ever, for Gaussian chains usually $N^{1/2}$ (or h) appears, rather than $h^{0.94}$. We are unable to provide a rationale for this unusual dependence, but just note that it fits the calculations significantly better than does a first-power dependence.

Acknowledgments. This work was supported in part by USPHS Research Grant GM 12555 and Biophysical Chemistry Training Grant 2G-722. It will be part of a thesis submitted by P. S. in partial fulfillment of the requirements for a Ph.D. at the University of Illinois.

Appendix

The sums are of the form

$$\sum_{k=1}^{\infty} A/(\lambda_k' + Bk^2)$$

where A and B are constants. This can be broken up into

$$\sum_{k=1}^{\nu} A/(\lambda_k' + Bk^2) + \sum_{k=\nu+1}^{\mu} A/(\lambda_{k,\mathrm{app}}' + Bk^2) + \sum_{k=\mu+1}^{\infty} A/(\lambda_{k,\mathrm{app}}' + Bk^2)$$

where $\lambda_{k,\mathrm{app}}'$ is the approximate analytical form for the kth nondraining eigenvalue.[8,9] The first ν eigenvalues have been tabulated numerically.[8,9]

We have therefore evaluated the first sum numerically, and summed the second out to fairly large μ ($\approx 10^3$) by digital computer. The third sum was replaced by an integral according to the Euler–MacLaurin procedure

$$\sum_{k=\mu+1}^{\infty} f_k = \int_{\mu+1}^{\infty} f(k)dk + {}^1\!/_2 f(\mu + 1)$$

and evaluated by numerical integration.

Adsorption of Polystyrene on Porous and Nonporous Adsorbents[1]

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ABSTRACT: A study was made of the adsorption of polystyrene from cyclohexane solution onto aluminum and aluminum oxide surfaces. Four polystyrene fractions, ranging in molecular weight from 67,000 to 1,800,000, were used. Brief studies were also made of the adsorption of polyisobutylene from benzene onto aluminum and of ethylbenzene from cyclohexane onto aluminum oxide. The surface areas of the two solids and the pore-size distribution of the aluminum oxide were measured by low-temperature nitrogen adsorption. The aluminum was essentially nonporous. For adsorption on aluminum, equilibrium appeared to be reached in a matter of hours; it is doubtful that true equilibrium was established even after 25 days in the case of aluminum oxide. Adsorption on aluminum is typical of the behavior of a variety of polymers adsorbed on nonporous adsorbents, exhibiting, for example, an increase of adsorbance with increasing molecular weight. The molecular weight dependence of adsorption on aluminum oxide was the reverse of normal behavior, the fraction of lowest molecular weight being adsorbed to the greatest extent. This is interpreted as a result of steric hindrance to penetration of the pore structure of the solid by large molecules. The estimated radius of the smallest pores penetrated by each fraction is approximately equal to the radius of gyration of the molecules in the solution. A study of the adsorption of ethylbenzene, a monomeric analog of polystyrene, from cyclohexane gives a value of −4220 cal/mol as the lower limit of the heat of adsorption of polystyrene segments. Polyisobutylene was not adsorbed from benzene onto aluminum, a result attributed to preferential adsorption of the solvent.

Current theories[3–7] of the adsorption of polymer molecules on solid surfaces use the idealized picture of a smooth plane at which the polymer chains are attached by many[4] or few[3] of the chain segments. While such a simplification is desirable for purposes of focusing attention on the types of conformations that are typical of chains, the fact remains that many common adsorbents for polymers are not well represented by the smooth surface model. There are the "porous" adsorbents, which have very large specific surface areas, a large fraction of which is present in inner recesses of the solid. Adsorption studies of polymers on porous adsorbents to date have shown that the time required for adsorption can be very long, and that the extent of adsorption is larger for smaller molecular weights than for larger molecular weights.[8–17] This has been

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(1) (a) Based on the Ph.D. thesis of Harris Burns, Jr., Georgia Institute of Technology, 1964. (b) Presented in part at the 148th National Meeting of the American Chemical Society, Polymer Division, Chicago, Ill., Sept 1964. An abstract is given in *Polym. Preprints*, **5**, 516 (1964).

(2) To whom all correspondence should be addressed.

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(10) S. Claesson and S. Claesson, *Ark. Kemi*, **19A**, No. 5 (1945); S. Claesson, *ibid.*, **26A**, No. 24 (1949).

