FUNDAMENTAL ASPECTS OF ADSORPTION CHROMATOGRAPHY OF POLYMERS AND THEIR EXPERIMENTAL VERIFICATION BY THIN-LAYER CHROMATOGRAPHY

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SUMMARY

The dependence of changes in the free energy $(-\Delta F/kT)$ accompanying the adsorption of polystyrenes on the energy of interaction of a polymer segment with the surface of a porous adsorbent $(-\varepsilon)$ has been investigated. It is shown that, for macromolecules of any molecular weight (MW), this dependence intersects the $-\varepsilon$ axis at the point $-\varepsilon = -\varepsilon_{cr}$ and, hence, the existence of the critical energy, ε_{cr}, has been verified experimentally. At $-\varepsilon < -\varepsilon_{cr}$, the probability of entry of macromolecules into the adsorbent pores is determined by the molecular-sieve effect, at $-\varepsilon > -\varepsilon_{cr}$ the adsorption effect begins to predominate and at $-\varepsilon = -\varepsilon_{cr}$ these two effects mutually compensate and the separation of macromolecules according to MW (or according to size) does not occur (the distribution coefficient, K_d, is unity for macromolecules of any MW). Since the molecular-sieve and the adsorption effects are interrelated, in the range of the molecular-sieve effect, the entry into the pores of macromolecules of higher MW is favoured by adsorption, whereas in the adsorption range the adsorption of macromolecules within the pores is favoured by the molecular-sieve effect. Over a wide range of energies, a continuous transition occurs from gel-permeation chromatography, in which the components are separated mainly owing to the macromolecular-sieve effect, to adsorption chromatography, in which the separation is due mainly to differences in the adsorption of components of different molecular weight. A linear calibration of K_d is possible as a function of MW, within the limits of a given homologous series, and it is desirable to use this calibration both for gel-permeation and for adsorption chromatography of polymers.

INTRODUCTION

At present, adsorption chromatography, in particular thin-layer adsorption chromatography (TLC), is the principal method for the separation of macromolecules according to their chemical structure[1,2]. However, the theory of the adsorption chromatography of polymers has not yet been developed. Even now, some workers have doubts as to the possibility of polymer fractionation by molecular weight (MW) on the basis of this method[3,4]. The outstanding theoretical problem in adsorption

chromatography is the interdependence of the molecular-sieve effect and the adsorption in the pores. The analysis of the extensive experimental data on the adsorption of macromolecules shows that it is of little use for elucidating the mechanism of the adsorption chromatography of macromolecules since most of the investigations were carried out at medium concentrations and with strong interactions[5] whereas chromatography is carried out at low concentrations of polymers and with weak interactions. There is a similarity between chromatography and the theoretical investigations on the adsorption of polymers, since in the latter the most interesting and fundamental results have been obtained for single macromolecules, *i.e.*, at the very low polymer concentrations used in chromatography.

It seemed desirable to consider the adsorption chromatography of polymers from the standpoint of the modern theory of adsorption of macromolecules[6-10]. We have already examined the similar problem of the TLC of polymers[11].

THEORY

The chromatographic mobility of macromolecules, R_F, is related to the ratio of the times of their existence in the mobile (t_m) and the stationary (t_s) phases; this ratio represents the probability of their existence in the mobile phase

$$R_F = \frac{t_m}{t_m + t_s} = \frac{1}{1 + \frac{V_p}{V_0} \cdot K_d} \tag{1}$$

where

$$K_d = \frac{c'}{c} = \frac{n'/V_p}{n/V_o} \tag{2}$$

Here n and n' are the numbers of moles of the macromolecule in the mobile phase of volume V_o and in the pore space of the adsorbent of volume V_p, respectively, c and c' are the concentrations of macromolecules in these phases, respectively, and K_d is the distribution coefficient.

The ratio of the concentrations of macromolecules in both phases, K_d, is related to the change in the free energy of a macromolecule on passing from the mobile into the stationary phase

$$K_d = \exp\left(-\frac{\Delta F}{kT}\right) = \exp\left(-\frac{\Delta H}{kT} + \frac{\Delta S}{k}\right) \tag{3}$$

where ΔH and ΔS are the changes in the enthalpy and the entropy of the macromolecule, respectively, when it enters a pore. Eqn. 3 is written on the basis of the fact that the change in the free energy of the chromatographic system when 1 mole of the macromolecule is distributed between the solution and the pore volume ($-\Delta \bar{F}$) is equal to the change in the free energy ($-N_A \Delta F$; N_A is the Avogadro number) of macromolecules adsorbed in the pores.

