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Gel Permeation Chromatography Using Porous Glass Investigations of the Influence of Silanization on Exclusion and Adsorption

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Abstract

The influence of silanization of glass beads on the exclusion process has been studied. Some attempts to evaluate the influence of adsorption properties of glass beads are made.

INTRODUCTION

In classical gel permeation chromatography, one of the means to simplify the separation of macromolecules is to assume a lack of adsorption interaction between the substance being separated and the column packing. Such an ideal process takes place only if we possess a gel characterized by a homogeneous, nonspecific surface which does not admit of any other interaction.

There are a number of materials which are used as column packings in sieve chromatography. One of them is glass of controlled porosity. Glass itself allows us to obtain not only a sorbent of anticipated porosity which can be easily regulated, but it can also be used in the form of beads as a perfect column packing of high mechanical resistance and, therefore,

possible to be utilized in cases of very high pressure. This material, however, possesses one significant disadvantage; namely, it shows considerable adsorption properties which disturb gel permeation, itself, particularly during the analysis of macromolecules with functional polar groups (*1*). In such cases the addition of a certain amount of substances that block the active centers or modify the surface is needed (*1*, *2*).

In this paper some attempts to evaluate the influence of the adsorption properties of glass beads of controlled porosity from the available data of gel chromatography are presented.

EXPERIMENTAL

Packings of Chromatographic Columns

The preparation of glass beads of controlled porosity (15 to 30 μ) was worked out in the Department of Physical Chemistry, Marie Curie-Skłodowska University, Lublin (*3–5*). For chromatographic measurements, both the initial and silanizing materials with DMDCS, and also with hexamethylodisilazane, were used. The silanization conditions were more rigorous than those recommended by Electro Nucleonics for glass CPG 10. Some properties of both packings are presented in Table 1. As can be seen from this table, silanization causes only a slight change in the average radius of pores and intragranular volume. Our studies have shown that the packings used in this work do not possess micropores (*6*).

Figure 1 presents distribution curves of pore radii in both materials as determined by the thermal method of nitrogen desorption. The solid line

TABLE 1

Some Surface Properties of Column Packings Used in Chromatographic Measurements[a]

Material	S_{N_2} (m^2/g)	D	r_{por} (Å)	V_{por} (ml/g)
Nonsilanized	51.9	—	220	0.98
Silanized	30.3	0.42	205	0.96

[a] S_{N_2} is the surface area, BET method, nitrogen adsorption. $D = S_{N_2} - S_{H_2O}/S_{N_2}$; where S_{H_2O} is the surface area determined by H_2O vapor adsorption. r_{por} is the average radius of pores determined by a mercury porosimeter. V_{por} is the intragranular volume.

