was verified by determining the specific surface area from different weighed amounts

TABLE I
SPECIFIC SURFACES OF UNIFLEX GELS

Gel	Specific surface (m^2/g)
Uniflex 40	142.30
Uniflex 70	1.29
Uniflex 100	1.29
Uniflex 200	3.09
Uniflex 300	77.77
Uniflex 500	131.50
Uniflex 700	15.28
Uniflex 1000	22.46
Uniflex 100,000	5.01

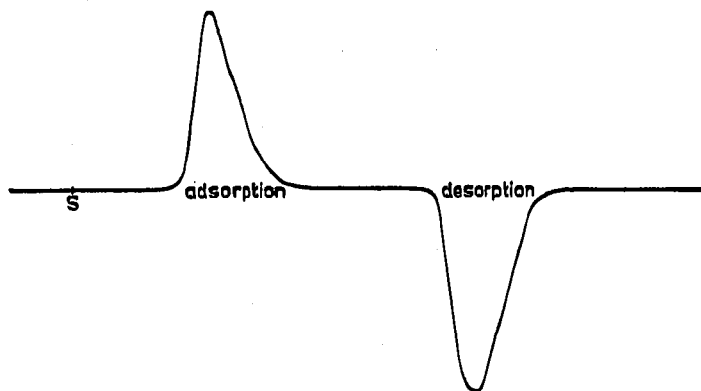


Fig. 2. Diagram of adsorption and desorption of nitrogen on Uniflex 300 macroporous gel.

of the same gel (Table II) and was $\pm 2\%$. For a repeated adsorption and desorption cycle of the sample, the relative reproducibility was better than 2.5%.

Together with the pore size distribution, the specific surface area is one of the main factors that influence the chromatographic properties of the material. It can be a very sensitive measure of the reproducibility of the quality of the individual polymer batches, as insignificant differences between the physical or chemical conditions during the suspension-precipitation polymerization will be reflected in the differences of the specific surfaces of the product. With the exception of gels with the smallest specific surface, when the accuracy of the method is not satisfactory, good agreement was found between gels from various charges (Table III). The accuracy attained by repeated measurements of the specific surfaces of the sample together with the differences between the specific surfaces of various gel types enable general relationships to be outlined between the polymerization conditions and the structure of the gel obtained.

The heats of adsorption of carbon dioxide, ethylene and propane measured in various temperature regions are presented in Table IV. The slope of the dependence of $\log V_{\theta}$ on $1/T$, where

$$V_{\theta} = \frac{V_N \cdot 273}{w_L T_C}$$

TABLE II

REPRODUCIBILITY OF SURFACE MEASUREMENTS BY THE THERMAL DESORPTION METHOD

Gel	Weighed amount (g)		Specific surface (m ² /g)	
	I	II	I	II
Uniflex 40	0.0466	0.0432	142.2	146.6
Uniflex 1000	0.1340	0.1401	24.4	21.2
Uniflex 100,000	0.2513	0.2500	4.9	5.1
H-39-54	0.1679	0.1939	8.1	8.2
H-79-54	0.0431	0.0331	158.3	161.2
H-97-54	0.0331	0.0458	149.1	154.5
TV-79-70	0.0274	0.0321	221.0	217.7
TV-79-82	0.0272	0.0319	150.2	145.1
TV-79-91	0.0317	0.0290	180.2	182.1
TV-59-70	0.0164	0.0200	172.5	176.7

TABLE III

REPRODUCIBILITY OF VARIOUS BATCHES OF HYDROPHILIC HYDROXYALKYL METHACRYLATE GELS

Gel	Specific surface (m ² /g)	
	I	II
Uniflex 40	142.30	151.70
Uniflex 1000	22.46	24.49
Uniflex 100,000	5.01	4.18
GPC-79-91	181.1	209.5
GPC-79-82	147.6	179.2
GPC-79-70	219.8	216.4
TV-24-91	5.12	3.42

