

Polymer Swelling. Molecular Structure-Affinity Correlation Studies that Involve Poly(styrene-*co*-divinylbenzene) Exposed to Cyclic Olefinic Liquids

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The adsorption parameter (α) values established for the cyclic olefinic liquids in this investigation were compared with those established for the corresponding cyclic hydrocarbons, and also with those for related acyclic hydrocarbons. These comparisons were based on the $\log \alpha_f = \log \alpha_i - D_s(N_f - N_i)$ relationships, characteristic of the respective subseries in each classification. The relationship ($\alpha_i = 1.87$ at $N = 4$, $D_s = 0.0519$) characteristic for *cyclo*-[CH=CH(CH₂)_{*n*-2}]- is uniformly above that ($\alpha_i = 0.863$ at $N = 4$, $D_s = 0.0875$) for the *cyclo*-(CH₂)_{*n*}, which in turn is above those for the many subseries of acyclic mono-, di-, tri- and tetra-substituted olefins, the highest α value of which is about 0.5. The portion of this study devoted to polyunsaturated cyclic olefins, *cyclo*-[(CH=CH)_{*q*}(CH₂)_{*n*-2*q*}]-, showed that the $\log \alpha$ vs N relationships for those subseries in which q is kept constant varies linearly with n , as described above, but those subseries in which n is kept constant do not vary linearly with q . In such correlations, α increases to a maximal value attained at about $q = 2-4$, depending on n , such that the maximal α value is ca. 2.8 when n is 4, ca. 1.8 when n is 8 and ca. 0.1 when n is 12. Benzene and styrene behave as cyclic polyolefins.

Introduction

Earlier publications¹ in this series, devoted to studies of liquid sorption by poly(styrene-*co*-divinylbenzene) [hereinafter referred to either as poly(Sty-*co*-DVB) or (Sty)_{1-*x*}(DVB)_{*x*}], reported the concept of an adsorption parameter for the sorbed liquid with respect to the sorbent polymer. This parameter is defined as the number (α) of adsorbed molecules per accessible phenyl group in the polymer at liquid saturation. It can be established gravimetrically, by means of a set of six (Sty)_{1-*x*}(DVB)_{*x*} samples having known values of x , as described in considerable detail elsewhere,¹⁻¹⁷ and recounted briefly here in the Experimental Section. The α values reported thus far (>500) range from 0 to 4, and they are reproducible to within ± 0.01 . These values reflect very sensitively the molecular structure of the adsorbed species and how it is accommodated by that of the repeat unit in the polymer. Consequently they are particularly useful in adsorption studies involving homologous series (based on the atom or functional group having the relatively much stronger affinity for the polymer), in which one variable in a homologous series having a given general molecular structure (GMS) is incremented systematically from 1 to its allowable limit while the others are held constant.

It was observed in such studies²⁻¹⁷ that the logarithms of the α values determined for a given homologous subseries exhibit a linear relationship with the total number (N) of methylene mass units (or equivalent) as expressed by eq 1.

$$\log \alpha_f = \log \alpha_i - D_s(N_f - N_i) \quad (1)$$

Here N_i and N_f are respectively the initial and final N values of the homologous series being considered, α_i and α_f are the corresponding α values, and D_s is the characteristic decrementation constant (i.e., the decrease in $\log \alpha$ per unit increase in N) for that series. Thus, after only a relatively few α values for some of the key smaller molecules were established experimentally, it was possible to calculate with reasonable confidence

those for many of the other molecular permutations that comprise the GMS classification.

The above studies also demonstrated that the mode of adsorption to the adsorption site (in this case the pendent phenyl group of the polymer at liquid saturation) is a most important uncontrolled variable that must remain constant, if the network of $\log \alpha$ vs N linear relationships (i.e., vectors in multidimensional space) is to reproduce the experimental data. For example the $\log \alpha$ vs N relationships for subseries of the GMS CH₃-*z*-Z_{*z*}(CH₂)_{*n*}H, in which Z is a Cl or Br atom⁸ or an alkoxy group,¹² are linear when n is incremented from 1 to 8 while z is kept constant, but they are not linear when z is incremented from 1 to 3 while n is kept constant. The latter exhibit maxima that vary with n , which reflect the modes of adsorption as influenced by the summation of the electronic and steric contributions from the hydrocarbon and Z substituents attached to the carbon atom adjacent to that Z substituent actually making liaison with the adsorption site. Consequently, each incrementation of Z is accompanied by a corresponding change in the mode of adsorption, which affects both constants α_i and D_s of eq 1.

In those cases dealing with polymethylene chains having functional groups at the terminal positions, i.e., Z(CH₂)_{*n*}CH₃-*z*-Z_{*z*}, the Z substituent making liaison with the adsorption site is the one on the carbon atom having the lesser number of Z substituents; the others are involved in dynamic associative interactions with the mobile sorbed-but-not-adsorbed molecules of their own kind in the system at liquid saturation, which affect accordingly the attitude of the adsorbed molecules with respect to the adsorption site. Here again both constant α_i and D_s in the $\log \alpha$ vs N linear relationships for the Z(CH₂)_{*n*}CH₃-*z*-Z_{*z*} series are affected, such that they are significantly different from those for the corresponding Z(CH₂)_{*n*}H series, and the magnitude of the differences vary inversely with the number of Z substituents in the terminal CH₃-*z*-Z_{*z*} group.