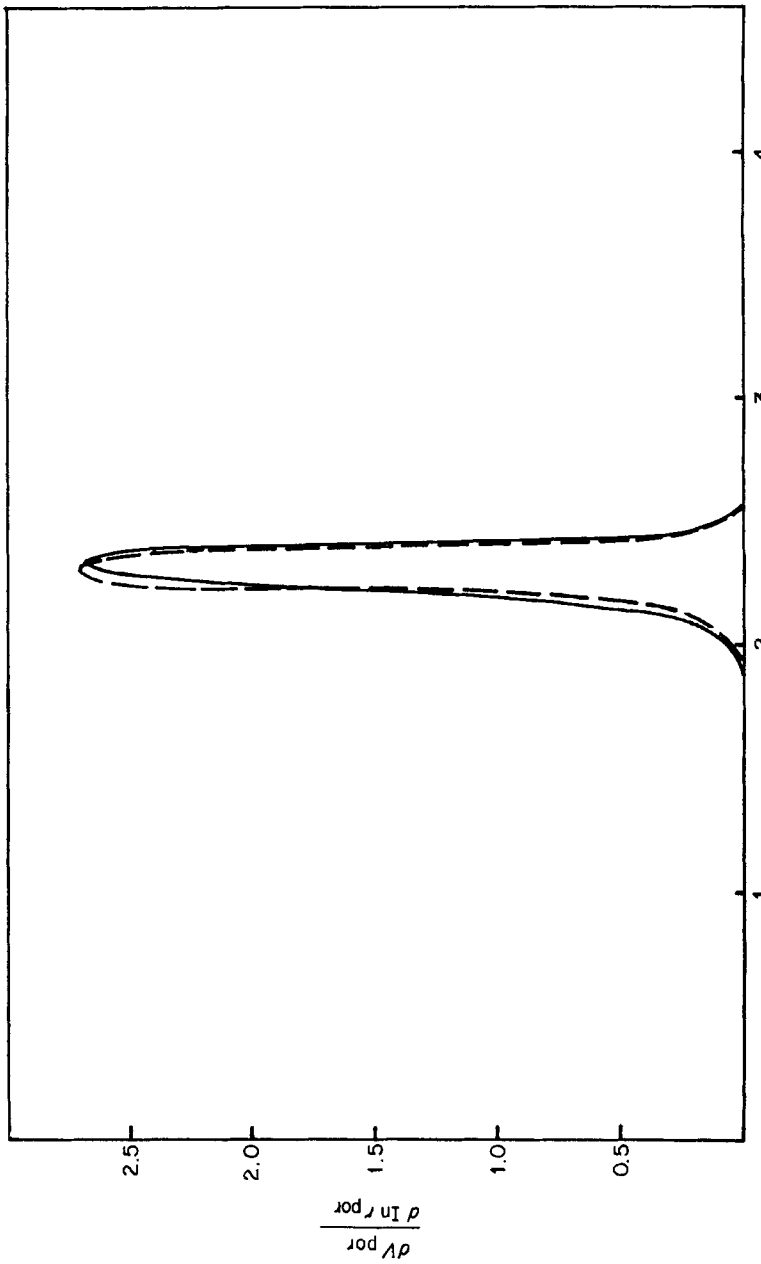


FIG. 1. Distribution functions of pore radii in both materials. The solid line denotes the distribution function for nonsilanized material, and the dashed line that for silanized material.