Hence, eqns. 1–3 permit a direct determination of $-\Delta F/kT$ for macromolecules adsorbed in the pores from chromatographic data

$$-\Delta F/kT = \ln[(1 - R_F)/R_F] + \ln(V_o/V_p) \tag{4}$$

DiMarzio and Rubin[9] have calculated that there was a change in the free energy of a macromolecule ($-\Delta F$) when it passes from the free volume to a slit-like pore depending on the energy of interaction of a macromolecular segment with the adsorption surface ($-\varepsilon = \Delta H/N_a kT$) ($N_a$ is the number of adsorbed segments of the macromolecule). It was established that when the energy of interaction ($-\varepsilon$) attains a critical value ($-\varepsilon_{cr}$) the value of $-\Delta F$ is first reduced to zero and then changes its sign (Fig. 1). At the point $-\varepsilon = -\varepsilon_{cr}$, the entropy losses ($T\Delta S$) of the macromolecule completely compensate for the gain in ΔF related to the energy of interaction, ΔH.
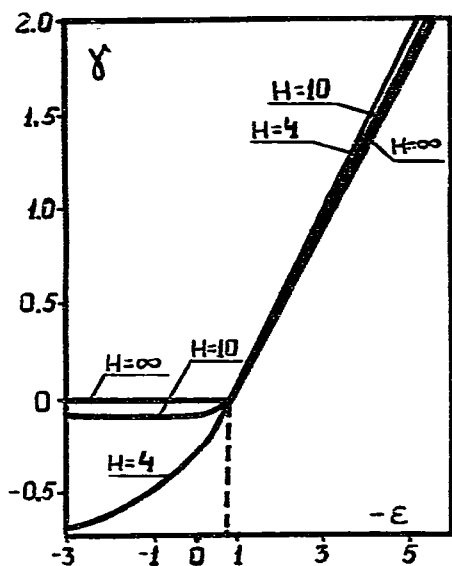

Fig. 1. Changes in the free energy (ΔF) per segment of macromolecule consisting of N segments. $\gamma \equiv \lim\limits_{N\to\infty} (-\Delta F/NkT)$ vs. the energy of interaction ($-\varepsilon$) of the segment with the adsorbent surface when the macromolecule passes from the free volume of the solution into a slit-like pore (according to ref. 9). H = Slit width in units of macromolecular segment length.

Since at $-\varepsilon_{cr}$ the value of ΔF is zero, then, according to eqn. 3, K_d is unity. In other words, when the energy $-\varepsilon$ attains the value $-\varepsilon_{cr}$, macromolecules are not thermodynamically influenced by the pore size of the adsorbent, and are distributed between the mobile phase and the pore space of the adsorbent as if this space consisted of one large cavity of volume V_p not separated into cells (pores). It follows that it is possible to determine the value of $-\varepsilon_{cr}$ by chromatography (when all of the macromolecules, irrespective of their MW, move at the same velocity) and also to determine the ratio V_p/V_o at $-\varepsilon = -\varepsilon_{cr}$ since under these conditions:

$$\frac{V_o}{V_p} = \left(\frac{R_F}{1 - R_F}\right)_{-\varepsilon \,=\, -\varepsilon_{cr}} \tag{5}$$

Fig. 1 shows the dependence of $-\Delta F/kT$ on $-\varepsilon$, calculated according to DiMarzio and Rubin[9]. It is clear that to the left of $-\varepsilon_{cr}$ the entrance of macromolecules into the pores leads to negative changes in the free energy, i.e., $-\Delta F$ decreases

$(K_d < 1)$; to the right of $-\varepsilon_{cr}$ the value of $-\Delta F$ increases $(K_d > 1)$. Moreover, as $-\varepsilon$ approaches $-\varepsilon_{cr}$ from the left, entropy losses $(T\Delta S)$ of macromolecules compensating for ΔH will continuously increase and, hence, the macromolecules of higher MW will be able to enter the pores. Thus, at $-\varepsilon < -\varepsilon_{cr}$, the limit of exclusion of macromolecules from the adsorbent pores will be determined not only by the molecular-sieve effect (by the ratio of the pore size to the size of the macromolecules in solution) but also by the value $(-\varepsilon)$ of the adsorption interaction of a macromolecular segment with the pore surface. In this sense it is possible to refer to the influence of adsorption on the molecular-sieve effect (on the exclusion limit of the polymer). This effect, which we have already reported elsewhere[11], follows directly from the above relation concerning the adsorption of macromolecules. On the other hand, the interdependence of the molecular-sieve effect and the adsorption is often described in the literature as the decrease of adsorption of macromolecules in narrow pores[12,13], whereas it follows from the theory of adsorption of single macromolecules that macromolecules in such pores should exhibit the highest adsorption.

