

## An Experimental Study of Adsorption of Polymers on Activated Carbon: Butadiene-Styrene Polymers and Poly(methyl Methacrylate)

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### Synopsis

An experimental study of the extents and rates of adsorption of several polymers from various solvents onto activated carbon has been carried out. The polymers studied included polystyrene, polybutadiene, butadiene-styrene copolymers and poly(methyl methacrylate). The solvents included toluene, cumene, decalin, 2-pentanone, and methyl ethyl ketone (MEK). Polystyrene is adsorbed from the different solvents in the order MEK, 2-pentanone, cumene, toluene, decalin. The adsorption from toluene, decalin, and cumene is in the order polystyrene, polybutadiene butadiene-styrene copolymer. The fact that the copolymer is adsorbed less than either homopolymer is striking. The variation of molecular weight distribution with extent of adsorption has been studied. It was found that low molecular weight polymer was preferentially adsorbed in the early stages of the experiment, but high molecular weight polymer was adsorbed at longer times. The apparent adsorption rate constants have been evaluated for the various systems and resolved into external mass transfer, internal (intraparticle) mass transfer, and adsorption rate constants. The experimental data have been applied to the prediction of the elution of the polymers from chromatographic columns packed with activated carbon.

### INTRODUCTION

We have undertaken an experimental study of the adsorption of polymers in our laboratories as a result of two distinct research interests, the chromatographic separation of mixtures of macromolecules and the reinforcement of elastomers by carbonaceous materials, which are essentially the same as the programs which have led to the development of this area. It was the chromatographic studies of Mark and Saito<sup>1</sup> on cellulose acetate in columns packed with blood charcoal which induced Baum, Broda, and Mark<sup>2,3</sup> to investigate this phenomenon in the mid-1930's. The second generation of investigators of polymer adsorption, whose work would seem to date from the Rubber Reserve Program of the 1940's, were concerned with the interaction of synthetic rubber with carbon black.<sup>4-7</sup> Later researchers studied this phenomenon from a scientific as opposed to an applications point of view. Various authors, beginning with Simha, Frisch, and Eirich,<sup>8</sup> have developed molecular theories of adsorption based upon the

configurational characteristics of macromolecules in the neighborhood of interfaces.<sup>9-11</sup> Few authors have given serious attention to adsorption rates of macromolecules as distinguished from equilibrium. Only the work of Hobden and Jellinek<sup>12</sup> seems worth noting. Recent experimental studies by various researchers, notably by Howard and his colleagues,<sup>13,14</sup> focus on two aspects of adsorption: (1) the effect of adsorbent structure, notably porosity and pore size distribution, and (2) the chemical and microstructural specificity of adsorption.

Our purpose here is to study the adsorption of a series of polymers of varying chemical composition and polarity, including the butadiene-styrene system, onto activated carbon from a variety of solvents. We specifically wish to investigate (1) how the extent of adsorption varies with the nature of the polymer and solvent, (2) the magnitudes of the rates of adsorption and how these magnitudes are related to the various mechanisms in the process, and (3) how the molecular weight distributions of the polymer in solution varies during the adsorption process or rather which molecular weight fractions are adsorbed. It was decided to use gel permeation chromatography<sup>15,16</sup> in carrying out the third aspect of this study. While the experimental results are of interest to us along the two lines suggested at the beginning of the paper, we will be primarily concerned with their interpretation as adsorption per se and their possible application to chromatographic separations. This paper represents a continuation of our studies of the characteristics of polymer solutions and their application to chromatography.<sup>17-21</sup> It is believed, however, that in choosing a number of polymers in the butadiene-styrene system for our study, the results will have some interest to rubber technologists.

## EXPERIMENTAL

### Materials

Four commercial polymers and five different solvents were used in this study. The polymers were polystyrene (Dow Styron 678), polybutadiene (Firestone Diene 35 NF), a 48% styrene-butadiene copolymer (Phillips Solprene 303), a 25% styrene-butadiene copolymer (Phillips Solprene 301), and a poly(methyl methacrylate) (du Pont Lucite 147). The number-average molecular weights of these samples were determined with a Hallikainen automatic recording osmometer, and the ratios of the weight-average to number-average molecular weights were determined with the gel permeation chromatograph. The experimental GPC curves can be readily converted to molecular weight distributions by presuming that the log molecular weight-elution volume curves are parallel to the near-linear line of the polystyrene standards and applying the value of the number-average molecular weight to obtain the factor separating the curves. Compare our earlier paper on this subject for butadiene-styrene polymers.<sup>21</sup> The results are summarized in Table I. The solvents used were methyl ethyl