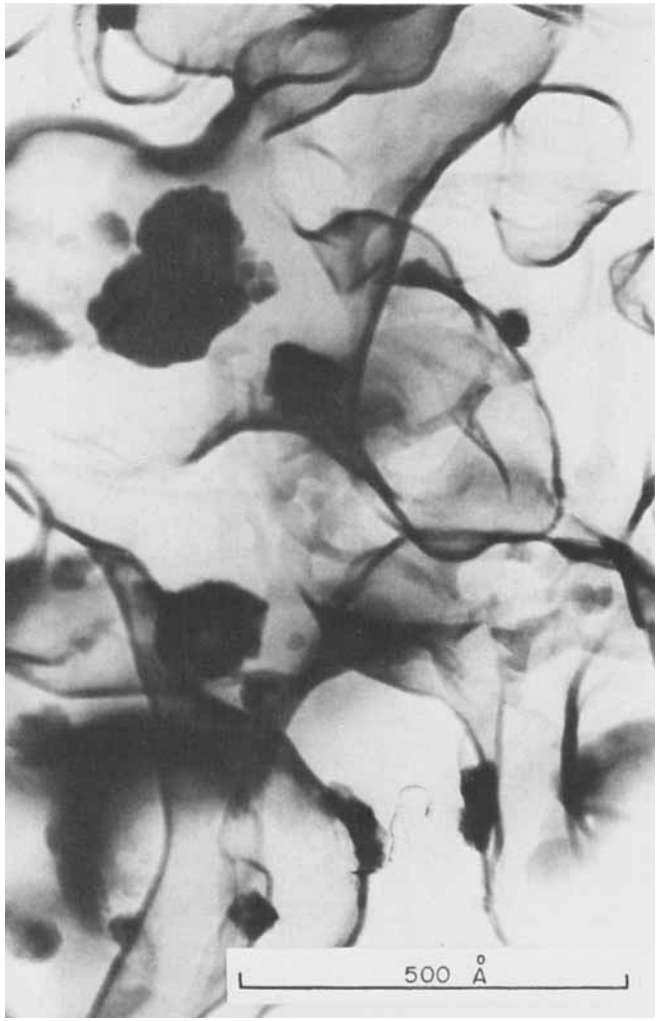


FIG. 2. Electromicrograph of nonsilanized material.

FIG. 3. Electromicrograph of silanized material.

denotes the distribution function of pores for the nonsilanized material; the dashed line that for the silanized material.

Electromicrographs for two packings are shown in Figs. 2 and 3. The photographs were made by the replica method.

Polystyrene Samples

Ultranarrow polystyrene (PS) standards obtained from Waters Associates were used.

Apparatus

Measurements were made in the Varian 4100 apparatus with a UV 254 detector equipped with a piston-membrane pump made of Orlit. The temperature of the column during work was regulated to an accuracy of 0.01 °K. The mobile phase for chromatography was THF (Loba-Chemie, Wien-Fischamend). The flow velocity was 1.2 ml/min (measured with an accuracy of 0.02 ml/min). Since the purpose of this work was to obtain some physicochemical characteristics of the systems discussed, a column 105 × 0.4 cm i.d., packed by the balanced density slurry method for both packings, was used. The ultranarrow PS was used as the macromolecule standard.

Chromatographic Measurements

Measurements of the relationship $M = f(V_e)$ were made, where V_e is the retention volume and M is molecular weight of the standards used. In the case of a column packed with nonsilanized glass, temperature measurements were made at 282, 288, 293, 298, 303, and 313 °K, whereas in the case of the silanized material the temperatures were 283, 293, 298, and 303 °K. The results of the measurements are presented in Figs. 4 and 5.

THERMODYNAMIC FUNCTIONS DETERMINED FROM CHROMATOGRAPHIC MEASUREMENTS

Evaluation of the adsorption effects on separation in GPC is a difficult problem (*7*). Studies of the thermodynamic relationships of the retention volume do not allow a direct evaluation of polymer–gel interactions. The thermodynamic functions of these measurements illustrate the total