The purpose of the present paper was to investigate experimentally the principal relation concerning polymer adsorption, in particular, to verify the existence of chromatographic systems having the critical energy $(-\varepsilon_{cr})$ and to study the mutual influence of the molecular-sieve effect and the adsorption of macromolecules with energies $-\varepsilon \gtrless -\varepsilon_{cr}$.

EXPERIMENTAL

The TLC of polystyrenes (PS) was carried out on glass plates (6 × 9 cm) coated with a suspension of 0.4 g of silica gel (grain size *ca.* 10 μm) and 10% of gypsum in 2.5 ml of water. The plates were activated at 120° for 30 min. The PS samples were applied in amounts of 2–3 μg (5 mg/ml of carbon tetrachloride) at a distance of 1.5 cm from the plate edge.

Chromatography was carried out in vessels (18.5 × 7.1 cm) containing 56 ml of the solvent. The plates were saturated in the solvent vapour in a chamber for 16 h. This time was sufficient for complete saturation (filling) of the pore volume of the adsorbent with the solvent. After saturation, the plates were placed in the solvent and ascending chromatography was carried out (the solvent ascends for 7 cm). Under these conditions, the dispersion of the R_F values of the polymers did not exceed 5%. After development, the plates were dried at 110° for 10 min, sprayed with a 3.3% solution of potassium permanganate in concentrated sulphuric acid and heated at 180° for 15 min. PS was developed as black spots on a white background. The solvents used were of the "chemically pure" grade. The following silica gels were used: Silochrome S-80 (pore size, $\varphi_p = 500$ Å), KSK ($\varphi_p = 100$ Å) and KSM-5 ($\varphi_p = 30$ Å). Narrow-disperse polystyrene standards ($M_w/M_n < 1.1$) of Waters Assoc. (Milford, Mass., U.S.A.) were used.

RESULTS AND DISCUSSION

Effects of critical energy on the chromatography of macromolecules on porous adsorbents

The effects described in the Theory section can be observed in the TLC of

PS (MW $= 2 \cdot 10^4 - 1.73 \cdot 10^5$) on silica gels in cyclohexane–benzene–acetone (40:16:X) system. The thermodynamics of this chromatographic system as a solvent for PS were investigated viscosimetrically. The measurements showed that, with an acetone content of up to 5%, i.e., in the entire concentration range investigated, this system is a good solvent for PS (its Mark–Kuhn constant, "a", is 0.7) and, hence, the size of the macromolecules of this polymer does not vary when X is increased from 0 to 5%. The results of experiments on KSK silica gel are shown in Fig. 2. It is clear that when the acetone content and, hence, the adsorption energy ($-\varepsilon$) of the polymer segment increase, macromolecules of greater MW can enter the pores (their R_F values approach those of PS having MW $= 2 \cdot 10^4$).

At $X = 1.8$ all of the PS samples move at the same level irrespective of their MW. This is the range of critical energies, $-\varepsilon = -\varepsilon_{cr}$. When the acetone content is lower than $X = 1.8$, the molecular-sieve chromatography changes into adsorption
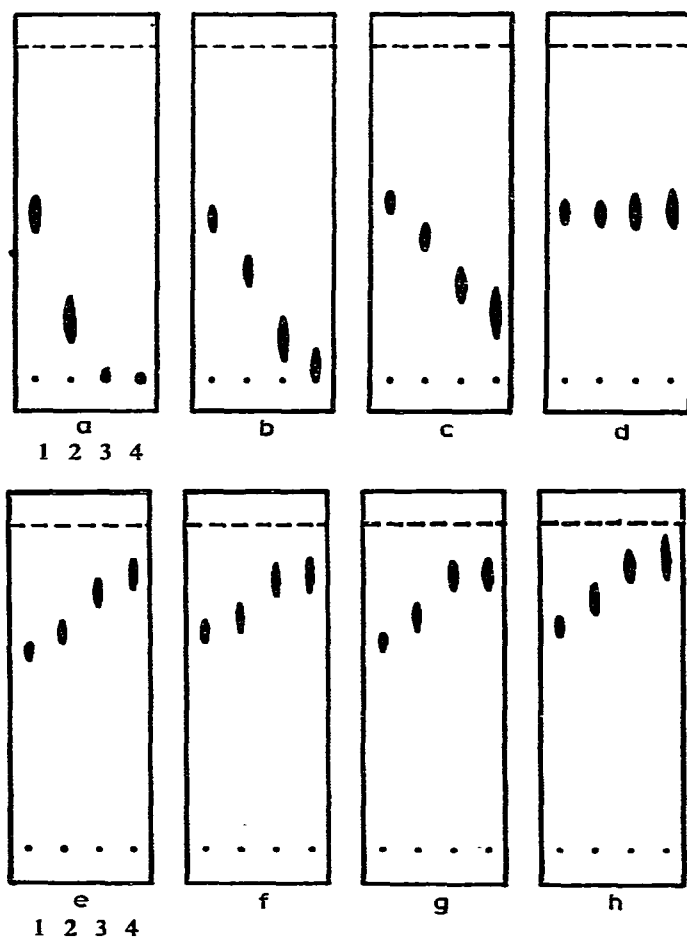