TABLE I  
Molecular Weights of Polymers

Polymer	Commercial name	Supplier	$M_n$ (osmometer)	$M_w/M_n$ (GPC)
Polystyrene	Styron 678	Dow	78,000	3.1
Polybutadiene	Diene 35 NF	Firestone	93,000	2.8
25% Styrene-butadiene	Solprene 301	Phillips	122,000	1.85
48% Styrene-butadiene	Solprene 303	Phillips	102,000	1.45
Poly(methyl methacrylate)	Lucite 147	du Pont	88,000	2.8

ketone (Fischer certified), toluene (Fischer certified), decalin (Eastman high purity), 2-pentanone (Eastman high purity), and cumene (Eastman high purity). Pittsburgh activated carbon type CPG was the activated carbon used; it is an acid-washed granular carbon produced from bituminous coal, with a density of 0.48 g/cm<sup>3</sup> and a BET surface area of 1000–1100 m<sup>2</sup>/g and a mean particle diameter of 0.08–0.10 cm. The carbon is porous, with about 45% of the pore volume being associated with pores less than 50 Å in diameter and about 15% being between 50 and 500 Å.

### Procedure

Polymer solutions of concentrations 0.2, 0.5, 1.0, and 1.5 wt-% were made up. About 20-g portions of each solution of a known concentration were placed in a wide-neck bottle with 3- to 5-g portions of activated carbon and shaken at different severity levels in a Burrell wrist action shaker. After the shaking process, the solutions were centrifuged to precipitate the activated carbon. About 10 g of the supernatant liquid from each sample was piped into a weighing bottle and placed in oven until dried. A vacuum system, operated by a Duo-Seal vacuum pump, which has 10<sup>-4</sup> mm Hg pressure was then applied at 60°C (120°C for the polystyrene) to remove the remainder of the solvent. The bottles were weighed and the polymer residue determined by difference. Gel permeation-chromatographic experiments were carried out on several of the polymer residues. Molecular weights of the residues were determined using calibration curves based upon presuming the calibration outlined.

### RESULTS

Figures 1 through 6 show the rates of adsorption of polystyrene, polybutadiene, the 48% styrene-butadiene copolymer, and the poly(methyl methacrylate) at various concentrations in the series of solvents considered. These results were based upon samples shaken at 5.5° amplitude. The slow approach to equilibrium is to be noted. The extents of adsorption may be seen to increase with concentration but vary significantly from polymer to polymer and in solvent to solvent. Some regularity is to be noted. In the solvents toluene, cumene, and decalin, the extent of adsorp-

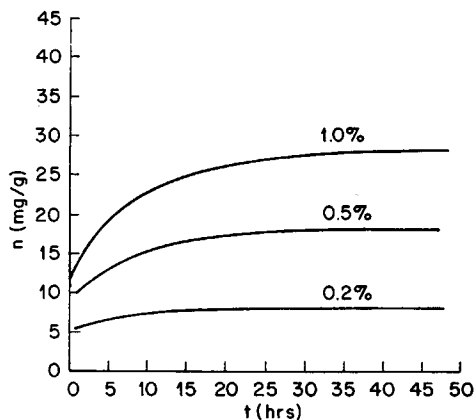


Fig. 1. Adsorption of polystyrene from methyl ethyl ketone solution of varying concentration.

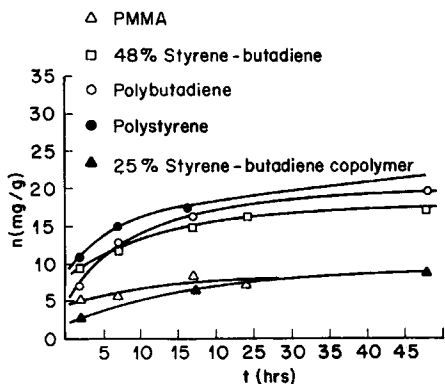


Fig. 2. Adsorption-time curves for various polymers including polybutadiene, polystyrene, and their copolymers from toluene onto activated carbon.

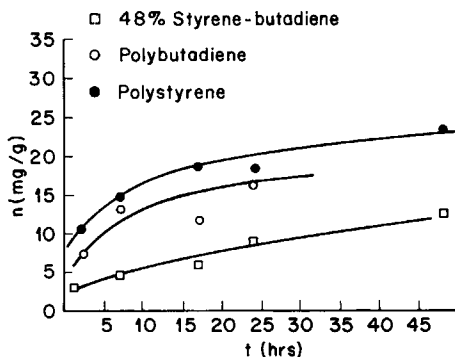


Fig. 3. Adsorption-time curves for polybutadiene, polystyrene, and a 48% styrene copolymer from decalin onto activated carbon.