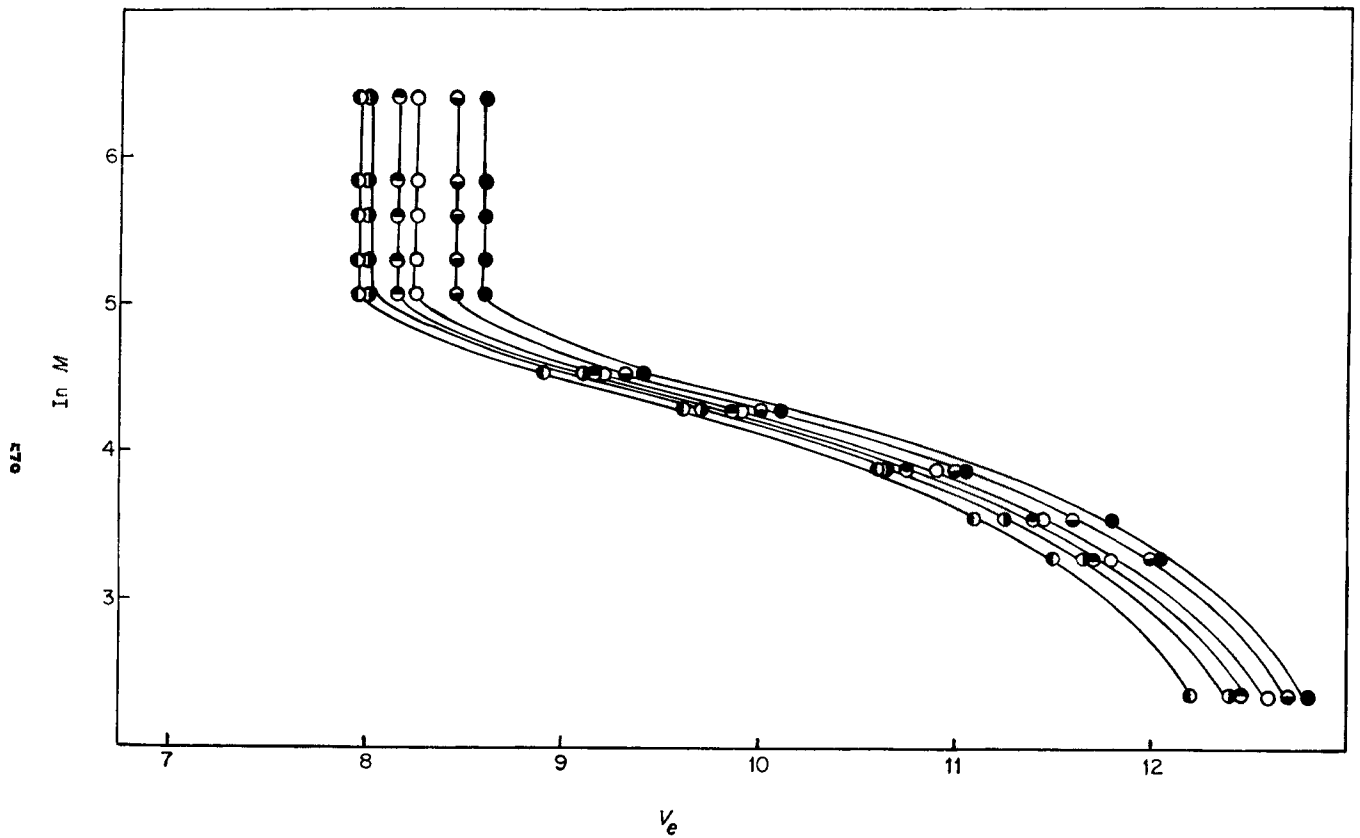


FIG. 4. The relationships $\ln M = f(V_e)$ for nonsilanized material. The points denote different temperatures: (●) 281 °K, (◒) 288 °K, (○) 293 °K, (◓) 298 °K, (◑) 303 °K, and (◐) 313 °K.