Fig. 2. TLC of narrow-disperse PS ($M_w/M_n < 1.1$) on KSK silica gel in cyclohexane–benzene–acetone (40:16:X) with preliminary saturation of the plate in solvent vapour for 16 h. $X =$ (a) 1.2, (b) 1.4, (c) 1.6, (d) 1.8, (e) 2.0, (f) 2.2, (g) 2.4 and (h) 3.0. M_w of samples of PS: (1) $19.85 \cdot 10^3$; (2) $51 \cdot 10^3$; (3) $111 \cdot 10^3$; (4) $173 \cdot 10^3$.

chromatography in which polymers of lower MW exhibit the highest R_F values. The values of $-\Delta F/kT$ were calculated according to eqn. 4.

The V_o/V_p ratio can be determined from the R_F values for PS at $-\varepsilon = -\varepsilon_{cr}$, when $-\Delta F/kT = 0$, *i.e.*, in the system cyclohexane–benzene–acetone (40:16:1.8) according to eqn. 5. The validity of the determination of V_p/V_o was confirmed by the agreement obtained with values of this ratio determined from the R_F values for low-molecular-weight PS (MW = 600) (Fig. 5). For our experiment on silica gels KSK and S-80, $\ln(V_p/V_o) = -0.447$. The energy of interaction $(-\varepsilon)$ of the segment with the surface of the adsorbent can be determined in kT units as the value of $-\varepsilon \approx \varepsilon_{pa} - \varepsilon_{sa}$, where the subscripts pa and sa indicate polymer–adsorbent and solvent–adsorbent contacts. The value of ε_{sa} can be obtained[14] per elementary surface area of 8.5 Å^2 for a ternary mixture of solvents from

$$\varepsilon_{sa} = \varepsilon_{ga} + \frac{\log (N_h 10^{an_h (\varepsilon_h - \varepsilon_g)} + N_g)}{an_h} \qquad (6)$$

which is valid at $\varepsilon_h > \varepsilon_g \gg \varepsilon^\circ$ (the third component) and at $N_h + N_g > 0.1$. Here N is the mole fraction and n is the molecular area (in 8.5 Å^2 units); for acetone (component h), $\varepsilon_h = 0.40$, $n_h = 4.2$; for benzene (component g), $\varepsilon_g = 0.25$, $n_g = 6$. From eqn. 6, we obtain the following values of ε_{sa} for different values of X:

X	1.2	1.4	1.6	1.8	2.0	2.2	2.4	3.0
ε_{sa}	0.169	0.172	0.175	0.178	0.181	0.184	0.187	0.196

Since the conformation of the adsorbed polymer is unknown, the value of ε_{pa} cannot be calculated. Consequently, the value of $-\varepsilon$ is taken as equal to $-\varepsilon_{sa}$ taking into account the fact that the lower is ε_{sa} the higher is $-\varepsilon$, the energy of interaction of a macromolecular segment with the adsorption surface. Fig. 3 shows that the dependence of $-\Delta F/kT$ on $-\varepsilon$ obtained from the TLC of polymers on KSK silica gel (Fig. 2) and Silochrome S-80 agrees with the theoretical dependence in Fig. 1. Fig. 3 also shows that the dependences for polymers of all MW, irrespective of the size of pores of the silica gel, intersect the abscissa at one point, *i.e.*, at $-\varepsilon = -\varepsilon_{cr} = 0.178\ kT$ units.

It is clear that the higher the MW of the polymer the greater are the changes in $-\Delta F/kT$ *vs.* $-\varepsilon$ near ε_{cr}. It is interesting that, in the case of TLC, adsorption effects can be observed only at energies of adsorption similar to $-\varepsilon_{cr}$ since further increases in $-\varepsilon$ lead to sharply increasing adsorption of the macromolecules and the R_F value tends to zero.

Fig. 3 shows that the dependence of $-\Delta F/kT$ (and, hence, of the chromatographic distribution coefficient, K_d) on energy $(-\varepsilon)$ is linear in the range of $-\varepsilon > -\varepsilon_{cr}$. The dependence of $-\Delta F/kT$ on the number of monomer units in the macromolecule, N(MW), is also linear, as can be seen from the experimental dependence on KSK and S-80 silica gels shown in Fig. 4 (see also ref. 1).