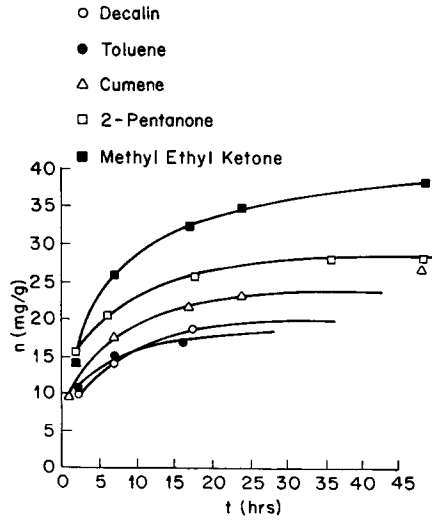


Fig. 4. Adsorption-time curves for polystyrene from various solvents (1.0% solutions) onto activated carbon.

tion is always in the order polystyrene, polybutadiene, butadiene-styrene copolymers. For the methyl ethyl ketone, in which only the polystyrene and the poly(methyl methacrylate) dissolve, the polystyrene is adsorbed to a greater extent.

The rates of adsorption were interpreted in terms of rate constants  $k_t$  defined by

$$\frac{dn}{dt} = k_t(c - c^*) \tag{1}$$

where  $n$  is the amount of polymer adsorbed per unit mass of adsorbent and  $c$  is the concentration in grams per unit volume;  $c^*$  is the concentration

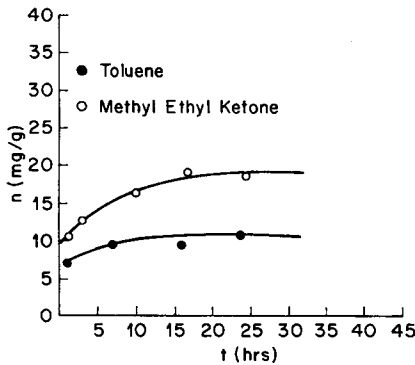


Fig. 5. Adsorption-time curves for poly(methyl methacrylate) from 1% toluene and methyl ethyl ketone solutions.

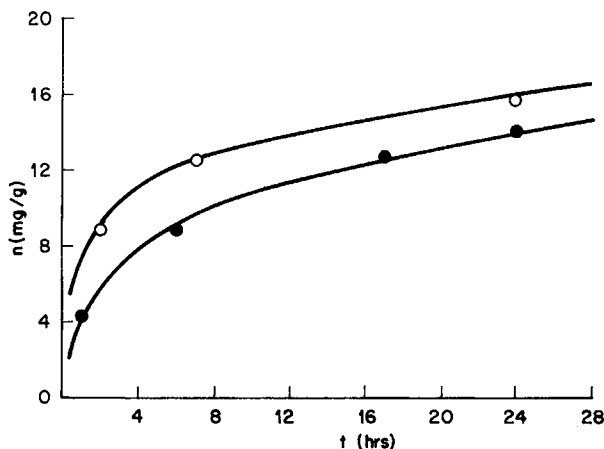


Fig. 6. Effect of shaking on the adsorption of polystyrene from a toluene solution: (○) shaken solution; (●) stagnant solution.

which would be in equilibrium with  $n$ . The  $k_t$  value was determined by two techniques, first by determining the limit

$$\lim_{t \rightarrow 0} \frac{1}{c} \left( \frac{dn}{dt} \right) = k_t. \quad (2)$$

As the  $n$ -versus- $t$  curves are steep at small times, a second method was used, based upon presuming a linear isotherm and taking  $c^*$  to be  $n/K$ , where  $K$  is an equilibrium constant. The linear isotherm was then substituted into eq. (1) and the resulting expression differentiated to yield

$$\frac{d^2n}{dt^2} = k_t \left[ \frac{dc}{dt} - \frac{1}{K} \frac{dn}{dt} \right]. \quad (3)$$

The variation in solution concentration with time is tied by conservation of mass to the rate of increase of adsorbed material. In particular,  $dc/dt$  is simply  $m \, dn/dt$ , where  $m$  is the mass of adsorbent per unit volume of solution. Substitution of this expression into eq. (3) leads to a second-order ordinary differential equation

$$\frac{d^2n}{dt^2} + k_t \left[ m + \frac{1}{K} \right] \frac{dn}{dt} = 0 \quad (4)$$

which may be solved to yield

$$\ln \left[ \frac{n(\infty) - n(t)}{n(\infty)} \right] = -k_t \left( m + \frac{1}{K} \right) t. \quad (5)$$