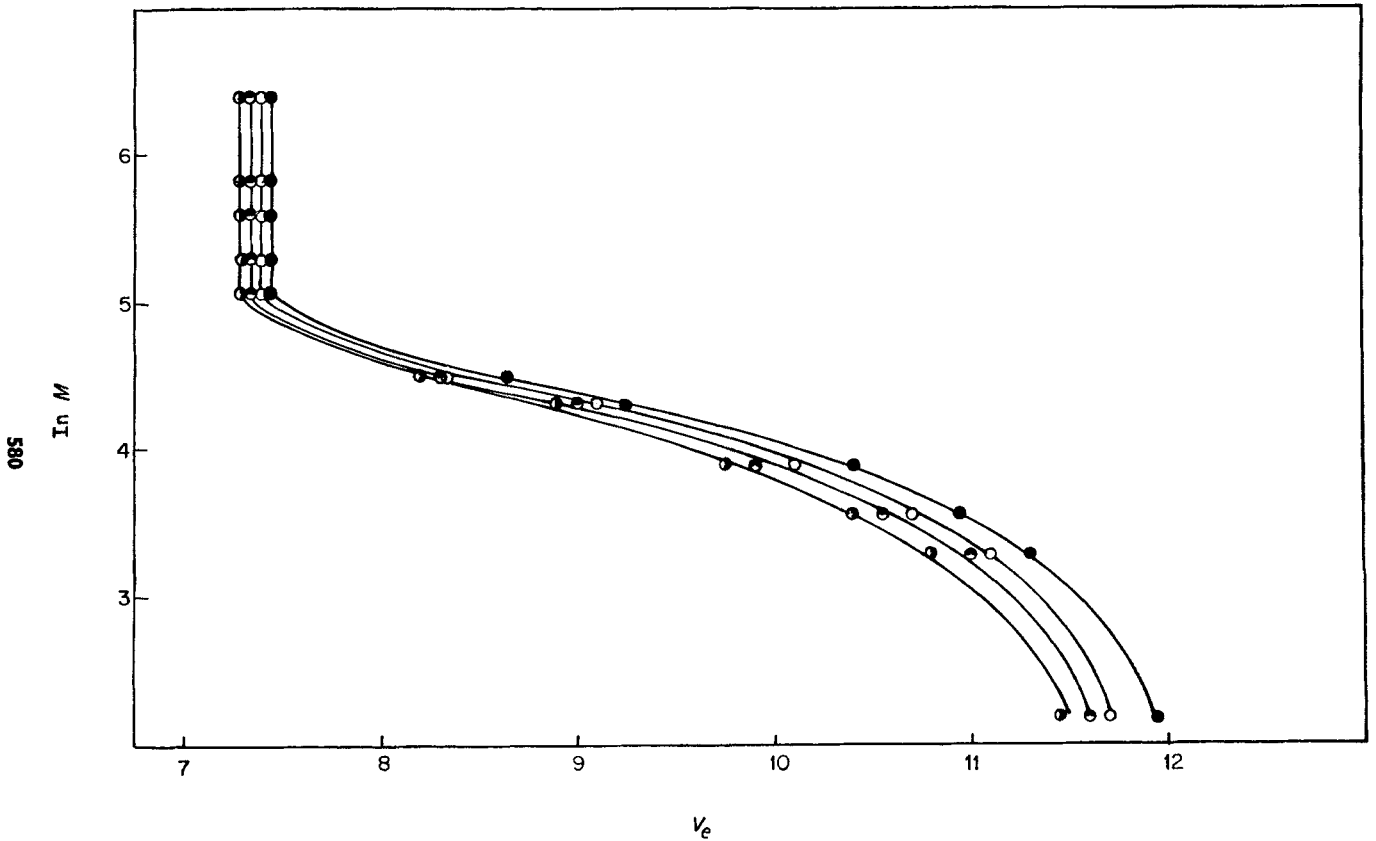
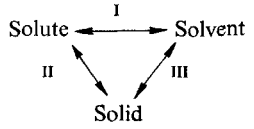


FIG. 5. The relationships ln $M = f(V_e)$ for silanized material. The points denote different temperatures: (●) 283 °K, (○) 293 °K, (◓) 298 °K, and (◑) 303 °K.

effects of the following processes (*8*):



In the typical systems used in gel permeation chromatography, Processes I, II, and III are exothermic. In the case of a polymer solution in which interactions with the gel skeleton are weak, the energy of the overall chromatographic process is determined by Processes II and III. In this case the temperature increase is accompanied by desolvation, with simultaneous solubility of the solute and a decrease in adsorption of the solvent on the solid. In the case where the polymer strongly interacts with the solid, the energy of the process is determined by Process II. In accordance with the exothermic character of this process, a temperature increase would cause a decrease in retention volume.

The total energy of interactions of the polymer molecule with the surface of the solid may be considered as the sum of the interactions of the particular energetic centers of the packing with the energetic centers of the polymer, though determination of at least an approximate analytical form of the function describing this energy is an exceptionally complicated problem. In the present paper, a "hard core" potential was used to describe this energy. In other words, it was assumed that the interaction energy of the polymer molecule is equal to zero at a certain distance r, and equal to infinity for distances smaller than r. The application of such a potential model resulted in the following analytical expression for the distribution coefficient K_d (*7, 9–11*):

$$K_d = \frac{V_e - V_0}{V_i} = 1 - dr \qquad (1)$$

where V_i is the internal volume, r is the radius of the spherical polymer molecule, d is a coefficient equal to $1/a$ for slab-shaped pores, $2/a$ for cylindrical pores, and $3/a$ for spherical pores, and a is the radius of the pores.