Thus, it was possible to verify that the critical energy determines the type of chromatographic behaviour shown by the macromolecules, *i.e.*, the molecular-sieve or the adsorption behaviour.
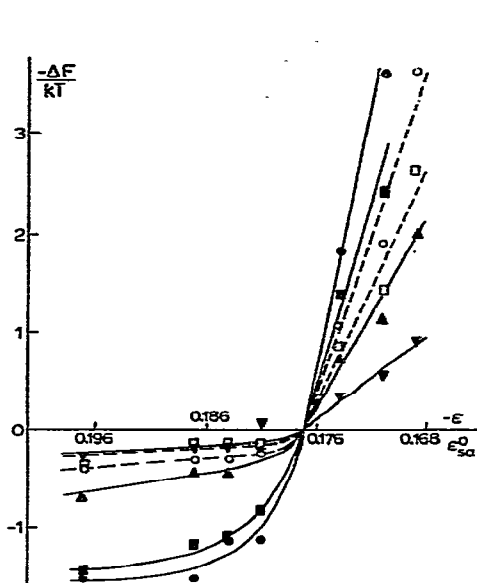
Fig. 3. Experimental dependence of $-\Delta F/kT$ on ε_{sa} ($-\varepsilon$), determined by TLC on KSK silica gel (see Fig. 2) (solid lines, filled symbols) and Silochrome S-80 (broken lines, open symbols); M_w of PS samples: ($\bullet$, $\bigcirc$) $173 \cdot 10^3$; ($\blacksquare$, $\square$) $111 \cdot 10^3$; ($\blacktriangle$) $51 \cdot 10^3$; ($\blacktriangledown$) $19.85 \cdot 10^3$.
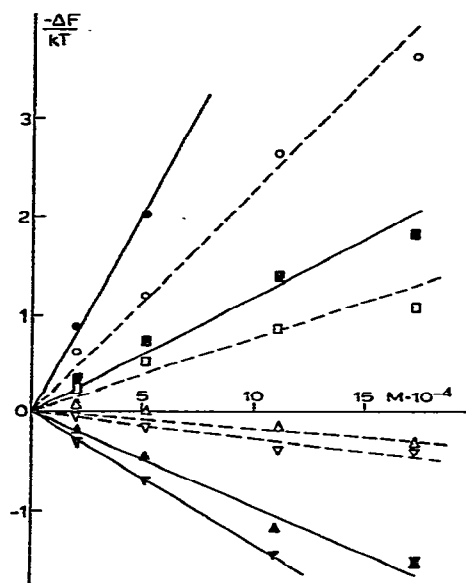
Fig. 4. Experimental dependence of $-\Delta F/kT$ on the molecular mass (M) of PS at different energies of interaction ε_{sa} determined by TLC on KSK silica gel (solid lines, filled symbols) and Silochrom S-80 (broken lines, open symbols). ε_{sa} = ($\bullet$, $\bigcirc$) 0.169, ($\blacksquare$, $\square$) 0.175, ($\blacktriangle$, $\triangle$) 0.187 and ($\blacktriangledown$, $\triangledown$) 0.196.

Interdependence of the molecular-sieve and adsorption effects in the chromatography of polymers

Fig. 3 shows that the probabiiity, $\exp(-\Delta F/kT)$, of the entry of macromolecules into the pores of the adsorbent increases with the energy of interaction ($-\varepsilon$). When $-\varepsilon$ increases, macromolecules of higher MW begin to enter the pores, and as the value of $-\varepsilon$ approaches $-\varepsilon_{cr}$ the separation of macromolecules based on the molecular-sieve effect becomes less pronounced and at $-\varepsilon = -\varepsilon_{cr}$ it disappears completely. Thus the influence of the interaction of macromolecules with the inner surface of the adsorbent (*i.e.*, the adsorption effect) on the molecular-sieve effect can be observed.