From plotting the left-hand side of this expression versus time, a straight line is obtained with a negative slope of  $k_t(m + 1/K)$ . To evaluate the term  $(m + 1/K)$ , we note that

$$n(\infty) = Kc(\infty) = \frac{c(0) - c(\infty)}{m} \quad (6a)$$

or

$$\frac{c(0)}{c(\infty)} = 1 + Km. \tag{6b}$$

It follows that we may write

$$k_t \left( m + \frac{1}{K} \right) = k_t \left( \frac{1 + Km}{K} \right) = k_t \left[ \frac{c(0)}{c(\infty)} \cdot \frac{c(\infty)}{n(\infty)} \right] = k_t \frac{c(0)}{n(\infty)}. \tag{7}$$

Table II summarizes values of the rate constant  $k_t$  determined from the two procedures. The values obtained using eqs. (5) and (7), where  $n(\infty)$  is taken to be  $n(48 \text{ hr})$  are generally two to three times larger than those obtained from the slopes. However, while there are major differences (we will discuss these in the next section), certain trends in the data among the various systems studied are clear. For example  $k_t$  decreases with increasing solution concentration and increases with intensity of shaking. This is shown in Figures 6 and 7.

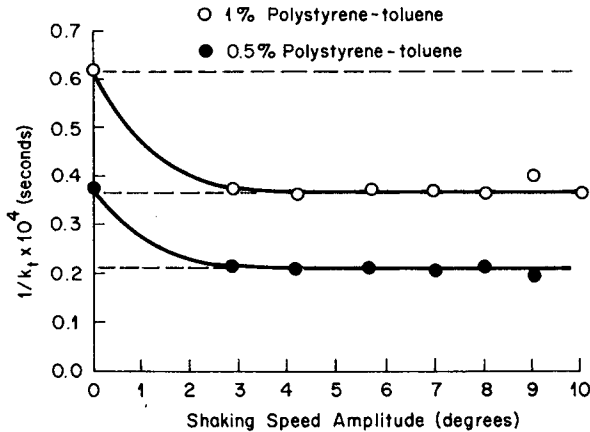


Fig. 7. Effect on shaking on  $k_t$  rate coefficient.

The variation of molecular weight distribution of the polystyrene and poly(methyl methacrylate) in methyl ethyl ketone and toluene, and of polystyrene in cumene with extent of adsorption was followed. The variations of the polybutadiene and butadiene-styrene copolymer in toluene were also measured. These results are summarized in Table III where the change in number-average molecular weight with time are indicated. With the exception of cumene, the data indicate that low molecular weight polymer is preferentially adsorbed at short times, but as the time increases, high molecular weight polymer starts to be adsorbed and is apparently adsorbed preferentially for very long times and perhaps at equilibrium. In cumene, high molecular weight polymer seems to be adsorbed even at short times (compare Kolthoff and Kahn<sup>4</sup>).

TABLE II. Adsorption Rate Constant  $k_t$ <sup>a</sup>

Polymers	Initial solution concentration, wt-%	Method 1 eq. (2)	Method 2 eq. (7) $n(\infty) = n(48 \text{ hr})$
Toluene			
Polystyrene	1.5	1.38	5.3
	1.0	2.70	5.38
	0.5	3.10	8.54
Polybutadiene	1.5	0.73	2.0
	1.0	1.07	2.77
	0.5	2.08	5.16
48% Styrene-butadiene copolymer	1.5	0.90	2.74
	1.0	1.42	4.12
	0.5	2.53	6.24
Poly(methyl methacrylate)	1.5	0.83	3.88
	1.0	1.46	4.78
	0.5	3.05	9.08
MEK			
Polystyrene	1	4.44	11.4
	0.5	7.08	17.6
	0.2	11.4	32.6
Poly(methyl methacrylate)	1.0	4.22	11.8
	0.5	7.10	17.0
	0.2	12.5	34.4
Decalin			
Polystyrene	1.5	1.35	3.76
	1.0	1.63	4.30
	0.5	2.20	5.57
Polybutadiene	1.5	0.43	1.06
	1.0	0.13	3.15
	0.5	1.17	2.84
48% Styrene-butadiene copolymer	1.0	0.86	2.16
	0.75	1.43	4.11
	0.50	0.63	1.66
2-Pentanone			
Polystyrene	1.0	4.66	12.20
	0.75	5.60	14.30
	0.5	7.02	16.24
48% Styrene-butadiene copolymer	1.0	4.5	10.95
	0.75	6.1	14.5
	0.5	7.7	18.6
Cumene			
Polystyrene	1.0	2.96	7.29
	0.75	3.65	8.88
	0.5	4.30	10.25
Polybutadiene	1.0	2.89	7.27
	0.75	3.27	8.19
	0.50	3.60	8.87
48% Styrene-butadiene copolymer	1.0	1.24	2.46
	0.75	1.55	3.72
	0.50	2.27	5.26

<sup>a</sup>  $k_t \times 10^4 \text{ sec}^{-1}$ .