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attributed to the long time which is required for the inner surface of the adsorbent to be reached by chains, and by the greater difficulty experienced by larger molecules in reaching these inner recesses, respectively. The number of such studies, however, is not great, the adsorbents used were not always characterized, and the results were not always compared to those obtained with the same polymer–solvent system and nonporous adsorbents.

The present work consists of a comparison of the adsorption behavior exhibited by a well-known polymer solvent system at its θ condition (polystyrene in cyclohexane) with reasonably well-characterized samples of a nonporous adsorbent (powdered aluminum) and a porous adsorbent (powdered aluminum oxide). In both cases measurements were made of the rate and the extent of adsorption by measuring the change in bulk concentration of the polymer solution caused by adsorption. Data were obtained as a function of molecular weight and temperature. Since aluminum always has an oxide layer, our work compares the adsorption on nonporous aluminum, which has at least a monlayer of oxide, with adsorption on porous aluminum oxide.

A brief study was made of the equilibrium adsorption of another θ system (polyisobutylene in benzene) with aluminum serving as the adsorbent. Also, the adsorption of ethylbenzene by Al_2O_3 from cyclohexane was studied in an effort to compare the behavior of polystyrene with its monomeric analog.

Experimental Section

Materials. The polystyrene used in this study was obtained from two sources. The high molecular weight material was prepared by thermal polymerization at room temperature. The bulk sample of lower molecular weight was prepared by polymerization at 45° of freshly distilled reagent grade styrene, using benzoyl peroxide as initiator. Both the high and the low molecular weight bulk samples were fractionated by fractional precipitation from benzene, using methanol as the precipitant. The fractions used in the adsorption studies were prepared by refractionation of these fractions. Fractions B and F were prepared using the fractional precipitation method for the refractionation. Fractions J and L were prepared by using an elution technique in a column containing Superbrite glass beads (Minnesota Mining and Manufacturing Co.) as the supporting material. The polymer was coated on the glass beads by very slow cooling of a benzene–methanol solution. The elution was accomplished by use of benzene–methanol mixtures, with the benzene concentration being increased gradually to elute successively higher molecular polymer from the beads. Fraction L was selected from the fractions prepared at 25° in this manner. Fraction J was selected from the fractions collected in another column fractionation in which the variation in the solvent composition was combined with a temperature gradient: in this case the solvent mixture contained methyl ethyl ketone and ethanol.

Values of the number average molecular weight, $\bar{M}_n$, and the weight average molecular weight, $\bar{M}_w$, were measured by osmometry and light scattering, respectively, with benzene as solvent. The results are shown in Table I.

The polyisobutylene sample was an unfractionated commercial Vistanex sample, for which $\bar{M}_v = 1 \times 10^6$.

The liquids used, cyclohexane, benzene, and ethylbenzene, were all reagent grade and were distilled before use. Spectroquality cyclohexane was used in all the adsorption measurements with polystyrene since traces of aromatic impurities would interfere with the spectrophotometric analyses of the solutions (*cf.* below).

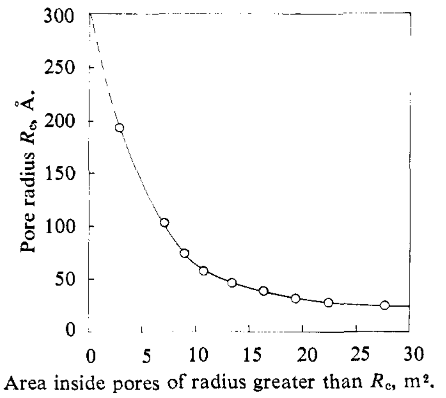

Figure 1. Distribution of area of aluminum oxide inside pores.

TABLE I

MOLECULAR WEIGHTS OF POLYSTYRENE FRACTIONS

Fraction	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
B	18.2		
	18.4[a]	15.0[a]	1.22
F	3.70	3.54	1.05
J	1.77	1.45	1.22
L	0.67	0.58	1.15

[a] Estimated from fractionation data on fraction B.

Adsorbent Characterization. The aluminum powder used was USP grade (J. P. Baker). The aluminum oxide was designated "Activated Alumina, Grade F-20" (Alcoa Corp.).

Surface areas were calculated by measuring the nitrogen adsorption as a function of pressure and interpreting the results with a conventional BET plot. The surface areas found were 1.14 ± 0.5 m²/g for aluminum and 310 ± 10 m²/g for aluminum oxide, respectively.

