Negative adsorption and liquid chromatography of polystyrene on silica

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The main factors that determine negative adsorption of polymers have been considered. These are the preferred (positive) adsorption of the solvent molecules and the sieve effect during the interaction of macromolecules with a porous adsorbent. Modification of the silica surface, solvent polarity, and the size of the macromolecular coils of polystyrene favor the negative sorption of polystyrene by porous silica and size-exclusion chromatography separation of macromolecules. The relations between the partition coefficient of a substance between the bulk and the adsorption phases and the excess values of retention, the capacity factor, and the adsorption coefficient (the Henry constant) are analyzed.

Key words: polystyrene, negative adsorption; chromatography; partition coefficient, the Henry constant; silica.

The study of the interaction of polymers with the surfaces of solids is of great importance for elucidating the mechanism of adhesion, creating composite polymer-containing materials, developing a theory of stabilization of colloid dispersions of polymers, and solving some problems of physicochemical mechanics of disperse systems (see, *e.g.*, Refs. 1 and 2). In most cases, when a polymer solution interacts with a solid, an adsorption monolayer of macromolecules forms on the surface of the adsorbent.[3] When there is competition between the polymer macromolecules and solvent molecules, the adsorption layers of polymers do not form in some systems because of the preferred adsorption of solvent molecules capable of complete displacement the polymer macromolecules from the surface of the adsorbent. The preferred adsorption of the solvent results in the negative adsorption of the polymer, *i.e.*, a deficiency of the polymer in the adsorption space in the vicinity of the adsorbent surface. Steric hindrances (sieve effects) during the adsorption of polymers on porous solids also favor the negative adsorption of macromolecules.

In this work, the adsorption of polystyrene on porous silica is studied and data on the liquid chromatography of polystyrene are presented.

The adsorption value of the polymer macromolecules (n^σ) determined experimentally is the amount by which the polymer content in the surface (adsorption) phase exceeds that in the bulk phase (polymer solution) far from the adsorbent surface:

$$n^\sigma = V(C_0 - C)/m, \qquad (1)$$

where V is the the volume of the solution; m is the weight of the adsorbent; C_0 and C (mg mL^{-1}) are the initial and equilibrium concentrations of the polymer.

The value of n^σ is connected with the total content of the polymer (n) on the adsorbent surface by the following relation:[4]

$$n = n^\sigma + V_a C, \qquad (2)$$

where V_a is the adsorption volume (the volume of the subsurface layer in which adsorption forces act). For the low-concentration range ($C \to 0$), $n \cong n^\sigma$ and the adsorption isotherm is linear (the Henry range).

$$n^\sigma = K_H C \qquad (3)$$

If the concentration of the macromolecules in the equilibrium solution increases during the interaction of the polymer solution with the adsorbent, then, according to Eq. (1), $n^\sigma < 0$ and, hence, $K_H < 0$; however, the total content of the polymer in the surface phase should be >0. If $n^\sigma < 0$, the adsorption of the polymer is negative.

Let us consider two cases of negative adsorption. In the first case, the negative adsorption of the polymer is due to the competition of the solvent molecules, which results in the partial or complete displacement of the macromolecules from the surface of the adsorbent. In this case, the concentration of the polymer in the surface solution is less than that in the bulk; consequently, the partition coefficient $K_p = C_s/C < 1$ (C_s is the concentration of the polymer in the surface solution). According to Eq. (3), $K_H < 0$ when there is negative adsorption. As follows from Eq. (2), the minimum value of K_H, which is equal to $-V_a$, is achieved at $n = 0$. The value $K_H = 0$ corresponds to $K_p = 1$. This means that the composition of the surface phase does not differ from that of the bulk phase and, consequently, in the Henry range, the isotherm $n^\sigma = f(C)$ coincides with the concentration axis.

In the second case, the negative adsorption of polymers is due to the sieve effect, *i.e.*, the pores of the adsorbent are partially or completely inaccessible to the polymer macromolecules. With allowance of the contribution of practically the whole volume of micro- and mesopores (V_s) of the adsorbent accessible to the eluent molecules, Eq. (2) should be written as

$$n_s = n^\sigma + V_s C, \qquad (4)$$

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because the composition of the solution in the mesopores of the adsorbent differs from that of the equilibrium bulk solution (far from the pore space) due to the sieve effect (*i.e.*, different accessibility of pores for macromolecules of different sizes).

For the case of bulk filling of pores in the low-concentration range, the adsorption isotherm $n^\sigma = f(C)$ is linear. At $n_s = 0$, the minimum value of K_H (pores are completely inaccessible to polymer macromolecules) is equal to $-V_s$, and the partition coefficient $K_p = 0$, because there are no macromolecules in the pores. Thus, the Henry constant K_H for the case of negative adsorption, in the framework of the model of the bulk filling of mesopores, changes from 0 to $-V_s$.