TABLE III  
*M<sub>n</sub>* of Polymers Absorbed from Various Solvents as a Function of Extent of Adsorption

Polymer	Before adsorption	1-2 Hours of adsorption	4-6 Hours of adsorption	7-9 Hours of adsorption	16-17 Hours of adsorption	24 Hours and over of adsorption
Polystyrene						
toluene	78,000	84,500	93,000	76,800	—	46,200
MEK	78,000	87,500	—	98,600	—	129,000
cumene	78,000	48,000	—	40,000	37,000	55,000
Poly(methyl methacrylate)						
toluene	88,000	114,000	116,500	104,500	78,500	85,000
MEK	88,000	99,500	—	125,000	—	100,000
Polybutadiene						
toluene	130,000	140,000	—	161,300	174,000	174,000
48% Styrene-butadiene toluene	114,000	189,500	—	196,000	155,000	163,000

An attempt has been made to estimate the equilibrium extents of adsorption at the different solution concentrations. Isotherms have been constructed and are shown in Figures 8, 9, and 10 for the various solvents.

## DISCUSSION

### Adsorption Equilibrium

Several aspects of the experiments are of considerable interest. First, the relative extents of adsorption are intriguing. In the butadiene-styrene system, generally the polystyrene was adsorbed more than the polybutadiene which was in turn adsorbed more than either of the copolymers.

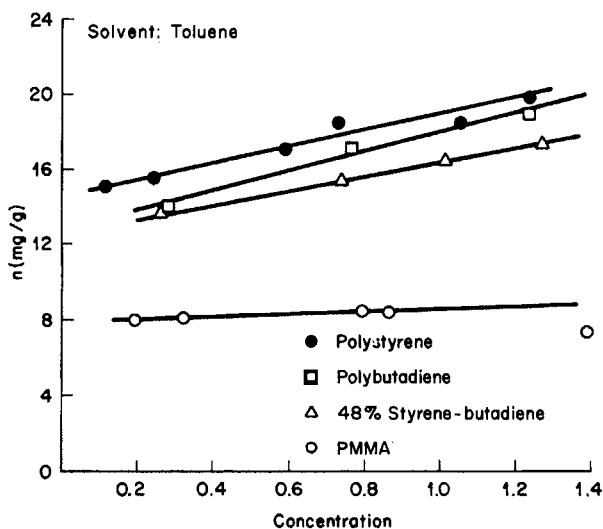
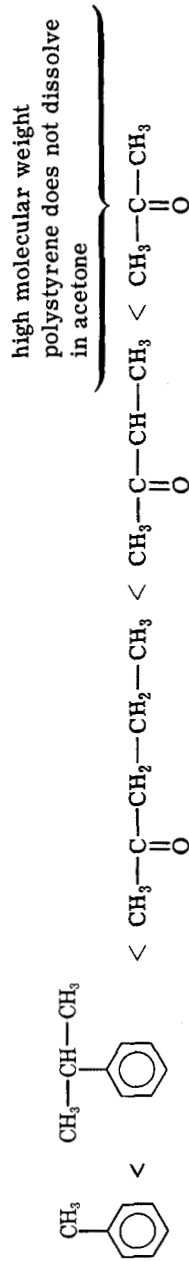


Fig. 8. Adsorption isotherms for various polymers from toluene onto activated carbon.

This was true in decalin, toluene, and cumene. In 2-pentanone, which does not dissolve the polybutadiene, the butadiene-styrene copolymer did adsorb more than the polystyrene. The decalin-toluene-cumene results are striking, as one would expect the copolymer to show intermediate adsorption characteristics. It does not! Perhaps molecular weight differences may have some influence, but one would not expect these to be so significant.