In order to determine the influence of the molecular-sieve effect on polymer adsorption, the TLC of PS was carried out on silica gels of different porosities: KSM-5 ($\varphi_p = 30$ Å), KSK ($\varphi_p = 100$ Å) and Silochrom S-80 ($\varphi_p = 500$ Å). First, it is necessary to ensure that the chemical structures of the surfaces of the gels are identical. The silica gels were treated with an aqueous HCl solution (1:1) followed by washing until free from chloride ions. As shown previously[15], when silica gel is treated with hydrochloric acid solutions, Lewis adsorption centres bonded to coordinatively unsaturated aluminium are destroyed (the amount of the centres is proportional to the percentage of aluminium in the silica gel). Only silanol hydroxyl groups remain; their surface concentration is approximately five groups per 100 Å² and does not depend on the size of the silica gel pores[16]. Thus, silica gels treated with hydrochloric

acid and exhibiting pores of different sizes are adsorbents with energetically equivalent surfaces. It should be noted that this conclusion concerning the energetic equivalence of silica gels of different porosity in PS adsorption can also be made for untreated silica gels, since, in our chromatographic system, untreated silica gel (Na^+) and silica gel (H^+) (after HCl treatment) exhibit the same adsorption activity (R_F) for PS of the same MW.

The composition of the system was selected so that the adsorption interaction of the PS segments with the silica gel surface corresponds to the critical energy ($X = 1.8$) and to greater energies ($X = 1.4$).

The chromatograms are shown in Fig. 5. It is clear that the value of the critical energy ($X = 1.8$) (when K_d of PS is unity irrespective of its MW) is almost the same for the macroporous silica gel S-80 and for silica gel KSK having large pores. Under these conditions the molecular-sieve effect is observed on microporous KSM silica gel. This suggests that $(-\varepsilon_{cr})_{KSM} > (-\varepsilon_{cr})_{KSK} \approx (-\varepsilon_{cr})_{S-80}$.
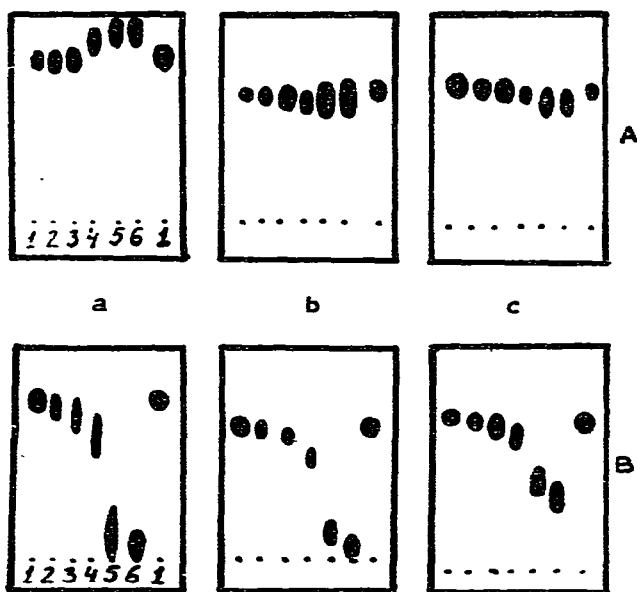

Fig. 5. Effect of pore size of the silica gels (H^+) [(a) KSM-5 ($\varphi_p = 30$ Å); (b) KSK ($\varphi_p = 100$ Å); (c) S-80 ($\varphi_p = 500$ Å)] on the R_F value of PS samples [$M_w = $ (1) 600, (2) $2 \cdot 10^3$, (3) $5 \cdot 10^3$, (4) $19.85 \cdot 10^3$, (5) $111 \cdot 10^3$ and (6) $173 \cdot 10^3$] in TLC with cyclohexane–benzene–acetone (40:16:1.8) (A) and (40:16:1.4) (B).

This behaviour cannot be interpreted by the DiMarzio–Rubin theory[9]: it is probably related to the excluded volume of the macromolecules, the effect of which is observed on microporous silica gel.

When the energy of interaction is sufficiently high, PS macromolecules penetrate the pores of the KSM silica gel and the result predicted by the theory[9] is observed; the smaller the pore size of the adsorbent, $\varphi_p(KSM) < \varphi_p(KSK) < \varphi_p(S-80)$, the greater is the adsorption of macromolecules and the greater is the decrease in the

free energy $(-\Delta F/kT)$. This effect increases with increasing MW of the polymer, but is not in accord with previous observations[17].

A comparison of the theory with the experimental data is based on two parameters: the number of statistical segments and, hence, their length for polymers of a certain MW, and the energy of interaction (ε). Since for flexible-chain polymers represented by Gaussian chains the length of the statistical Kuhn segment is approximately constant and the energy is determined by the chromatographic conditions, it may be concluded that the experiments made for PS completely confirm the suitability of this theory for describing the adsorption of all flexible-chain polymers on porous adsorbents. Hence, the theoretical and experimental relations reported here are fundamental to the adsorption chromatography of this class of polymers.