One of the most important retention parameters in liquid chromatography is the capacity factor (K'):

$$K' = (V_R - V_0)/V_0, \quad (5)$$

where V_R is the retention volume of a polymer in the column; V_0 is the volume of the mobile phase. At $K_p = 0$, the minimum value of the capacity factor K' becomes equal to $-V_s/V_0$, because in this case the difference $V_R - V_0$ is negative.[5]

Experimental

Polystyrene standards (Pressure Chem. Corp., USA) with molecular weights M_w = 10000, 97200, and 450000, as well as the suspended polystyrene PS1 (Kuskovo Chemical Plant, Moscow) were used as the objects of studying. The PS1 samples were purified by reprecipitation from a toluene solution with methanol and dried at 80 °C. The molecular weight of PS1 estimated by viscosimetry (M_η) in a toluene solution at 25 °C was equal to 48000. The polydispersity of PS1 was equal to 3.6, which was evaluated with the aid of a Waters 240 liquid chromatograph (Millipore, USA) on standard columns packed with styragels.*

The solvents, *n*-heptane, CCl_4, and toluene of chemically pure grade (Reakhim, Moscow), were purified with rectification and stored in dark vessels over dehydrated NaA zeolite. *n*-Heptane was used as a marker for the estimation of the "dead" volume of the chromatographic column.

Samples of the mesoporous silica, silochrom S-80G (Luminofor, Stavropol'), served as the adsorbents. According to the literature data,[6,7] the average pore size of silochrom S-80G is equal to 55 nm, the total pore volume is 1.20 $cm^3 g^{-1}$, and the specific surface area is 96 $m^2 g^{-1}$. The fraction with grain sizes 0.25—0.50 mm was used for the adsorption experiments. In the chromatographic experiments, a metal column (350×4.6 mm) was packed with silochrom particles 10 mm in size. Before experiments, the silochrom was dried for 4 h in a vacuum at 150 °C. The concentration of the OH groups on the surface of silochrom S-80G was equal to 4.1 groups per 1 nm^2, which is close to the data of Ref. 8. The concentration of the OH groups was determined from the weight loss of the silochrom sample after calcination at 1100 °C in a crucible furnace.

In order to dehydroxylate the surface, one portion of silochrom S-80G was heated at 900 °C for 6 h. As a result, the density of the OH groups of the dehydroxylated sample of silochrom (S-80D) descreased to 0.6 groups per 1 nm^2. Another portion of silochrom S-80G was treated with a 10% solution of trimethylchlorosilane in toluene for 4 h and additionally, after a single washing with toluene, with a 10% toluene solution of dimethyldichlorosilane.[9] According to the data of elemental analysis performed on a C,H,N-analyzer (Perkin-Elmer, USA), the carbon content on the surface of the silanized sample (S-80M) was 2.4%; this corresponds to practically complete coverage of the inner surface of the mesopores of the S-80M silochrom.

The procedure used for the adsorption measurements has been previously described in detail.[10] The change in the polymer concentration in the bulk of the solution during adsorption was monitored with an LIR-2 interferometer.

The chromatographic measurements of the retention of polystyrene standards were carried out on a Tsvet-304 liquid chromatograph (Khimavtomatika, Dzerzhinsk). An R-1107 flow differential refractometer (Perkin-Elmer, USA) with a cell volume of 5 μL was used as the detector. Chromatograms were recorded on a self-registering T34820 instrument (Laboratornye Pribory, Prague). The flow rate of the eluent (toluene) was equal to 1 mL min^{-1}, and the temperature of the thermostat of the column was 25±0.5 °C. The retention times of three PS standards were measured on two samples of silochrom, hydroxylated S-80G and S-80M modified with trimethylsilane. The volume of the mobile phase was estimated from the retention time of *n*-heptane.

Results and Discussion

Polystyrene macromolecules in CCl_4 solutions are adsorbed mainly on hydroxylated silica and form a monolayer on the surface of silica at the equilibrium concentration >3 mg mL^{-1} (Fig. 1, curve *1*). The negative adsorption of PS on silanized silica (see Fig. 1, curve *3*) is due to the replacement of silanol groups with trimethylsilyl groups, which weaken substantially the interaction of the PS macromolecules with the adsorbent. Dehydroxylation of the surface of silica decreases the specific interaction of phenyl groups of the PS macromolecules with the adsorption sites, resulting in a decrease in adsorption (see Fig. 1, curve *2*). Replacing CCl_4 with toluene significantly decreases the adsorption of the PS macromolecules on the dehydroxylated surface of silica and favors the negative adsorption of PS at the hydroxylated surface of silochrom S-80 (Fig. 2, curve *3*). The toluene molecules interact specifically with the silanol groups of silica and displace the PS macromolecules from the surface solution.