The question arises as to the relationship between the quality of the solution and the extent of adsorption from it. The effect of solvent-polymer interactions show in the adsorption of polystyrene from toluene, cumene, and MEK, where the extent of adsorption increases as the solvent power (as measured, say, by the second virial coefficient) decreases:



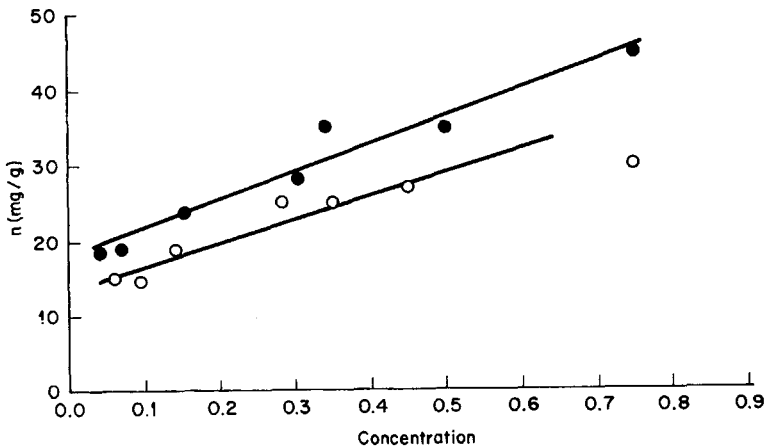


Fig. 9. Adsorption isotherms for polystyrene (●) and poly(methyl methacrylate) (○) from methyl ethyl ketones.

Similarly, the greater adsorption of the butadiene-styrene copolymer than that of polystyrene from the 2-pentanone can be explained by polymer-solvent interaction. This rule does not apply to the adsorption of polystyrene from decalin, where the extent of adsorption is less than from toluene in spite the fact that the former solution has a lower solvent power than the polystyrene-toluene solution. Again, it does not apply to adsorption of the butadiene-styrene copolymer relative to the homopolymers from

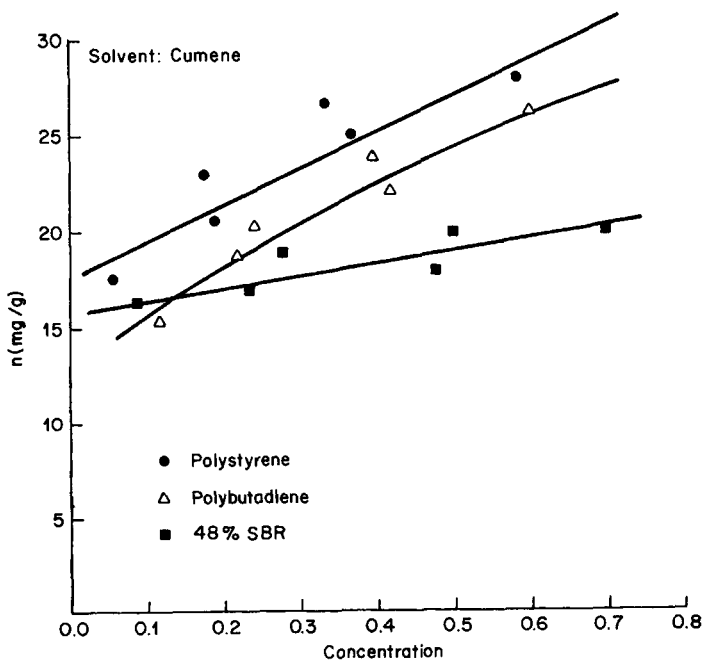


Fig. 10. Adsorption isotherms for various polymers from cumene onto activated carbon.

decalin, cumene, and toluene. A reasonable conclusion on surveying the data is that solution quality only determines extent of adsorption when all solutions are poor or when a good solution is compared to a poor one. Among good solutions (if we include polystyrene-decalin as such) there is no correlation.

### Adsorption Rate Mechanism

We now turn to the adsorption rate process. The reason for the disagreement between the value of  $k_t$  determined by the two methods is (1) that application of eq. (1) to our data underestimates  $k_t$  because we do not have data at very short times; and (2) the use of eq. (7) neglects nonlinearities in the isotherm and presumes that the polymer is completely adsorbed in 48 hr. The calculations from eq. (1) are lower, as expected. Presumably both sets of results are of the correct order. The errors would seem to be reasonably constant within both sets of measurements, and either might be used in themselves for purposes of comparison.