This theory (exclusion volume approach) assumes that the coefficient K_d is independent of temperature.

It is evident that the true course of changes in the potential of polymer–solid interactions inside pores is far from the hard core potential, which completely neglects adsorption effects. As a matter of fact, the potential inside pores may possess minima which will depend on the shape and orientation of the polymer molecule in relation to the pore walls.

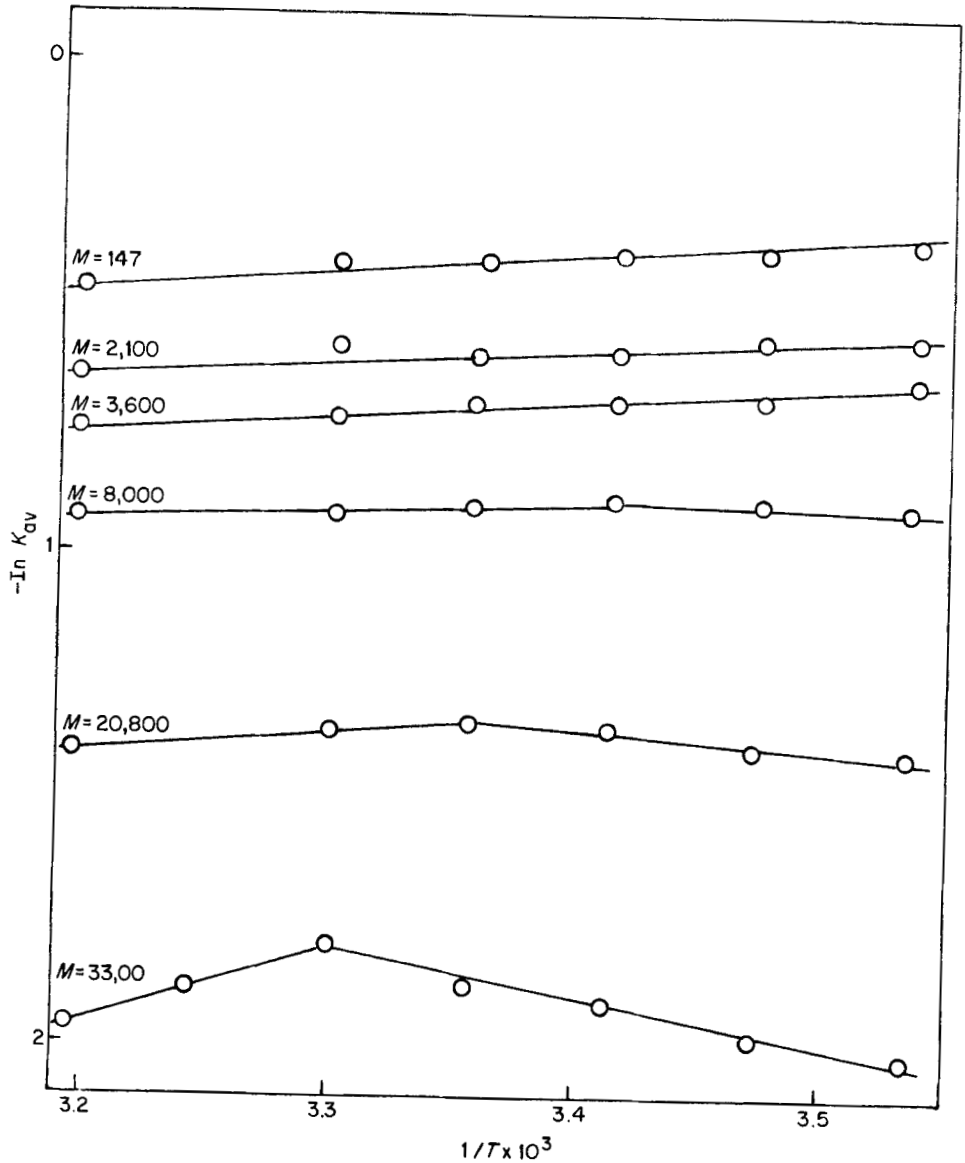


FIG. 6. The relationships ln $K_{av} = f(1/T)$ for nonsilanized material and different PS samples.