The K_H and K_p values for the adsorption equilibrium in the PS1—silica system presented in Table 1 indicate that chemical changes in the state of the silica surface and the nature of the solvent molecules have substantial influence on the sign and value of the Henry constant. It is noteworthy that in spite of the high error in the evaluation of K_H by graphic extrapolation, the predominant role of the surface chemistry of the adsorbent and the structure of the solvent molecules in the behavior of the PS macromolecules on the interface is beyond doubt.

The molecular weight of the polymer and size of the molecular coil determine the accessibility of the pore space. Comparatively small PS macromolecules (M_w =

* The estimation of polydispersity of PS1 was carried out by A. I. Kuzaev (N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences).

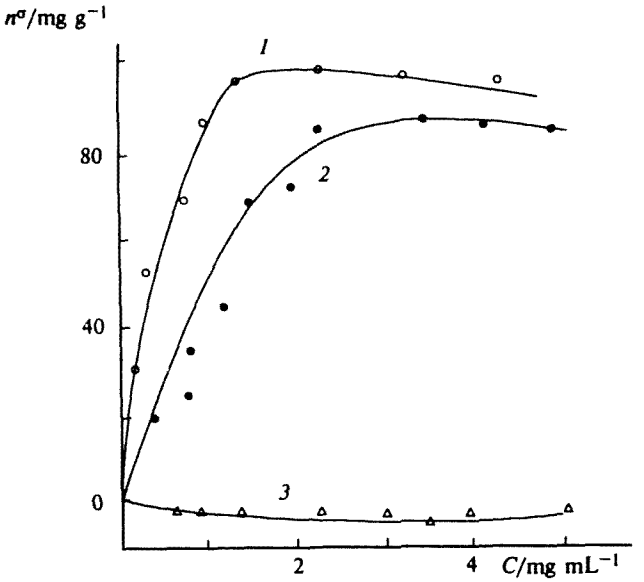

Fig. 1. Adsorption of polystyrene (M_η = 48000) from solutions in CCl_4 on hydroxylated (*1*), dehydroxylated (*2*), and silanized (*3*) samples of silica.

10000) diffuse slowly into the mesopores of silochrom S-80G particles and partially displace the toluene molecules from the pores (Fig. 3, curve *3*), whereas large PS macromolecules (M_w = 450000) cannot penetrate because of their size into the mesopores of S-80G silochrom, which have an average size of 55 nm (see Fig. 3, curve *1*). Curve *2* in Fig. 3 reflects the kinetics of competitive sorption of both toluene molecules and PS macromolecules with M_w = 97200 by mesoporous silica. The macromolecules of this sample of polymer, unlike the higher molecular weight PS (M_w = 450000), retard to a higher extent the diffusion of toluene molecules into the 55 nm mesopores. The subsequent intense displacement of toluene molecules by PS macromolecules with M_w = 97200 during mutual diffusion finishes in 2 h. The toluene molecules concentrate on

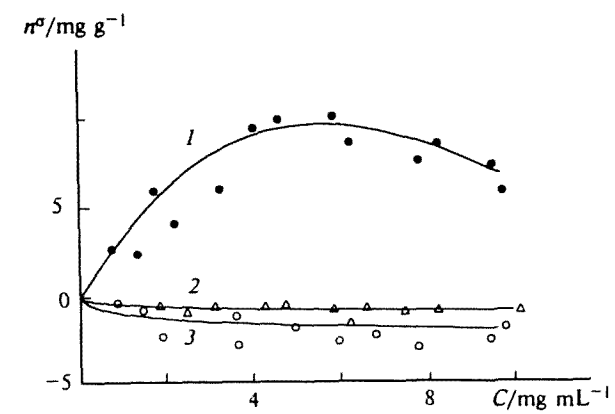

Fig. 2. Adsorption of polystyrene (M_η = 48000) from solutions in toluene on silochrom S-80 with dehydroxylated (*1*), silanized (*2*), and hydroxylated (*3*) surfaces.

Table 1. The Henry constants (K_H/mL g^{-1}) and partition coefficients (K_p) for the PS1*—silochrom S-80—solvent system at 25 °C

Sample	CCl_4		PhMe	
	K_H	K_p	K_H	K_p
S-80G	>200	>170	−0.28	0.77
S-80D	48	41	2.7	3.2
S-80M	−0.24	0.80	−0.22	0.82

* M_η = 48000.

the surface of the accessible pores and in the thin pores of S-80G silochrom.

The Henry constant was calculated from the data of the chromatographic experiment according to the equation

$$K_H = (V_R - V_0)/m, \quad (6)$$

i.e., as the corrected retention volume per the unit weight of the sorbent in the column.