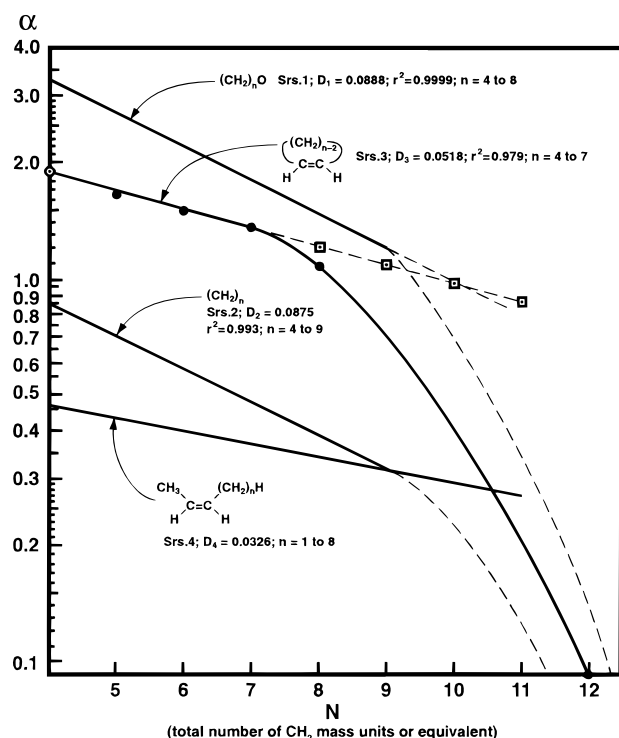


Figure 1. Comparisons of the $\log \alpha$ vs N relationship for cyclic mono ethylenes $[(CH_2)_{n-2}CH=CH]$ with those for $cis\text{-}CH_3CH=CH(CH_2)_nH$, $(CH_2)_nO$, and $(CH_2)_n$.

Similar results were noted¹⁷ in our studies involving sorption of olefinic liquids, $R_aR_bC=CR_cR_d$, where each R substituent is a $(CH_2)_nH$ group that can be incremented from 0 to 8. Liaison of such molecules with the adsorption site involves the carbon atom bearing the greater number of hydrogen atoms (or smaller alkyl group). In such series the constants α_i and D_s for the respective $\log \alpha$ vs N linear relationships reflect nonlinearly the number of hydrogen atoms replaced by an alkyl substituent and the respective relative positions of these groups (cis, trans, or gem or combinations thereof), depending on their relative electronic and steric contributions to the olefinic carbon atom making liaison with the adsorption site.¹⁷ These relationships were then used as criteria for inferring the respective modes of adsorption and the attitudes characteristic of the subseries in the adsorbed state (see Figures 2a–f in ref 17), which exhibited quantitative differences in accordance with the molecular architecture for that subseries in its adsorbed state.

The subseries of the disubstituted ethylenes assumed to have the most effective attitude in its mode of adsorption (based on its $\log \alpha$ vs N linear relationship; $\alpha_i = 0.464$ at $N = 4$ and $D_s = 0.0326$) is that characteristic for $cis\text{-}CH_3CH=CH(CH_2)_nH$, all the others being uniformly below this reference line. Having established this relationship, it can now be used as a valid basis for adjudicating the effect on α caused by ring closure to afford the corresponding *cyclo*- $[CH=CH(CH_2)_{n-2}]$ series, since the mode of adsorption in both cases should be essentially the same. It was suggested that liaison with the adsorption site in the case of the cis-disubstituted acyclic olefins involves the cis- π -orbitals of the double bond with an adjacent pair of π -orbitals on the same side of a pendent phenyl group of the polymer, such that both cis-hydrogen atoms of the olefin are thrust onto the phenyl ring while both $(CH_2)_nH$ groups attached to the olefinic double bond extend away from the adsorption site at a relatively sharp angle, as shown in Figure 2f of ref 17. This should also be true for the cyclic olefins, but the markedly increased constraint on random motion imposed by the ring configuration should favor

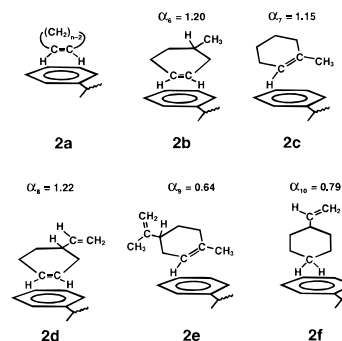


Figure 2. Suggested modes of adsorption for cyclohexenes and related molecules.

better packing at the adsorption site, which should be manifested in a large difference in α_i but only a small difference in D_s for their respective $\log \alpha$ vs N linear relationships.

The purpose of this publication is to report and compare the results observed in this study with those recorded in Figure 1 for the *cis*- $CH_3CH=CH(CH_2)_nH$, the cyclic $(CH_2)_n$, and the cyclic $(CH_2)_nO$ series, and also to report the conclusions derived therefrom.