The pore-size distribution in the aluminum oxide was determined by the method of Pierce.[18] Hysteresis was observed in this system and the desorption data were used in the calculations.[19] The results of the pore-size distribution are shown in Figure 1, where the area inside the pores (assumed to be cylindrical in the analysis) greater than a given value of the radius R_c are shown as a function of R_c. These results show that the aluminum oxide sample is quite porous, as would be expected from the large surface area measured by the BET method.

The low value of the surface area of the aluminum powder suggests that this sample is essentially nonporous. Further support of this conclusion was obtained by measuring the distribution of particle diameters using a Coulter counter. This instrument measures directly the volume of the particle.[20] The volume is then converted into an equivalent spherical diameter using the known density of the aluminum. From the calculated distribution of particle diameters a surface area can be calculated, which in the present case turned out to be one-half of the value measured by the BET

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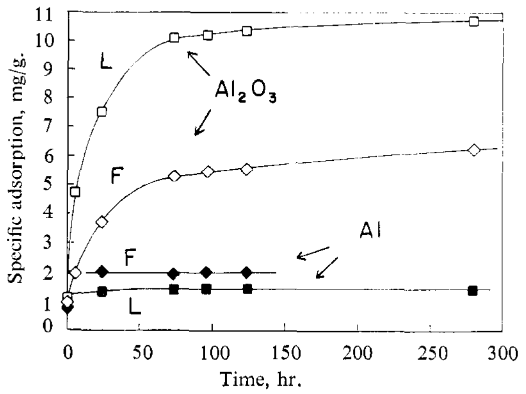

Figure 2. Rate curves for adsorption of polystyrene on aluminum oxide and aluminum.

method. The close correspondence between these two values depends upon the absence of extensive porosity in the particles and thus confirms the fact that the aluminum is not porous.

Adsorption Measurements. The adsorption measurements were made by shaking polymer solutions of known initial concentrations with weighed portions of adsorbent, and then measuring the concentration of the bulk solution afterward. The amount of polymer adsorbed per gram of adsorbent was expressed by the specific adsorbance, A

$$A = W(c_0 - c)/w \qquad (1)$$

where W is the weight of the solution in decagrams, w is the weight of the adsorbent in grams, c_0 and c are the initial and final concentrations of the solution, respectively, expressed in milligrams of polymer per decagram of solution. In our experiments W was approximately 0.075 dg and w varied between 0.5 and 4.0 g.

In the measurements of polystyrene solutions, the concentrations were measured spectrophotometrically, using the prominent peaks of 2595, 2615, and 2690 Å. Calibrations were made on cyclohexane solutions of known concentrations at all three wavelengths. Analysis of the data obtained leads to the conclusion that the precision of the values of the concentrations determined in this manner is between 1 and 2%.

Concentrations of polyisobutylene solutions were obtained by a gravimetric technique, owing to the absence of any characteristic adsorption bands of this polymer in the ultraviolet and visible regions of the spectrum. Analyses of two solutions of known concentration by this technique yielded errors of 0.3 and 4.2%, respectively.

Before making an adsorption run, the adsorbent was heated in a 20-cc glass ampoule at about 140° for 24 hr. After this, 10 cc of a polymer solution of known concentration was added to the ampoule. The ampoule was sealed off while the contents were frozen by immersion in a Dry Ice–acetone mixture, then shaken gently in a rack suspended in a constant-temperature bath for the time allotted for adsorption. The solid was allowed to settle, the ampoule removed from the bath, opened, and the solution was gently decanted and its concentration determined by analysis.

The technique just described is open to the possible objection that the adsorbent and the solution were in contact for some time before placing the ampoule in the constant-temperature bath. Furthermore, the effect of the sudden drop in temperature which occurred while the contents were frozen when the ampoule was sealed off is difficult to determine. Accordingly, some of the kinetic measurements described below were accomplished using a different technique designed to postpone the occasion of contact between adsorbent and solution. In this technique the dried adsorbent was placed inside a thin-walled tube which was sealed off and placed inside a larger tube which contained the polymer solution. After sealing off the larger tube and placing it in the constant-temperature bath to attain thermal equilibrium, violent shaking was used to break the inner tube and allow adsorbent and solution to make contact. Although this method is in principle superior, the experimental difficulties involved proved to be considerable; although several efforts were made to obtain kinetic data in this way, the results were fragmentary and generally unsatisfactory. The results obtained, however, are indistinguishable to within experimental error from those obtained using the first technique.