The negative values of K_H and, hence, K' (see Eq. (3)) reflect the fact that the retention volume of the polymer macromolecules is less than V_0, the volume of the mobile phase. This is resonable because V_0 involves the total pore volume V_s, and the retention volume of the polymer is only a fraction of the total volume V_s. Relations between K' and K_p values have been presented previously[11] and can be written for the case of the sieve chromatography of polymers as

$$K' = [(K_p - 1)V_s]/V_0. \quad (7)$$

The V_s volume characterizes the capacity of the chromatographic column in which the size-exclusion separation of macromolecules proceeds. From Eq. (7) one can obtain expression (8) for the calculation of K_p.

$$K_p = 1 + K'V_0/V_s \quad (8)$$

Similarly, one can write relationship (9) between the partition coefficient and the Henry constant.

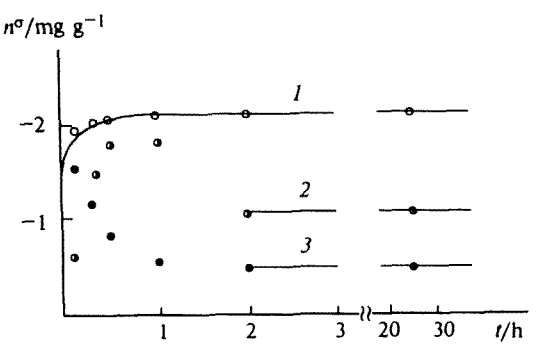

Fig. 3. Kinetics of the adsorption of PS1 polystyrene standards on silochrom S-80G from solutions in toluene: M_w = 450000 (*1*), 97200 (*2*), and 10000 (*3*).

Table 2. The K' and K_H values for the polystyrene standards on hydroxylated silochrom S-80G (the eluent is toluene, 25 °C, V_0 = 5.62 mL, m = 2.7 g, V_s = 1.2 mL g^{-1})

M_w	d	Chromatography			Statics	
	/nm*	V_R /mL	$-K_H$ /mL g^{-1}	$-K'$	$-K_H$ /mL g^{-1}	$-K'$
10000	7	5.2	0.15	0.07	0.14	0.07
97000	27	4.7	0.84	0.42	0.68	0.34
498000	68	2.5	1.15	0.55	1.12	0.56

* The size of the macromolecular coil (d) is calculated according to the Flory—Fox formula.[12]

$$K_H = [(K_p - 1)V_s]/m \quad (9)$$

From expession (9) we obtain the $K_{H,min}$ value for the case of the limiting negative chromatography of polymers ($K_p = 0$).

$$K_{H,min} = -V_s/m \quad (10)$$

On the basis of the results of measuring the excess adsorption of polymers on porous adsorbents, one can calculate coefficients K_p and K'.

$$K_p = (n + V_sC)/(V_sC) = n/(V_sC) + 1 \quad (11)$$

$$K' = K_Hm/V_0 \quad (12)$$

Table 2 presents a comparison of the K_H and K' values estimated from the chromatographic and adsorption experiments. Eqs. (3) and (12) were used, respectively, for calculating K_H and K' from the data on static adsorption. The results give evidence for satisfactory agreement of the K_H and K' values obtained by different methods.

In the case of the negative chromatography of the polystyrene standards on silochrom S-80G during elution with toluene, the sieve effect, *i.e.*, a decrease in accessibility of mesopores as the molecular size increases, should be assumed to be the dominant factor that influences the partition function of the macromolecules in the column.

During elution of the polymers solutions in the regime of liquid sieve chromatography, the chemical state of the surface of sorbents can favor the occurrence of positive adsorption of the macromolecules on the surface of mesopores. In this case, low-molecular fractions of the polymer eluted (M_w < 10000) will evolve from a chromatographic column, when $K' > 1$ ($V_R - V_0 > 0$). The temperature at which the chromatography is performed is another factor that affects the behavior of the macromolecules in the pores of the hydroxylated silica. When the temperature of the chromatographic column is higher, adsorption of both the polymer and the solvent decrease. However, an increase in temperature decreases to a greater extent the adsorption of a solvent capable of specific (donor-acceptor) interaction with the adsorbent. In these cases of the liquid chromatography of polymers, both the sieve and adsorpton mechanisms of the retention of the macromolecules in the column are operating.

* * *

Thus, the main factors leading to negative values of coefficient K' in the liquid chromatography of polymers are stronger interaction of the eluent molecules with the surface of the adsorbent than with the macromolecules (the energetic factor) and steric hindrances to the penetration of macromolecules of solutes into the pores of the adsorbent (the geometric factor).

The coincidence of the values of the Henry constants and partition coefficients calculated from the adsorption and chromatographic experiments indicates that the chromatographic process occurs in a quasi-equilibrium regime.

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