The adsorption process takes place in a series of consecutive steps: (1) diffusion from the bulk fluid to the adsorbent particle surface, (2) diffusion through the same structure to the internal surface area of the particle, (3) adsorption. It is not apparent at first which of these processes is the rate-determining one. We have thus attempted to look into this problem. The concentration difference between that in the bulk of the solution and that in equilibrium with the adsorbate may be divided into three concentration differences corresponding to the three steps noted above:

$$c - c^* = (c - c_s) + (c_s - c_i) + (c_i - c^*) \tag{8}$$

bulk to	external	internal
external	surface	region
adsorbent	to inter-	adsorption
surface	nal region	process

If we divide these expressions through by the mass flux or rate of adsorption, we may write<sup>22</sup>

$$\frac{1}{k_t} = \frac{1}{k_{ext}} + \frac{1}{k_{int}} + \frac{1}{k_{ads}} \tag{9}$$

where  $k_{ext}$  is the external mass transfer coefficient,  $k_{int}$  is the internal mass transfer coefficient, and  $k_{ads}$  refers to the actual rate of adsorption within the particle.

The quantity  $k_{ext}$  is important as witnessed by the influence of solution concentration (which probably should be interpreted as viscosity) and shaking intensity. Certainly,  $k_{ext}$  may be expressed in terms of a shaking Reynolds number and a Schmidt number.<sup>22</sup> The value of  $k_{ext}$  may be determined if one presumes that this quantity is a continually increasing function of shaking intensity. Eventually, if the system is shaken very severely,  $k_{ext}$  will become very large, and

$$\frac{1}{k_t} \left( \begin{matrix} \text{intense} \\ \text{shaking} \end{matrix} \right) = \frac{1}{k_{int}} + \frac{1}{k_{ads}} \tag{10}$$

Such an experiment has been carried out and is illustrated in Figure 7. For the systems studied,  $k_i$ ,  $k_{\text{ext}}$ , and the term on the right-hand side of eq. (10) have values of order  $10^{-4}$  sec (g solution)/(g adsorbent);  $k_{\text{ext}}$  is approximately twice the value of  $k_i$ .

There would seem to be no direct experimental method for determining  $k_{\text{int}}$ . However, this quantity may be estimated through expressions variously derived by several authors<sup>23-26</sup> which consider diffusion through pores in a sphere. These have the form

$$k_{\text{int}} = 15 \frac{D_{\text{int}}}{R^2} \quad (11)$$

where  $D_{\text{int}}$  is the molecular diffusivity within the pore, and  $R$  represents the distance the pores penetrate into the adsorbent particle. If they pores penetrate to the center of the particle, then  $R$  represents the radius. The radius of the particle is thus the maximum value of  $R$  and leads to the smallest rate constant  $k_{\text{int}}$ . Estimation of the diffusivity  $D_{\text{int}}$  is a more difficult problem since we are concerned with the movement of macromolecules through pores. Diffusivities of macromolecules in solutions, especially dilute solutions, have long been available in the literature,<sup>27</sup> and they may be estimated through either the Stokes-Einstein equation<sup>28</sup> or its modification by Flory.<sup>29</sup> However, these diffusivities are measured in containers large compared to the size of the molecule, while in the adsorbent particle there are interacting walls which are frequently of the same order of magnitude in diameter. Diffusivities of macromolecules such as polystyrene of molecular weight 100,000 in a dilute toluene solution are of the order  $10^{-7}$  cm<sup>2</sup>/sec. This leads to values of  $k_{\text{int}}$  of the order  $10^{-3}$  sec<sup>-1</sup> where we have used the radius of the particle. It follows that if the diffusivity is of the right order of magnitude,  $k_{\text{int}}$  is perhaps close to  $k_i$ , but may be large by a factor of 10 (even when the solution-adsorbent system is subject to rapid shaking).

From the discussions of the above paragraphs it would seem to follow that  $k_{\text{ext}}$ ,  $k_{\text{ads}}$  (and perhaps  $k_{\text{int}}$ ) are significant in determining  $k_i$  and that by rapid shaking one may eliminate the contribution of  $k_{\text{ext}}$ . If  $k_{\text{int}}$  is larger as suggested above, the results summarized in Table IV for  $k_i$  will be essentially  $k_{\text{ads}}$ , the basic physically property with which we are concerned. These are based on  $k_i$  calculated from eq. (7). The results are of some interest. The rates of adsorption from the two ketones are somewhat large compared with the data from the hydrocarbon solvents. This is especially the case with the methyl ethyl ketone.