Experimental Section

The set of six composite film samples, employed as the polymeric sorbent in all our previous studies of $(Sty)_{1-x}(DVB)_x$ swelling-to-saturation in hundreds of test liquids, were used again in this study of sorption of cyclic olefinic liquids. A large portion of this study was carried out before each of the original set of composite film samples had been subdivided into five unequal smaller portions (as described in our publication regarding sorption of sulfur-containing liquids¹⁵), which was done to permit us to use a "scaled-down" version of the original protocol in the evaluation of liquid samples that were only available to us in small amounts (<10 mL). The procedure for making these composite film samples, comprised of $(Sty)_{1-x}(DVB)_x$ particles (>80 wt %) enmeshed in PTFE microfibers, and the distribution of these particles in the microporous composite films produced thereby (see Figures 1, 6, 7, and 20 of ref 1) are described in considerable detail elsewhere.^{1–12} Reagent grade samples of test liquids were obtained from commercial sources, and they were used as such without further purification. The only exception was cyclooctatetraene, which was purified just before use by fractional distillation (bp = 50 ± 1 °C at 20 Torr, $n_D^{24} = 1.5352$; lit bp = 48 °C at 17 Torr, $n_D^{25} = 1.5350$)¹⁸ to remove higher molecular weight products that had formed during storage.

A set of composite film samples, each having a known value of x (i.e., $x = 0.01, 0.02, 0.03, 0.04, 0.08$, or 0.11), was allowed to swell to saturation in excess test liquid at 23 ± 1 °C. Thereafter, the volumes (S) of sorbed liquid per gram of enmeshed particles in these samples were determined gravimetrically in the usual way.^{1–12} The slope of the straight line, obtained when the S values are plotted as a function of the corresponding cube root of the average number λ [i.e., the ratio $(1+x)/x$ calculated for the sample having the average composition $(Sty)_{1-x}(DVB)_x$] of backbone carbon atoms between covalent cross-linked junctions in the respective samples, identifies the relative swelling power (C , in mL of adsorbed liquid per gram of particles) of the sorbed test liquid, in accordance with eq 2.

$$S = C(\lambda^{1/3} - \lambda_0^{1/3}) \quad (2)$$

TABLE 1: Sorption Data for Cyclic Olefins

(A) Monounsaturated $[-CH=CH-(CH_2)_n]-$								
no. of compound	molecular structure	N^a	d^b	$\lambda_o^{1/3}$	C^d	α^e	χ_1^f	
1	cyclopentene, $n = 3$	5	0.774	1.70	1.39	1.65	0.65	
2	cyclohexene, $n = 4$	6	0.811	1.72	1.47	1.51	0.60	
3	cycloheptene, $n = 5$	7	0.824	1.70	1.45	1.30	0.62	
4	<i>cis</i> -cyclooctene, $n = 6$	8	0.846	1.71	1.33	1.07	0.69	
5	cyclododecene, $n = 10$	12	0.863	1.70	0.16	0.09	1.40	
(B) Substituted Cyclohexenes and Related Olefins								
no. of compound	molecular structure	fig ^g	N	d	$\lambda_o^{1/3}$	C	α	χ_1
6*	(±)4-methyl-1-cyclohexene ^b	2b	7	0.799	1.70	1.39	1.20	0.65
7*	1-methyl-1-cyclohexene	2c	7	0.813	1.72	1.31	1.15	0.70
8	(±)4-vinyl-1-cyclohexene	2d	8	0.832	1.82	1.52	1.22	0.57
9	(±)limonene, 50/50 mix	2e	10	0.842	1.66	0.99	0.64	0.90
9a	(+)limonene, $n_D^{20} = 1.4722$		10	0.840	1.70	1.01	0.65	0.88
9b	(-)limonene, $n_D^{20} = 1.4718$		10	0.844	1.70	1.01	0.65	0.88
10	vinyl cyclohexane	2f	8	0.805	1.70	1.04	0.79	0.87
(C) Polyunsaturated Cyclic Hydrocarbons								
no. of compound	molecular structure		N	d	$\lambda_o^{1/3}$	C	α	χ_1
11	1,4-cyclohexadiene		6	0.847	1.77	2.06	2.26	0.24
12	benzene		6	0.879	1.75	2.14	2.50	0.19
13	cycloheptatriene ⁱ		7	0.888	1.80	2.11	2.12	0.21
14	1,5-cyclooctadiene ⁱ		8	0.882	1.90	2.14	1.81	0.19
15*	styrene		8	0.909	1.85	2.09	1.91	0.23
16*	cyclooctatetraene		8	0.916	1.90	2.15	1.96	0.19
17	1,5,9- <i>trans,trans,cis</i> -cyclododecatriene ^j		12	0.890	1.76	1.89 ^j	1.08	0.35

^a N : is the total number of methylene mass units or equivalent. ^b d : is the density of the liquid. ^c $\lambda_o^{1/3}$: is the value of $\lambda^{1/3}$ (eq 2) extrapolated to $S = 0$. ^d C : is the relative swelling power, as defined in eq 2. ^e α : is the adsorption parameter, as defined in eq 3. ^f χ_1 : is the Flory–Huggins interaction parameter, calculated using eq 4. ^g Figure: reference to Figures 2b–f, which show the molecular structure and mode of adsorption to the pendent phenyl group of the polymer at liquid saturation. ^h (±): indicates that the sample is a mixture of optically active isomers. (–) indicates *leavo*-rotatory; (+) indicates *dextro*-rotatory. ⁱ Mixture of *cis*–*trans* isomers. ^j More than a week was required to attain swelling equilibrium at 23 °C.