Sensitivity of the R_F value to the molecular weight and the chemical composition of the polymer

The sensitivity of the R_F value in the TLC of polymers can be investigated by analyzing the expression for R_F obtained from eqn. 4

$$R_F = \frac{1}{1 + \dfrac{V_p}{V_g} \cdot K_d} = \frac{1}{1 + \dfrac{V_p}{V_0} \cdot \exp(-\lambda N)} \tag{7}$$

where $-\lambda$ is the change in the free energy of a segment of the macromolecule per kT unit and N is the number of segments. Near the critical energy, to a first approximation, this change is proportional to the difference between $-\varepsilon$ and $-\varepsilon_{cr}$, i.e., $-\lambda = -\gamma(\varepsilon - \varepsilon_{cr})$, where γ is a proportionality coefficient.

If eqn. 7 is differentiated with respect to N and λ, it can be seen that the sensitivity, $\partial R_F/\partial N$, of the R_F value to the MW of the polymers decreases with increasing N, whereas $\partial R_F/\partial N$ as a function of λ (the value proportional to the interaction energy) has an extremum near $-\varepsilon_{cr}$, both in the range of the adsorption chromatography $(-\lambda > 0)$ and in the range of the molecular-sieve chromatography $(-\lambda < 0)$, and becomes zero at ε_{cr}. Moreover, for each MW an extremum of λ exists (according to the eluent composition). These theoretical relations correspond to experimental TLC data for PS which show that, in order to obtain an effective separation of polymers according to MW, it is necessary to select an eluent of a specific composition for each range of MW (Fig. 6). If the composition of the solvent is not changed, then λ is determined by the polymer composition. In this case the dependence of the R_F value on λ is a monotonically decreasing function. The dependence of $\partial R_F/\partial \lambda$ on N, passes through a maximum, the position of which is related to the value of λ. It can be concluded from the experimental data that the sensitivity of the R_F value to the copolymer composition is retained at least up to a MW of *ca.* $5 \cdot 10^5$ (ref. 3).

CONCLUSIONS

The relations investigated provide a basis for interpretation of the mechanism of the adsorption chromatography of polymers, and describe the peculiarities of both the adsorption chromatography and those of the molecular-sieve chromatography.
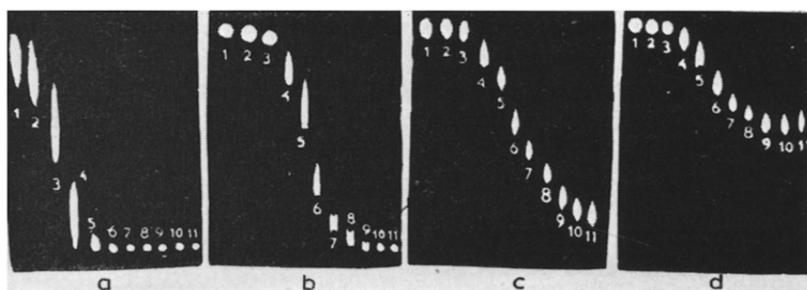
Fig. 6. TLC of narrow-disperse PS ($M_w/M_n < 1.1$) in cyclohexane–benzene–acetone systems: (a) 13:3:1.1; (b) 12:4:0.4; (c) 12:4:0.7; (d) 12:4:1. MW of PS samples: (1) 900; (2) $2 \cdot 10^3$; (3) $5 \cdot 10^3$; (4) $10.3 \cdot 10^3$; (5) $19.85 \cdot 10^3$; (6) $51 \cdot 10^3$; (7) $98.2 \cdot 10^3$; (8) $173 \cdot 10^3$; (9) $411 \cdot 10^3$; (10) $867 \cdot 10^3$; (11) $2.145 \cdot 10^3$.

This suggests that these types of chromatography are related to the positive and negative adsorption of polymers on porous adsorbents by a single mechanism. In particular, the relations permit effective fractionation of polymers according to MW by using adsorption chromatography (positive adsorption). It should be noted, however, that some workers[3,4] have expressed doubts concerning the possibility of polymer fractionation according to MW by using adsorption TLC. It seems to us that these doubts are due to the difficulties of selecting a solvent in which the change in $\exp(-\varDelta F/kT)$ with increasing MW of the polymer within the range of MW necessary for analysis would range from 0 to 3 (*e.g.*, for PS of MW $= 10^4$–$4 \cdot 10^5$, as shown in Fig. 6c). In many cases it may be impossible to find a solvent that would give the required value of ε_{sa}. This problem can be solved if a binary or a ternary solvent mixture is used. In such a mixture it is not difficult to select a solvent composition which would give the value of ε_{sa} necessary for the required range of MW. The best components for such a mixture will be those for which the R_F value of polymers of all MW is zero in one solvent and unity in the other solvent. Nevertheless, similar values of dielectric permittivity of these solvents (as a criterion for their selection for the separation of polymers according to MW[4]) are of no importance.