Moreover, in the case of a solvent strongly interacting with the surface of the solid, adsorption occurs.

The glass beads used in our chromatographic measurements show fairly strong adsorption properties (*4*, *12*). In the case of some solvents, the presence of hydroxyl groups and boron atoms on the surface may result in the formation of hydrogen bonds (specific interactions). Silanization of the initial material leads to replacement of hydroxyl groups by much less active siloxane groups. Thus the adsorption properties of the silanized material are much weaker. The silanization of the surface of the bed causes a change in the energy of Processes II and III. In the case discussed here, Process III undergoes a fundamental change (decrease in solvent adsorption on silanized material).

The thermodynamic functions for both packings and for a number of PS standards were calculated from the temperature dependence of the coefficient K_{av} (*8*, *13*):

$$K_{av} = \frac{V_e - V_0}{V_t - V_0} \tag{2}$$

where V_t is the total volume according to the equations

$$\Delta G^\circ = -RT \ln K_{av} \tag{3}$$

$$\Delta H^\circ = -R \frac{\partial \ln K_{av}}{\partial 1/T} \tag{4}$$

Diagrams of temperature relationships ($\ln K_{av}$) are presented in Figs. 6 and 7. In Tables 2 and 3 the values of ΔG° for the standards of both column packings are summarized. Table 4 presents the values of ΔH° calculated for the particular PS standards of both packings at 298°K.

DISCUSSION

From a comparison of the data contained in Tables 2 and 3, the following can be observed. First, for a given standard, an increased ΔG° with a temperature increase is generally observed except for the standards of the highest molecular weight on nonsilanized material. Second, for a given temperature the values of ΔG° are higher for higher molecular weights. Third, the values of ΔG° are higher in the case of silanized material.

It is also of interest to follow the course of $\ln K_{av}$ for nonsilanized material for the standards with the highest molecular weight. A distinct change can be observed: at higher temperatures the slope is positive