Here λ_0 is the value of λ extrapolated to $S = 0$. The corresponding adsorption parameter (α) was calculated from the observed C values by means of eq 3

$$\alpha = 104Cd/M \quad (3)$$

The letters d and M refer to the density and formula weight, respectively, of the test liquid.

The Flory–Huggins interaction parameter (χ_v) is also calculated from C by means of eq 4, as described elsewhere.¹⁹

$$\chi_v = 0.49 + 1.01v - 0.61vC \quad (4)$$

Here v is the volume fraction of polymer in the polystyrene–liquid system. Since it was noted that χ_v is most sensitive to the molecular structure of the sorbed species at $v = 1$ (see Figure 4 of ref 19), only the χ_1 values are reported in Table 1. The χ_v values at any other value of v can be calculated using eq 5.

$$\chi_v = 0.49 + v(\chi_1 - 0.49) \quad (5)$$

Results and Discussion

Accumulation of Sorption Data. The sorption data accumulated in these studies using cyclic olefinic liquids are recorded in Table 1. These are subdivided into three categories: *cyclic monoolefins* (1–5); *miscellaneous substituted cyclohexenes* (6–10); and *multi-unsaturated cyclic hydrocarbons* (11–17). The test liquids that were evaluated using the “scaled-down” version of the original protocol are identified by an asterisk placed next to the respective identification numbers, which were assigned to the corresponding molecular structure in accordance with the numerical order listed in Table

1. The relative swelling powers (C , eq 2) established for these liquids were used to calculate the corresponding adsorption parameters (α) and the Flory–Huggins interaction parameters (χ) by means of eqs 3 and 4, respectively, as described in the Experimental Section.

Interpretations of the Sorption Data. *Cyclic Olefinic Liquids.* The data points for the five available samples of the *cyclo*-[CH=CH(CH₂) _{$n-2$}]- (members $n = 5-8$ and 12, (1–5 in Table 1) are recorded in Figure 1, which shows that the first four data points (filled circles) lie between the observed linear portions of the reference lines for the cyclic ethers (CH₂) _{n} O ($n = 3$ to 9, series 1 in Table 2) and the cyclic hydrocarbons (CH₂) _{n} ($n = 4$ to 10, series 2 in Table 2).

Consistent with expectation, the fifth data point (filled circle at $N = 12$ in Figure 1) lies between the upper and lower dashed line extensions of these reference lines (series 1 and 2 in Table 2), which represent the respective anticipated sharp deviations from linearity established by the lower members of these cyclic series. In the case of the cyclic ethers, deviation from linearity beginning at about $n = \text{ca. } 8$ was expected on the basis of analogy with the observations of Prelog and others^{20–24} who noted that cyclic homologous series of the type (CH₂) _{n} A, where A is a functional group such as >CHOH, >CHNH₂, and >C=O, react normally with chemical reagents when n is less than 9, but are insensitive toward those reagents when n is in the range 9–12. These investigators attributed the observed anomalous chemical behavior to steric hindrance owing to the compacted cyclic polymethylene chain that causes the functional group to be directed inward rather than outward, thereby rendering the normally reactive group inaccessible to the reagent even when dissolved therein.

TABLE 2: $\log \alpha_f = \log \alpha_i - D_s(N_f - N_i)$ Relationships for Various Cyclic Homologous Series^d

homologous series	no. of compound	$\alpha_i:N_i$	D_s	$\alpha_f:N_f$	r^2
$(\text{CH}_2)_m\text{O}, m = 3-9$	1	3.31:4	0.0888	[0.97]:10	0.9999
$(\text{CH}_2)_m, m = 4-10$	2	0.863:4	0.0875	[0.258]:10	0.993
$\text{CH}_3\text{CH}(\text{CH}_2)_{m-1}, m = 4-10$	2a	0.481:5	0.0875	[0.143]:10	
$[\text{CH}=\text{CH}(\text{CH}_2)_{m-2}], m = 4-8$	3	1.99:4	0.0518	[0.97]:10	
<i>cis</i> - $\text{CH}_3\text{CH}=\text{CH}(\text{CH}_2)_n\text{H}, n = 1-8$	4	0.464:4	0.0326	0.0412:11	
$\text{CH}_3\text{O}(\text{CH}_2)_n\text{H}, n = 1-8$	5	0.82:4	0.0505	0.59:11	
<i>cyclo</i> - $\text{C}_6\text{H}_{11}(\text{CH}_2)_n\text{H}, n = 0-8$	6	0.570:6	0.2537	0.00539:14	0.9997
<i>cyclo</i> - $\text{C}_5\text{H}_9(\text{CH}_2)_n\text{H}, n = 0-8$	7	0.72:6	0.0998	0.00673:14	
<i>cyclo</i> - $\text{C}_6\text{H}_{11}\text{CH}(\text{CH}_3)(\text{CH}_2)_{n-1}\text{H}, n = 1-9$	6a	0.10:9	0.2537	0.00539:14	
<i>cyclo</i> - $\text{C}_6\text{H}_{11}\text{CH}(\text{CH}_3)_2(\text{CH}_2)_{n-1}\text{H}, n = 1-9$	6b	0.053:10	0.2537	0.00539:14	
†Srs 8					
<i>cyclo</i> - $\text{C}_6\text{H}_{11}\text{CH}_3-q(\text{CH}_3)_q, q = 0-3$	8	0.32:7	0.2552	0.053:10	0.9996
2- $\text{H}(\text{CH}_2)_n[\text{C}_m\text{H}_{2m-1}\text{O}]$					
$n = 0-8 \quad m = 3$	9a	3.31:4	0.174	0.134:12	
$n = 0-8 \quad m = 4$	9b	2.70:5	0.174	0.109:13	
$n = 0-8 \quad m = 5$	9c	2.21:6	0.174	0.090:14	
$n = 0-8 \quad m = 6$	9d	1.74:7	0.174	0.073:15	
†Srs 1					
3- $\text{H}(\text{CH}_2)_n[\text{C}_m\text{H}_{2m-1}\text{O}]$					
$n = 0-8 \quad m = 3$	10a	3.31:4	0.157	0.184:12	
$n = 0-8 \quad m = 4$	10b	2.70:5	0.154	0.158:13	
$n = 0-8 \quad m = 5$	10c	2.21:6	0.151	0.137:14	
$n = 0-8 \quad m = 6$	10d	1.74:7	0.147	0.119:15	
†Srs 1					
4- $\text{H}(\text{CH}_2)_n$ -1-cyclohexene	11				
$n = 0-8$		1.51:6	0.0998	0.240:14	