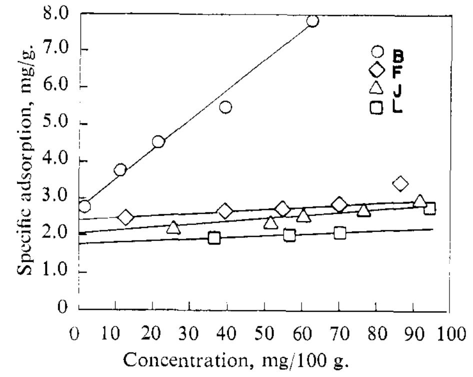

Figure 3. Adsorption of polystyrene fraction on aluminum at 34.8° after 25 days.

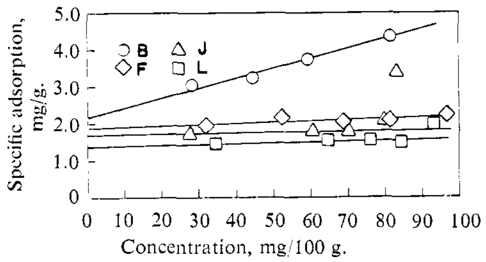

Figure 4. Adsorption of polystyrene fractions on aluminum at 50° after 25 days.

Results and Discussion

Adsorption rates were determined by measuring the specific adsorption A (*cf.* eq 1) as a function of time. Adsorption of polystyrene from cyclohexane occurred much more rapidly on the nonporous aluminum than on the porous aluminum oxide. The data in Figure 2 show that an apparent equilibrium was established within several hours on aluminum, but it is doubtful that equilibrium was attained on aluminum oxide even after 25 days. Figure 2 also shows that during the time interval encompassed by these measurements that the extent of adsorption increased with decreasing molecular weight on aluminum oxide, whereas the more normal molecular weight dependence, an increase, occurred on aluminum. In what follows these general features will be explained in terms of the different porosities possessed by the two adsorbents.

Polystyrene on Aluminum. The isotherms for the adsorption of polystyrene onto aluminum are qualitatively similar to those observed for other polymers

TABLE II

COMPARISON OF RADII OF ADSORBED AND FREE POLYSTYRENE MOLECULES

Fraction	$10^{-5} \times \bar{M}_w$	R_a (34°), Å	R (34°), Å	$R_a(34°)/R(34°)$	R_a (50°), Å	R (50°), Å	$R_a(50°)/R(50°)$
B	18.2	202	379	0.52	225	440	0.51
F	3.70	96.4	171	0.56	107	192	0.56
J	1.77	72.1	118	0.61	79.2	131	0.61
L	0.67	47.9	73	0.67	54.5	79	0.68

studied by other investigators using metal and glass as adsorbents.[8,21–25] The isotherms for three of the four fractions are nearly horizontal lines over the entire concentration range studied, with no apparent decrease in specific adsorption even at the lowest concentration (Figures 3 and 4). The amount adsorbed increases with increasing molecular weight and decreases with increasing temperature. Since the isotherms did not exhibit truly horizontal plateaus, especially in the case of the highest molecular weight, fraction B, it was decided to express the extent of adsorption by the quantity A_0, the intercept of the linear isotherm at infinite dilution. This corresponds to the procedure commonly followed in determining surface areas of solids by gas adsorption using the BET method, wherein an extrapolation is made to zero gas pressure of the linear portion of the isotherm. Thus the values of A_0 correspond closely to the "knees" of the complete isotherms, the lower portions of which are missing in the present work.

If these data are interpreted by assuming that the molecules are adsorbed in a monolayer as distorted random coils of radius R_a, then R_a (in ångströms) may be calculated from the equation

$$R_a = (S_m/\pi)^{1/2} = (SM/6.023\pi A)^{1/2} \tag{2}$$

where S_m = the area occupied by a single molecule, S = specific surface area of the adsorbent in square meters per gram, M = molecular weight of the polymer, and A = specific adsorption in milligrams per gram. Values of R_a calculated in this manner are shown in Table II, along with values of the root-mean-square radius of gyration R of the free chains (*i.e.*, in the bulk solution). The values of A were taken to be equal to A_0, the values at infinite dilution. Values of R were calculated for each molecular weight and temperature by using the light scattering data for PS in cyclohexane obtained by Notley and Debye.[26] The values of R_a/R in Table II indicate a significant degree of compression of the coils occurs upon adsorption with the apparent radius being *ca.* 40% lower than that of the free coil. The degree of compression is unchanged over the temperature interval 34–50°. The degree of distortion increases somewhat with molecular weight, but due to the gross simplification of this model we prefer to not place too much emphasis upon this point.