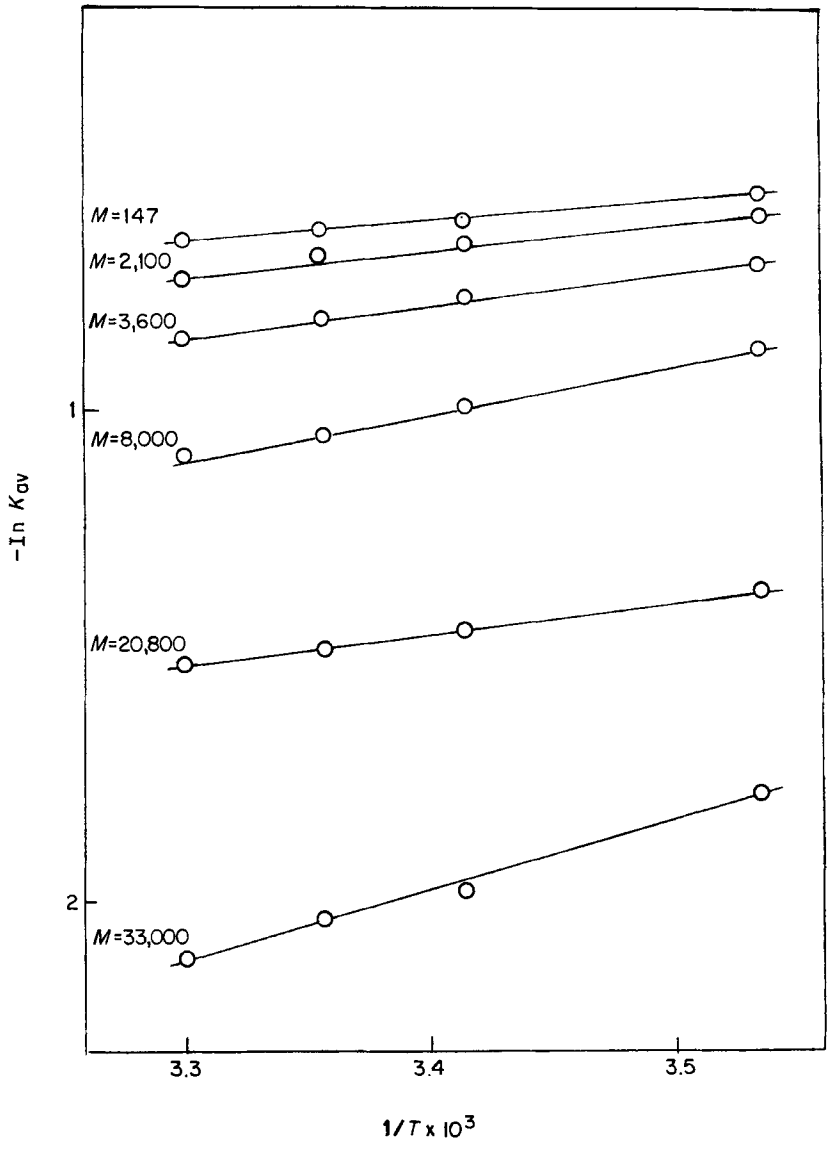


FIG. 7. The relationships ln $K_{av} = f(1/T)$ for silanized material and different PS samples.

TABLE 2

Free Energy for PS Standards on Nonsilanized Glass Beads (in cal/mole)

Molecular weight	Temperature (°K)					
	283	288	293	298	303	313
33,000	1,145	1,145	1,120	1,120	1,090	1,225
20,800	790	800	795	800	830	880
8,000	510	515	520	535	550	580
3,600	360	390	410	415	435	470
2,100	320	320	345	360	350	400

TABLE 3

Free Energy for PS Standards on Silanized Glass Beads (in cal/mole)

Molecular weight	Temperature (°K)			
	283	293	298	303
33,000	1,020	1,160	1,215	1,285
20,800	790	850	890	925
8,000	510	580	630	670
3,600	410	460	490	520
2,100	355	400	410	450

TABLE 4

Enthalpy Change for PS Standards on Silanized and Nonsilanized Materials at 298°K (in kcal/mole)

Molecular weight	ΔH° nonsilanized	ΔH° silanized
33,000	−2.10	2.80
20,800	0	1.10
8,000	0.40	1.80
3,600	0.60	1.20
2,100	0.70	1.00

(negative ΔH°) and at lower temperatures it is negative. With a decrease in molecular weight the point at which the slope is equal to zero is shifted in the direction of lower temperatures. When $M = 33{,}000$, this is accompanied by practical stability up to $T = 303\,^\circ\text{K}$, and then there is a distinct increase. These changes are illustrated by Table 4. Though in the case of silanized material a systematic increase in the value ΔH° with an increase in M is observed, in the case of nonsilanized material this relationship is reversed, and when $M = 33{,}000$, a negative value is observed.

The presence of an oxygen atom in the solvent molecule results in the formation of hydrogen bonds between molecules of the solvent and surface OH groups in the case of nonsilanized material. The adsorption of the solvent is high, and the polymer molecules interact with the surface of the solid where it is covered with the solvent. With a temperature increase, the solvent adsorption decreases. On silanized material the adsorption of solvent molecules is much weaker, hence screening of solid–polymer interactions by solvent molecules is weaker, too.

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