^a α_i and α_f refer to the initial and final α -value in the homologous series being considered. N_i and N_f refer to the corresponding total number of methylene mass units. D_s is the decrementation constant for the series being considered. r^2 is the square of the correlation coefficient determined by linear regression for the homologous series being considered. m , n , and q are integers that indicate the number of methylene units in the structural variable being considered.

In the case of sorption involving cyclic ethers $[(\text{CH}_2)_n\text{O}]$ having $n > 9$, such sequestering would render the oxygen atom unavailable for association with the polymer. Hence the α values for these molecules should decrease sharply from the $\log \alpha$ vs N linear relationship established for the lower members, shifting downward to the α values characteristic of the corresponding $(\text{CH}_2)_n$ liquids. The latter also exhibit a similar sharp negative deviation from linearity beginning at about $n = 9$ (Figure 1), but for a different reason: self-association involving its methylene units eliminates the entropic advantages that favor adsorption in the cases of the smaller members, and in the cases of the yet higher members leads to formations of microcrystalline domains.²⁵ That the α value for cyclododecene (0.09, **5** in Table 1) lies between the extrapolated α values for $(\text{CH}_2)_{11}\text{O}$ and $(\text{CH}_2)_{12}$ (0.16 and 0.06, respectively, at $N = 12$ in Figure 1) is consistent with the observations made by the earlier investigators,²⁰⁻²⁴ and it supports the rationale offered by them to explain the anomalous behavior exhibited by cyclic molecules having 9–12 members. Thus in both cases the sharp deviation from the linearity established for the lower members was caused by a marked change in the mode of adsorption.

It must be stressed here that the cause of the above sharp negative deviations, beginning at about $n = 8$ or 9 (Figure 1), is not the same as that for the change which occurs in a linear $\text{A}(\text{CH}_2)_n\text{H}$ series when n is > 8 , as exhibited for example in Figure 1 of ref 16 by the $\log \alpha$ vs N relationship for the $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{H}$ series. The deviation exhibited by the higher members of such linear series is caused by correlated molecular orientation of the methylene units between molecules without change in the mode of adsorption, as discussed previously.^{3-6,26-28}

Because as expected, the data points for the higher members of *cyclo*- $[\text{CH}=\text{CH}(\text{CH}_2)_{n-2}]$ deviated sharply from linearity, only the first three observed data points (**1**, **2**, and **3** in Table 1) were used to calculate by linear regression its characteristic \log

α vs N linear relationship (series **3** in Table 2; $\alpha_i = 0.188$ at $N = 4$, represented by an empty circle in Figure 1; $D_2 = 0.05177$; $r^2 = 0.979$). This relationship was then used to calculate the “phantom” values for the $n = 8-11$ members, i.e., the values (indicated in Figure 1 by empty squares) that would have been exhibited by these members if the cause for negative deviation from the linearity established by the lower members were absent.

Comparison of the $\log \alpha$ vs N linear relationships established for the types of cyclic molecules (series **1**, **2**, and **3** in Figure 1 and Table 2), show clearly that their relative affinity (α_i at $N = 4$) for polystyrene is in the order $-\text{O}- > -\text{CH}=\text{CH}- \gg -\text{CH}_2-$. The negative effect on $\log \alpha$ caused by incrementation of ring size, as indicated by the decrementation constant (D_s) for these homologous series, however, is in the order $-\text{O}- \approx -\text{CH}_2- > -\text{CH}=\text{CH}-$, such that the extrapolations of the $\log \alpha$ vs N linear relationships for the cyclic ethers and the cyclic olefins intersect at the “phantom” data point, $\alpha = 0.97$; $N = 10$. This large difference in sensitivity to ring incrementation is believed to reflect the relative product of (A) the forces of attraction times (B) the molecular area at the interface between the adsorption site and the respective functionalities making liaison thereto (i.e., AB); in the case of the ethers, this involves only a single atom, as suggested in Figure 9 of ref 14, whereas in the case of the olefins it involves the length of the carbon-carbon double bond, as suggested here in Figure 2a. The approximately 2-fold greater area in the latter case is responsible for the greater stability, or perhaps the greater loss of degrees of freedom, which is reflected in a smaller decrementation constant for the series. Similar results were noted when the $\log \alpha$ vs N linear relationship established for the thioethers, $\text{CH}_3\text{S}-(\text{CH}_2)_n\text{H}$, was compared with that for the corresponding $\text{CH}_3\text{O}-(\text{CH}_2)_n\text{H}$ series. This was interpreted to mean¹⁵ that the product of greater affinity times wider adsorption base afforded by the