A slightly more refined interpretation of the isotherm data is suggested by Silberberg's theory.[4] Defining Γ as the number of chain segments adsorbed on a surface site, then

$$\Gamma = 6.023 a_0 A_0 / M_0 S \tag{3}$$

where a_0 = the area of an adsorption site (in square ångströms), M_0 = the molecular weight of a chain segment, and A_0 and S have been defined above. To calculate Γ, it is necessary to estimate a_0. The area of a polystyrene segment could be estimated to be *ca.* 50 Å^2 by assuming it to be slightly less than the sum of the areas (obtained from vapor adsorption studies) of benzene (32.3 Å^2) and ethane (22.5 Å^2). If, however, a segment is sterically hindered from lying flat on the surface, then a smaller value of a_0 would be appropriate. Silberberg, for example, has suggested that values of 20 Å^2 or even 10 Å^2 may be appropriate. Calculations of Γ based upon values of a_0 equal to 10, 20, and 50 Å^2 give results which are compatible with either a two-dimensional structure of the film ($\Gamma = 1$ for $a_0 = 10$ Å^2) or a three-dimensional structure ($\Gamma = 5$ for $a_0 = 50$ Å^2). Uncertainty regarding the proper value of a_0 precludes a distinction between these possibilities. Furthermore, the values of Γ are proportional to the extrapolated specific adsorption, $\mathring{A}_0$, and this quantity may be influenced by factors other than the number of adsorption sites on the surface. Thus a randomly coiled molecule might be adsorbed at relatively few sites, yet make many other sites inaccessible to other chains by steric restrictions. This situation is indistinguishable (by this type of calculation) from that in which a molecule is extended on the surface and adsorbed at many sites without interfering significantly with adsorption at unoccupied sites. In the former case a large value should be used for a_0, but there seems to be no way to predict what this value should be.

Accordingly, we do not attempt to draw any conclusions from our isotherm data about the structure of the adsorbed layer of chains. To do this it is necessary to supplement the study of isotherms with a technique which probes the nature of the adsorbed layer more directly. Such techniques include a measurement of the film thickness by the flow-rate method of Rowland and Eirich[24] or the ellipsometric method of Stromberg, *et al.*,[25,27,28] and the spectrophotometric methods which measure the fraction of chain segments directly attached to the surface.[29]

The intercepts of the isotherms found on aluminum

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(29) B. J. Fontana and J. R. Thomas, *J. Phys. Chem.*, **65**, 480 (1961).

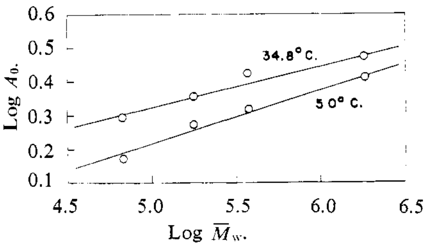

Figure 5. Relation between specific adsorption on aluminum at zero concentration and molecular weight.

(Figures 3 and 4) are found to be related to the molecular weight by the empirical equation

$$A_0 = K\bar{M}_w^{\,a} \qquad (4)$$

where K and a are constants. These data are represented in Figure 5 and the constants are shown in Table III, which also shows the constants of eq 4 which have been found for other systems.

It is seen from these data that polystyrene is adsorbed by aluminum to an extent which is comparable to that observed in other systems containing nonporous adsorbents. Adsorption is also seen to increase with molecular weight and to decrease slightly with increasing temperature; these features are also commonly observed in other systems.[8]

Several experiments were performed to examine the extent of the reversibility of the adsorption observed on aluminum. In the first of these fraction F was adsorbed for 6 days at 34.8°, after which the temperature was raised to 50°. Although the isotherm data (Figures 3 and 4) indicate that the extent of adsorption decreases with temperature, this type of experiment gave no indication, to within experimental error, of desorption after 6 days at 50°. On the other hand, when adsorption from cyclohexane for 6 days at 34.8° was followed by contact with benzene (a good solvent) for 4 days at 50°, 94% of the adsorbed polymer was removed. The failure of desorption to take place in cyclohexane at 50.0° indicates that true equilibrium was probably not attained in the data represented in Figures 3 and 4. This type of result has also been observed in experiments on PMMA by Ellerstein and Ullman,[22] and is due to the fact that an adsorbed polymer chain can be removed from the adsorbent only with difficulty, since all of the surface–segment contacts must be broken in order for desorption to occur. The success obtained in desorbing polystyrene when it was immersed in benzene is due partly to the fact that benzene is a much better sovent than cyclohexane, and the fraction of segments adsorbed in a given chain is smaller in a benzene medium than in a cyclohexane medium. Furthermore, benzene molecules probably interact more strongly with the aluminum surface than do those of cyclohexane and are consequently more effective in removing polymer segments.