It is noteworthy that the adsorption chromatography of polymers is also complicated by slow adsorption–desorption kinetics. Fig. 7 shows chromatograms of PS in a cyclohexane–benzene system where, for MW exceeding 10^5, the chromatographic process does not occur owing to slow adsorption–desorption kinetics. A part of the polymer remains at the start and another part migrates with the solvent front.
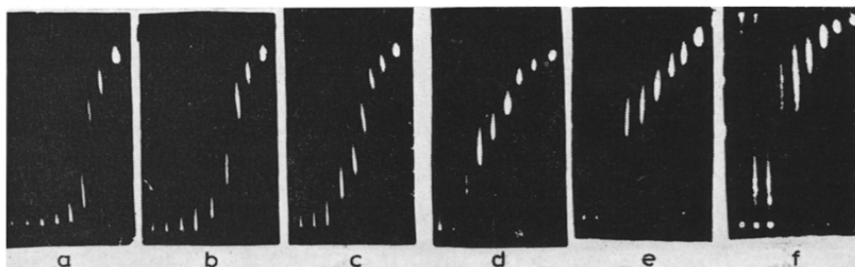

Fig. 7. TLC of PS samples 3–11 (Fig. 6) (from right to left) on KSK silica gel in benzene–cyclohexane systems; (a) 15•7; (b) 15:6.5; (c) 15:6; (d) 15:5.5; (e) 15:5.3; (f) 15:5.

This situation is changed if adsorption-active acetone ($\varepsilon^\circ = 0.40$) is added to the system, and if the plate is initially saturated with the eluent vapour (Fig. 6). It is easy to show that in this case the adsorption–desorption kinetics do not affect the R_F value: polymer samples are spotted along the diagonal of the plate. The intersection of the line joining the chromatographic spots of the polymer, the line joining the starting spots of the polymer and the line of the solvent front at one point (Fig. 8) shows that, under our experimental conditions, exclusively elution chromatography (in our case adsorption chromatography) takes place (Fig. 6). This would not occur if the desorption time were comparable to the development time.
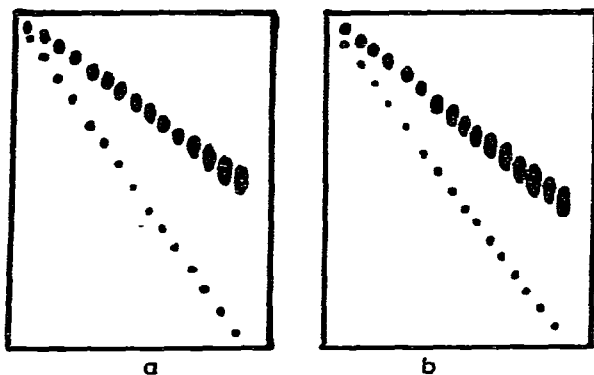

Fig. 8. TLC of PS samples of MW $19.85 \cdot 10^3$ (a) and $51 \cdot 10^3$ (b) in the cyclohexane–benzene–acetone (40:16:1.6) with preliminary saturation for 2 h. The samples were spotted along the diagonal of the plate.

The question arises as to whether the relations described actually correspond to polymer adsorption inside the pores. The GPC of PS on these sorbents (Figs. 2 and 5) indicates that macromolecules enter the pores of the adsorbent. Macromolecules can also partially enter the pores and be partially adsorbed on the adsorbent surface. The linear dependence of $-\Delta F/kT$ on N in the investigated MW range of PS shows that all of the PS segments are adsorbed under identical conditions, i.e., inside the pores. Moreover, the particle size, i.e., the area of the external surface of the adsorbent, does not affect the dependences in Figs. 2 and 3, which also supports this suggestion.

The most effective chromatographic separation of polymers according to the adsorption mechanism can be carried out in the range $-\varepsilon_M > -\varepsilon > \varepsilon_{cr}$, where $-\varepsilon_M$ is the energy of interaction at which K_d attains a value of ca. 2–3. At $-\varepsilon < -\varepsilon_M$, chromatography does not proceed owing to the strong adsorption capacity of the macromolecules. When $-\varepsilon \approx -\varepsilon_{cr}$, chromatography is not effective, and when $-\varepsilon < -\varepsilon_{cr}$ its effectiveness increases again with decreasing $-\varepsilon$. Since the dependence of $\ln K_d$ on the MW of the polymer is linear (Fig. 4) over the entire range of ε, it follows that $K_d = \exp(-\lambda N)$. We suggest that this dependence may be used to calibrate all chromatographic systems.

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