sulfur atom (relative to the oxygen atom) renders the thioethers less sensitive to incrementation of $(\text{CH}_2)_n\text{H}$ from $n=1$ to ca. 4.

As stated in the Introduction, the α values for the cyclic molecules studied thus far are uniformly much greater than those for the corresponding acyclic molecular structures, provided that the mode of adsorption of the species being considered is essentially the same. This is attributed to a marked decrease in steric hindrance to further adsorption, owing to cyclization which imparts severe constraints on random motion of the substituents covalently bonded to the atom (or functional group) making liaison with the adsorption site. Such constraints also result in higher densities for the cyclic liquids. It was suggested that the mode of adsorption for *cis*- $\text{CH}_3\text{CH}=\text{CH}(\text{CH}_2)_n\text{H}$ (see Figure 2f of ref 17) should be essentially the same as that (Figure 2a) for *cyclo*- $[\text{CH}=\text{CH}(\text{CH}_2)_{n+1}]$ -, which implies that the log α vs N linear relationship for the cyclic series (**3** in Table 2) should be uniformly above that for the acyclic series (**4** in Table 2).

This is indeed the case: Figure 1 shows that the log α vs N linear relationship for series **3** is significantly above that for series **4**. It is noted, however, that the decrementation constant ($D_4 = 0.0326$) for the acyclic series is somewhat less than that ($D_3 = 0.0518$) for the cyclic series. Similarly, the decrementation constant ($D_5 = 0.0505$) for $\text{CH}_3\text{O}(\text{CH}_2)_n\text{H}$ is less than that ($D_1 = 0.0888$) for $(\text{CH}_2)_{n+1}\text{O}$ (series **5** and **1**, respectively, in Table 2). These observations can be rationalized on the basis that incrementation in the acyclic series affects only one substituent attached to the atom (or functional group) making liaison with the adsorption site, whereas each incrementation in the cyclic series affects both substituents attached thereto.

The excess in α (i.e., $\Delta\alpha = \alpha_{\text{cyclic}} - \alpha_{\text{linear}}$) observed in such comparisons appears to increase markedly with the affinity of the functionality making liaison with the adsorption site, i.e., ethers > olefins > saturated hydrocarbons. This is interpreted to mean that when random motion of the attached $(\text{CH}_2)_n\text{H}$ substituent is tethered by cyclization the result is a marked improvement in the entropic considerations that favor more efficient self-assembly (i.e., higher density) at the adsorption site, such that the magnitude of $\Delta\alpha$ reflects the affinity of the functional group (or atom) making liaison with the adsorption site. This observation is in qualitative agreement with the observations noted for similar comparisons involving cyclization of linear $\text{ZCRH}(\text{CH}_2)_n\text{H}$ to give the corresponding cyclic $\text{ZCR}(\text{CH}_2)_n$,¹⁴ where R is H or CH_3 and Z is I, Br, or Cl.

Substituted Cyclohexenes. We noted in the preceding section that the α values for molecules that comprise homologous series having the cyclic GMSs $(\text{CH}_2)_m$, $(\text{CH}_2)_{m-1}\text{O}$, and $-\text{CH}=\text{CH}(\text{CH}_2)_{m-2}-$ are affected by incrementation of m from 4 to 10, and that the respective log α vs N linear relationships thereof are influenced by the relative affinities of the members of these series for the pendent phenyl groups of polystyrene at liquid saturation [here m is used to refer to the number of methylene units that comprise the ring structure to differentiate this from the number of methylene groups in a $(\text{CH}_2)_n\text{R}$ side chain covalently bonded thereto]. It was now of interest to investigate the effects on cyclohexene caused by systematic structural permutations of these $(\text{CH}_2)_n\text{R}$ substituents and to compare these results with those reported in Parts 20 and 22 of this ongoing study of sorption based on molecular structure, which deal respectively with sorption of alkyl-substituted cyclic ethers¹⁴ and cyclic hydrocarbons.¹⁶

The marked effect on α caused by incrementation of methylene units in $(\text{CH}_2)_n\text{H}$ substituents covalently bonded to cyclohexane (series **6** in Table 2) is recorded in Figure 3 of ref 16, which shows that the negative slope ($D_2 = 0.0875$) of the

log α vs N linear relationship for incrementation of m in *cyclo*- $(\text{CH}_2)_m$ from 4 to 10 (series **2** in Table 2) is about a third of that ($D_6 = 0.254$) for incrementation of n in $\text{H}(\text{CH}_2)_n$ -cyclohexane from 0 to 8. The latter reflects the magnitude to which the entropic effects that favor adsorption in the cases of *cyclo*- $(\text{CH}_2)_m$ molecules having $m < 10$ is negated by $\text{H}(\text{CH}_2)_n$ substituents covalently bonded to the ring-structure. The above comparative results show that this negative influence, owing to incrementation of n from 0 to 8 while m is kept constant at 4–10, is about half that which occurs at constant n per unit increase in m greater than 10.