TABLE IV

HEATS OF ADSORPTION OF SOME GASES ON HYDROXYALKYL METHACRYLATE GELS

Adsorbent	Adsorbate	Temperature range (°C)	Heat of adsorption (kcal/mole)
GPC-59-54	Propane	40-80	6.8
GPC-59-54	Ethylene	35-90	5.0
Uniflex 300	Ethylene	40-90	4.8
Uniflex 300	CO ₂	26-40	3.6
Uniflex 300	CO ₂	40-80	5.9
GPC-59-54	CO ₂	26-40	4.8
GPC-59-54	CO ₂	40-80	5.5

in which V_θ = specific volume; V_N = net elution volume; w_L = weight of the adsorbent; and T_C = operating temperature (°K), from which the heat of adsorption has been calculated (Fig. 3), is constant for both hydrocarbons over the whole temperature range under investigation. With carbon dioxide there is a change in the slope at a temperature T_z , and the heat of adsorption for temperatures above T_z is increased. A similar phenomenon has been observed also for the Porapak-type polymer carriers⁹; this is the subject of a further study. In contrast with Porapaks,

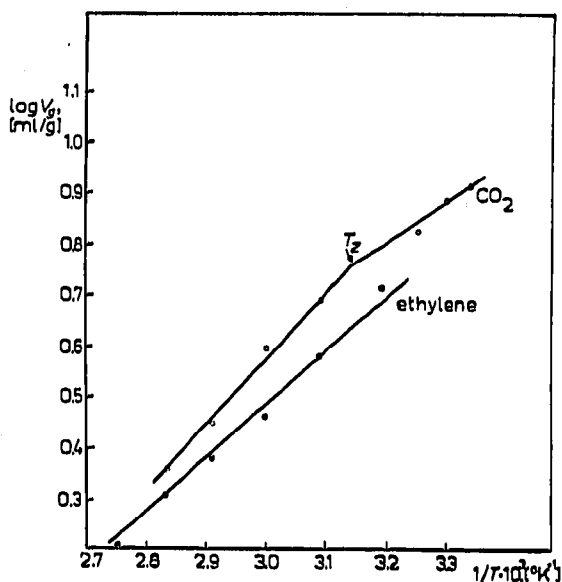


Fig. 3. Dependence of logarithms of corrected retention volumes of carbon dioxide and ethylene on the reciprocal values of the column temperatures. Adsorbent: Uniflex 200.

$$\text{Log } V_\theta = f\left(\frac{1}{T_k}\right), \quad V_\theta = \frac{V_a - V_d}{W} \cdot \frac{273}{T_k}$$

where V_a = component retention volume; V_d = column free volume; W = adsorbent weight; and T_k = column temperature (°K).

which are sorbents of the third type, Uniflex is a hybrid between sorbents of the second and third types. The break observed in the curve of the dependence of $\log V_0$ on $1/T$ for carbon dioxide can probably be explained¹⁴ by a morphological change of the polymer at T_z . Owing to the fact that the elution data were measured with a relative accuracy of $\pm 1\%$ and their dependence on the reciprocal value of the operating temperature was unambiguous, the calculated heats of adsorption can also be regarded as being the true values.

Measurements of the specific polymer surfaces by the thermal desorption method, as well as the determination of the heats of adsorption from the elution data at different temperatures, are methods that are both time-saving and make no excessive demands on the equipment used. They enable information on polymeric macroporous materials to be obtained that is interesting from the viewpoint of their application in gas and gel chromatography.

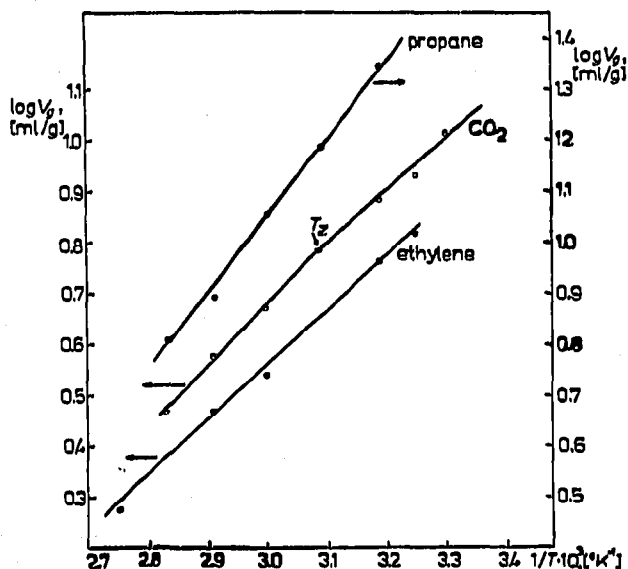


Fig. 4. Dependence of logarithms of corrected retention volumes of carbon dioxide, ethylene and propane on the reciprocal of the column temperatures. Adsorbent: GPC-59-54. (For explanation of symbols, see Fig. 3.)

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