Table III
Parameters K and a in Equation 4

System	K	a	Ref
PS, cyclohexane, Al, 34.7°	0.39	0.13	
PS, cyclohexane, Al, 50°	0.20	0.16	
PDMS, benzene, glass, 30.4°	0.97	0.40	23
PDMS, *n*-heptane, glass, 30.4°	2.94	0.35	23
PDMS, benzene, Fe, 30.4°	0.34	0.43	23
PDMS, *n*-heptane, Fe, 30.4°	4.9	0.23	23
PMMA, benzene, Fe	0.35	0.04	22
PMMA, benzene, glass	2.00	0.00	22
PMMA, 1,2-dichloroethane, Fe	0.14	0.08	22

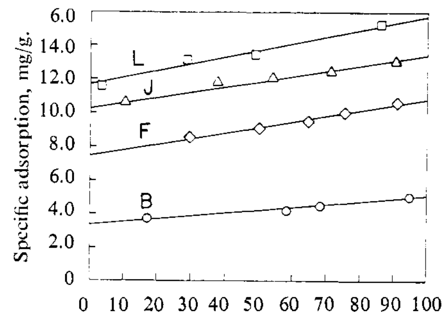

Figure 6. Adsorption of polystyrenes fractions by aluminum oxide at 34.8° after 25 days.

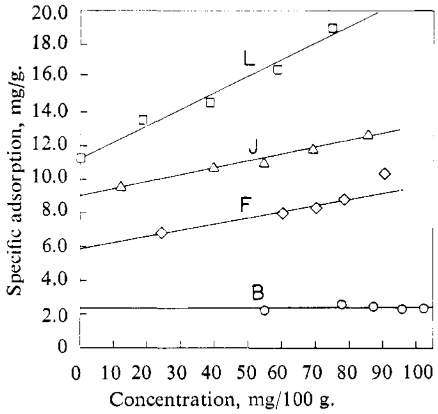

Figure 7. Adsorption of polystyrene fractions on aluminum oxide at 50° after 25 days.

To summarize, the adsorption of polystyrene from cyclohexane by aluminum is typical of the behavior observed in other systems which contain a nonporous adsorbent.

Polystyrene on Aluminum Oxide. Adsorption of polystyrene on the porous adsorbent aluminum oxide (Figures 6 and 7) shows a reversal of the normal molecular weight dependence, with the low molecular weight fractions being adsorbed to the greatest extent. We attribute this behavior, as others[10,30] have done, to the greater ability of the smaller molecules to penetrate the pore structure of the adsorbent. It is possible to put this picture on a semiquantitative basis by assuming that a given weight of polymer is adsorbed in a film of the same area on either aluminum or aluminum oxide. It then follows that

$$S(\mathrm{Al_2O_3}) = S(\mathrm{Al})[A_0(\mathrm{Al_2O_3})/A_0(\mathrm{Al})] \qquad (5)$$

where $S(\mathrm{Al_2O_3})$ = accessible area of adsorbed film per gram of $\mathrm{Al_2O_3}$, $S(\mathrm{Al})$ = specific surface area of aluminum, and A_0 = specific adsorption on the indicated adsorbent at infinite dilution. The area of the adsorbed film so calculated may then be assumed to be

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(30) E. Jenckel and B. Rumbach, *Z. Elektrochem.*, **55**, 612 (1951).

TABLE IV
CHARACTERIZATION OF ALUMINUM OXIDE BY VALUES OF LIMITING PORE RADIUS, R_{c1}

Fraction	$\bar{M}_w \times 10^{-5}$	$S(Al_2O_3)$, m²/g 34°	50°	R_{c1}, Å 34°	50°	R_{c1}/R 34°	50°
B	18.2	1.36	1.23	240	260	0.62	0.59
F	3.70	3.53	3.12	177	188	1.03	0.98
J	1.77	5.79	5.29	102	112	0.86	0.86
L	0.60	7.54	8.15	94	92	1.28	1.16