The data point observed for methylcyclopentane ($\alpha = 0.39$; $N = 6$ in Figure 3 of ref 16) was used to verify that the log α vs N linear relationship for $\text{CH}_3\text{CH}(\text{CH}_2)_{m-1}$ (series **2a** in Table 2), which passes through this data point and that ($\alpha = 0.32$; $N = 7$) for methylcyclohexane, is parallel to the log α vs N linear relationship for *cyclo*- $(\text{CH}_2)_m$ ($m = 4$ to 10, series **2** in Table 2), and also that the log α vs N linear relationship for *cyclo*- $(\text{C}_5\text{H}_9)(\text{CH}_2)_n\text{H}$ ($n = 0$ –8, series **7** in Table 2), which passes through the data points for cyclopentane and methylcyclopentane, is parallel to the log α vs N linear relationship for $\text{H}(\text{CH}_2)_n$ -cyclohexane ($n = 0$ to 8, series **6** in Table 2). Since this is consistent with expectation based on our earlier studies,^{10–15} it was assumed that the α values for all the permutations of the GMS *cyclo*- $[(\text{CH}_2)_{m-1}\text{CH}](\text{CH}_2)_n\text{H}$, in which n is incremented from 0 to 8 while m is kept constant at 4–10, are given by the intersections of the set of seven relationships that are parallel to that for *cyclo*- $(\text{CH}_2)_m$ and the set of nine relationships that are parallel to that for *cyclo*- $(\text{C}_6\text{H}_{11})(\text{CH}_2)_n\text{H}$ (series **2** and **6** respectively in Table 2), as indicated in Figure 3 of ref 16.

It was interesting to note that the data points observed for isopropyl- and *tert*-butylcyclohexanes are essentially the same as the corresponding data points for *n*-propyl- and *n*-butylcyclohexanes, which means that the α values for such R-substituted cyclic hydrocarbons are affected only by the mass of the R substituent covalently bonded thereto and virtually independent of its molecular architecture. Thus, the decrementation constants for the log α vs N linear relationships characteristic of the three cyclohexane series in which R is $-\text{CH}_3$, $-\text{CH}(\text{CH}_3)(\text{CH}_2)_n\text{H}$ and $-\text{C}(\text{CH}_3)_2(\text{CH}_2)_n\text{H}$ (series **8**, **6a**, and **6b**, respectively, in Table 2) are essentially the same as that ($D_6 = 0.254$) observed for the series in which R is $(\text{CH}_2)_n\text{H}$ (series **6**).

This insensitivity to branching at the carbon atom adjacent to the ring structure is interpreted to mean that the location of R on the ring structure is on a ring carbon atom that is not adjacent to the adsorption site. The above results also show that each member of the *cyclo*- $(\text{CH}_2)_m$ series is the first member of the respective series having the GMS *cyclo*- $[(\text{CH}_2)_{m-1}\text{CH}](\text{CH}_2)_n\text{H}$, which means that the decrementation constants for the latter set of series can be established with reasonable confidence via eq 1 after the α value for only one additional member ($n = 1$ –8) in the series being considered is determined experimentally, as indicated in Figure 3 of ref 16.

The above observations have important significance for consideration of the data accumulated for the alkyl-substituted cyclic ethers, because only the α values for methyl substituted members of such series have been established experimentally, as summarized in Figure 5 of ref 14. In these series liaison with the adsorption site involves the ether oxygen atom; consequently, the decrementation constant for incrementation of an attached $(\text{CH}_2)_n\text{H}$ group from $n = 0$ to 8 will depend on the proximity of this group to that atom, i.e., it should vary inversely with the number of ring carbon atoms between the two sites.

This is indeed the case as indicated by the $\log \alpha$ vs N linear relationship for series **9a–d** and **10a–d** in Table 2, which were deduced from the data recorded in Figure 5 of ref 20 for the 2- and 3-methyl- and dimethyl-substituted cyclic ethers. The decrementation constants (D_s , eq 1) for each series of 2-substituted cyclic ethers (i.e., 2- $\text{H}(\text{CH}_2)_n[\text{C}_m\text{H}_{2m-1}]\text{O}$ having $m = 3–6$, series **9a–d** in Table 2) is $D_9 = \text{ca. } 0.174$, which means that D_s for this series is independent of m . The D_s values for each of the corresponding 3-substituted series (i.e., 3- $\text{H}(\text{CH}_2)_n[\text{C}_m\text{H}_{2m-1}]\text{O}$, series **10a–d**), however, decrease monotonically with m from $D_{10a} = 0.157$ at $m = 3$ to $D_{10d} = 0.147$ at $m = 6$, which reflects how the influence of dynamic associative interaction of the branched substituents with the mobile sorbed-but-not-adsorbed molecules in the gelled system at liquid saturation increases with the number of ring carbon atoms between the branching site and the adsorption site, as discussed previously.¹⁴