### Application to Chromatography

The adsorption equilibrium data may be interpreted so as to estimate the possibility of chromatographic separation experiments. Relative elution volumes and dispersion were computed from the adsorption data using well-known results from the theory of chromatography.<sup>17,30-32</sup> In the formulation of White and Kingry,<sup>17</sup> it may be seen that possible molecular sieving

TABLE IV

$$\text{Rate Constant } \frac{1}{1/k_{\text{int}} + 1/k_{\text{ads}}}^{\text{a}}$$

System	Rate constant × 10 <sup>4</sup> sec <sup>-1</sup>
Polystyrene-toluene	8.54
Polybutadiene-toluene	5.16
48% Styrene-butadiene copolymer-toluene	6.24
48% Poly(methyl methacrylate)-toluene	9.08
Polystyrene-decalin	5.57
Polybutadiene-decalin	2.84
48% Styrene-butadiene copolymer-decalin	1.66
Polystyrene-cumene	10.25
Polybutadiene-cumene	8.87
48% Styrene-butadiene copolymer-cumene	5.26
Polystyrene-pentanone-2	16.24
48% Styrene-butadiene copolymer- Pentanone-2	18.6
Polystyrene-methyl ethyl ketone	32.6
Poly(methyl methacrylate)-methyl ethyl ketone	34.4

<sup>a</sup> Based on eq. (7).

effects are lumped together with the adsorption phenomenon. According to this theory, one may write the elution volume of the peak concentration as

$$\frac{V_i}{V_{\text{col}}} = \alpha + K_i(1 - \alpha) \tag{12}$$

where  $K_i$  is the equilibrium constant  $K_i = n_i/c_i$  for species  $i$  and  $\alpha$  is the void fraction. Application of eq. (12) implies a linear equilibrium. From Figures 8, 9, and 10, this may seem not to be the case. However, representing the adsorption results in this manner should be of at least qualitative value for the purpose of predicting chromatographic column response. Table V summarizes  $K_i$  values estimated from our long-duration adsorption data. Predicted chromatographic separations for typical solvents are summarized in Table VI. The impossibility of separating heterogeneous butadiene-styrene copolymers according to composition in all solvents may be appreciated. Such chromatographic separations have, however, been

TABLE V  
Apparent Adsorption Linear Equilibrium Constant  $K_i$

	Toluene	Methyl ethyl ketone
Polystyrene	2.5	10.0
Poly(ethyl methacrylate)	1.0	6.7
Polybutadiene	2.0	—
48% Styrene-butadiene copolymer	1.83	—

TABLE VI  
Band Width and Elution Volume in a Column 20 cm in Length and 1.0 cm in Diameter

Polymer	Solvent	$\frac{V_i}{V_{\text{solvent}}}$	Band width $4\sigma$ , cm <sup>3</sup>	$V_i$ pulse, cm <sup>3</sup>
Polystyrene	Toluene	4.75	188	30
Polybutadiene	Toluene	4.0	208	25
48% Styrene-butadiene copolymer	Toluene	3.7	154	23
Poly(methyl methacrylate)	Toluene	2.5	80	16
Polystyrene	MEK	16.0	128	100
Poly(methyl methacrylate)	MEK	11.0	52	70

carried out in our laboratories in the thin-layer mode using silica gel.<sup>21,33</sup> Interestingly, the adsorption properties of silica gel are much different from those of activated carbon. For instance, poly(methyl acrylate) is usually adsorbed more rather than less than polystyrene.

The amount of dispersion may also be estimated using linear chromatography theory. We use the van Deemeter equation<sup>21,26,31,34</sup> for the volumetric dispersion  $\sigma^2$ ,

$$\sigma^2 = 2A^2Z \left[ \frac{E}{U} (\alpha + K_i) + \frac{K_i^2 U}{k_t} \right] \quad (13)$$

where  $U$  is the linear velocity of the solvent,  $E$  is the axial dispersion coefficient, and  $Z$  is the distance along the column. We take  $E$  to be  $2.5d_p U$  where  $d_p$  is the adsorbent particle diameter. This is equivalent to an axial Peclet number of 0.4. The band width  $4\sigma$  may be computed and the length of the column required to obtain a meaningful separation estimated. Computed results are summarized in Table VI. As a chromatographic column, this leaves much to be desired. The slow adsorption-desorption process is undoubtedly the reason that chromatographic columns using activated carbon have never really been successful in separating mixtures of macromolecules.

## CONCLUSIONS

The adsorption of various polymer-solvent systems on activated carbon has been studied experimentally. In particular, extent of adsorption-versus-time curves and the equilibrium isotherms for several systems have been obtained. The butadiene-styrene system has been studied in some detail, and it has been found that in many solutions polybutadiene and polystyrene are absorbed more strongly than their copolymers. It has been shown that low molecular weight polymer is usually adsorbed during the early stages of adsorption. Rates of adsorption have been analyzed and an attempt has been made to resolve the apparent adsorption rate coefficient



in terms of external mass transfer, intraparticle diffusion, and true adsorption.

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