the area of the aluminum oxide surface which is accessible to polymer molecules of a given fraction. Access to the remainder of the total area of the adsorbent is denied due to the inability of the polymer molecules of this molecular weight to pass through the small pores. By using Figure 1, which is a plot of the area contained in pores of radius greater than R_c *vs.* R_c, the limiting pore radius can be read off, if the areas are identified with the values calculated from eq 5. Table IV shows the values of the limiting pore radius, R_{c1}, so obtained. Also shown in Table IV are the ratios R_{c1}/R, where R is the radius of gyration of the molecule in the bulk solution. The values of R are shown in Table II. The ratios R_{c1}/R are approximately equal to unity at both 34 and 50°, indicating that the coils are adsorbed into the pores without significant distortion. The agreement is sufficiently good to encourage the use of adsorption on porous adsorbents as a means of measurement of molecular dimensions of well-fractionated samples, and also as a method of selective fractionation, as has also been suggested by others.[16,17]

Ethylbenzene on Al_2O_3. The adsorption of ethylbenzene from cyclohexane by Al_2O_3 was studied at 35.0 and 50.0°. Since ethylbenzene is the monomeric analog of polystyrene, it was hoped that such data would allow an estimate to be made of the heat of adsorption per adsorbed polystyrene unit. A spectrophotometric technique was used to analyze the solutions. The data obtained are shown in Figure 8. The value of ΔH, the heat of adsorption at constant coverage, is independent of ethylbenzene concentration, since the isotherms are linear. Using the equation

$$\frac{d \ln c}{dT} = \frac{\Delta H}{RT^2} \tag{6}$$

the value of ΔH is found to be -4220 cal/mol. This is *ca.* 7*RT*, a value almost sufficient to cause collapse of chain molecules to a two-dimensional film according to the SFE theory.[31] However, the adsorption of ethylbenzene may be very different from that of polystyrene. The molecules of ethylbenzene are adsorbed independently of one another and are able to assume low-energy orientations with respect to the surface. Units of polystyrene, being connected to other units, may not be free to assume the configurations of lowest energy. In this case, the effective heat of adsorption per unit would be higher than the value of -4220 cal/mol, which must therefore be considered as a lower limit. The adsorption of ethylbenzene on aluminum was too small to permit a calculation of ΔH to be made.

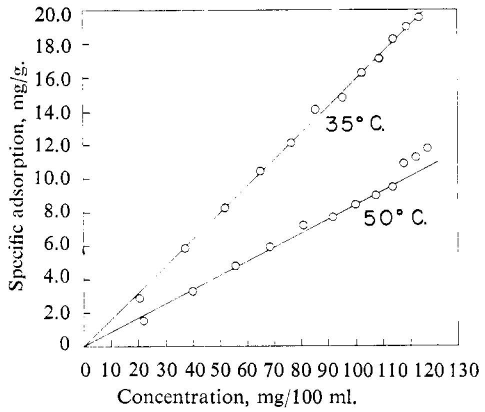

Figure 8. Adsorption isotherms for ethylbenzene on Al_2O_3.

Adsorption of Polyisobutylene. A limited number of measurements were made by using a gravimetric technique on the system PIB–C_6H_6–Al. The results indicate a slight extent of negative adsorption, *i.e.*, averaged over eight runs the final bulk concentration exceeded the initial concentration by *ca.* 3%. Since PIB and C_6H_6 also constitute a θ mixture, the difference between this system and PS–C_6H_{12} must be due to the difference in interactions with the adsorbent. Quite likely, the phenyl groups of PS are more tightly bound to the surface than C_6H_{12} molecules, whereas the C_6H_6 molecules are more tightly bound than the aliphatic units of PIB.

By contrast, Binford and Gessler[32] find that although PIB is not absorbed from CCl_4 solutions, that there is no tendency for CCl_4 to be selectively adsorbed from CCl_4–hexane mixtures. Thus the failure of PIB to be adsorbed from CCl_4 is to be attributed to the fact that CCl_4 is a good solvent for this polymer.

Conclusion

The adsorption behavior of polystyrene on aluminum powder is qualitatively similar to that observed previously for other polymers on nonporous adsorbents. There appears to be no anomaly in this system attributable to the thermodynamic poorness of the solvent. This suggests that adsorbate–adsorbent interaction is of substantially greater importance in determining the degree of adsorption than is the solute–solvent interaction. This conclusion is supported by the failure of polyisobutylene to be adsorbed from benzene. Thermodynamically, these two systems would have behaved in similar fashion if solute–solvent interactions were controlling. On the other hand, preferential adsorption of molecules containing conjugated rings would explain both results.

The nature of "equilibrium" in systems containing polymers is perhaps poorly defined. Failure to achieve significant desorption of polystyrene at a high temperature after initial adsorption at low temperature may reflect only a very slow desorption process which requires desorption of a large number of segments. On the other hand, it may indicate that the observed steady state is not a condition of true equilibrium at all but only a condition in which the adsorption process is sterically hindered from approaching thermodynamic equilibrium more closely. Further study of this prob-

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lem is indicated, and a more careful definition of equilibrium for systems of this type from a statistical point of view is desirable.

The adsorption of polystyrene on porous alumina is limited by the ability of the polymer molecules to penetrate the pore structure of the adsorbent. Such penetration is limited by the dimensions of the polymer molecule in solution. This result is in accord with the results of Moore[33] who used the differential diffusion rates in cross-linked polymers as the basis of molecular weight fractionation in gel-permeation chromatography.

Kiselev and Eltekov[16,17] have drawn conclusions similar to ours regarding the possibilities of estimating molecular dimensions of polymer molecules and of effecting fractionation by adsorption on porous polymers. These authors, however, characterize the porosity of their adsorbents by a single parameter, a "predominant size of pore openings." It is preferable to obtain the distribution of pore sizes, as in Figure 1 of the present work.

In a recent investigation[15] Howard and McConnell have presented results for the adsorption of polyethylene oxide onto porous adsorbents (charcoal and nylon) from a variety of solvents and conclude, as we have done, that with a porous adsorbent the area of surface available to solute molecules has no unique value but depends on the size of the adsorbate molecule. Furthermore, they measured the pore-size distributions of their adsorbents. However, whereas we find that the absorbance of polystyrene on Al_2O_3 decreases with increasing molecular weight, Howard and McConnell find that for most of their solvent systems that there is no molecular weight dependence of the adsorbance of polyethylene oxide when charcoal was used as the absorbent. The molecular weights of all except one of their polymers are less than 20,000; furthermore, they do not appear to have fractionated their samples. Thus it is difficult to compare their work directly with ours.

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Specific Counterion Effects on the Viscosity Behavior of Protonated Poly(ethylenimine)

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ABSTRACT: The viscosity of poly(ethylenimine), PEI, was measured as a function of the degree of protonation, α, in aqueous solutions of sodium chloride, sodium nitrate, and sodium perchlorate. The intrinsic viscosities of protonated PEI in solutions containing chloride or nitrate ions are not surprising; they may be explained by the compensating effects of the modified electrostatic repulsion of the polyelectrolyte chain and the decrease of the solvent power for the polyion. However, the intrinsic viscosities of protonated poly(ethylenimine) in aqueous perchlorate solutions are peculiar; $[\eta]$ decreases to a minimum and then increases with increasing α. An intramolecular association of the polymer chain in these aqueous perchlorate solutions is believed to be the cause for the contraction of the polymer coil. This intramolecular association appears to be the result of hydrogen bonding of two nitrogens on polymer chain by a proton; the role of the anion here is to stabilize the complex. Viscosity measurements were also made on protonated poly(ethylenimine) in mixed ethanol–water media. The only counterion present was introduced by the acid used (hydrochloric or perchloric acid) in the protonation process; no salt was added. The results are completely consistent with those obtained in aqueous systems in the presence of excess salts. This excludes the possibility that the intramolecular contraction might be caused by the induced intramolecular hydrophobic associations of the polymer chain. This study shows that, in the presence of simple counterions, a physical picture of polyelectrolytes in solution may sometimes be difficult to obtain in terms of electrostatic interactions of structureless charged units only, but often requires a detailed consideration of all specific counterion effects on the charged macromolecules. This includes, not only the electrostatic repulsion of the polyion and the decrease of solvent power for the polymer, but also the possiblity of induced intramolecular associations of the polyelectrolyte.

It is well known that introduction of ionized groups into uncharged polymer chains results in chain expansions because of electrostatic repulsion. These electrostatic effects, which are much greater than those resulting from solvent effects, are markedly reduced by the addition of simple monovalent ion (counterions). A number of polyelectrolyte theories using purely electrostatic models have been developed to explain this behavior.[1] With the exception of the analysis given by Flory,[1g] these theories neglect effects which are nonelectrostatic in nature.[2] As Flory has pointed out, such effects may contribute to chain expansion, but they may also render chain expansion more difficult.[1g] An extreme example of such nonelectrostatic effects is given by the "polysoaps,"[3-6] where the polyions carry long aliphatic hydrocarbon side chains, that tend to

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