It should be noted here that the D_s values observed for the series in which the number of methyl substituents in the 2- or 3-positions of the respective cyclic ether series that was increased from 0 to 2 (see Figure 5 of ref 14) are the same as that for the corresponding $\text{H}(\text{CH}_2)_n[\text{C}_m\text{H}_{2m-1}]\text{O}$, in which n is incremented from 0 to 3 (series **9a–d** and **10a–d** in Table 2), which here again suggests that the $\log \alpha$ vs N linear relationship for R-substituted cyclic molecules depends primarily on the mass of the R substituent and is relatively independent of its molecular architecture, as was observed to be the case for the cyclic $(\text{CH}_2)_{m-1}\text{CHR}$ molecules.¹⁶

Since the D_s values for the 2-RCH $(\text{CH}_2)_{m-1}\text{O}$ series are somewhat greater than those for the set of 3-RCH $(\text{CH}_2)_{m-1}\text{O}$ series, which decrease monotonically with increase in m , it can be assumed that the D_s values for the 4-RCH $(\text{CH}_2)_5\text{O}$ series will be equal to or only slightly less than that observed for the corresponding 3-RCH $(\text{CH}_2)_5\text{O}$ series.

Having established the above relationships for the cyclic $(\text{CH}_2)_m$ and $(\text{CH}_2)_m\text{O}$, it is now possible to use this information as a reference base that permits meaningful interpretation of the α values observed for the five substituted cyclic molecular structures (6 to 10) recorded in Table 1. The data collected in the above reference base demonstrates that the unsubstituted cyclic moieties are the first member of the corresponding $\text{H}(\text{CH}_2)_n$ -substituted series. Hence it is reasonable to assume that this is also true for the $\text{H}(\text{CH}_2)_n$ -cyclohexenes (series **11** in Table 2).

Thus, the decrementation constant (D_{11}) for the 4-substituted cyclohexene series was calculated, by means of eq 1 using only the α values for cyclohexene and ± 4 -methyl-1-cyclohexene (1.51 and 1.20, respectively; **2** and **6** in Table 1), to be $D_{11} = 0.0998$, which is only about two-thirds of that ($D_{10c} = 0.151$) for the corresponding $\text{H}(\text{CH}_2)_n$ -substituted cyclic ethers (series **10c** in Table 2), and less than two-fifths of that ($D_6 = 0.254$) for the $\text{H}(\text{CH}_2)_n$ -substituted cyclic saturated hydrocarbons (series **6** in Table 2). The above order of relative sensitivity to incrementation of methylene units in the polymethylene side chain parallels that for the corresponding products (P) of (A), the relative affinity of the group making liaison with the adsorption site, times (B), the relative area of the interface between the adsorbed molecule and that adsorption site (i.e., $P = AB$). This observation is qualitatively similar to that noted earlier for the corresponding comparisons regarding D_s for incrementation of m in the cyclic series $(\text{CH}_2)_m$, $(\text{CH}_2)_m\text{O}$, and $-\text{CH}=\text{CH}(\text{CH}_2)_{m-2}-$. The differences noted in the earlier comparisons for incrementation of m , however, are markedly less than those noted in the present comparisons for incremen-

TABLE 3: $\log \alpha_f = \log \alpha_i - D_s(N_f - N_i)$ Relationships for Subseries of Hydrocarbons Having the GMS $\text{cyclo}-(\text{CH}_2)_{n-2q}(\text{CH}=\text{CH})_q$ —^a

n	q	no. of series	$\alpha_i:N_i$	D_s	$\alpha_f:N_f$	r^2
4–12	0	2	0.863:4	0.0875	0.172:12	$\Leftarrow 0.993$
4–12	1	3	1.87:4	0.0518	0.724:12	$\Leftarrow 0.979$
4–12	2	12	2.82:4	0.0482	1.16:12	
6–12	3	13	2.50:6	0.0601	1.08:12	$\Leftarrow 0.9991$
8–12	4	14	1.96:8	ca. 0.09	0.86:12	
10–12	5	15	ca. 0.9:10	ca. 0.014	0.47:12	
12	6	16	ca. 0.01:12			

^a n , q , α_i , α_f , N_i , N_f , D_s , and r^2 are as defined in the footnotes of Table 2.

tation of n in the side chain, which supports the point of view that the product $P = AB$ is an important consideration that determines the relative D_s for such incrementations.

Since a liquid sample of a 3- $[\text{H}(\text{CH}_2)_n]$ -substituted cyclohexene having $n = 1$ to 8 is not yet available to us, we were not able to determine the D_s value for this series in the manner described above for the corresponding 4-substituted cyclohexenes (series **11** in Table 12). It is reasonable to expect, however, that D_s for the 3-substituted cyclohexene series will be somewhat greater than that ($D_{11} = 0.0998$) for the 4-substituted cyclohexenes, because of the relative proximities to the adsorption site, and consequently the former should impart greater steric hindrance to adsorption than the latter. Hence, the α values for the $n = 1–8$ members for the former series should be uniformly slightly less than those for the corresponding members of the latter series. The $\log \alpha$ vs N linear relationships for the two series, however, should meet at the data point $\alpha = 1.51:N = 6$ for cyclohexene ($n = 0$, **2** in Table 1), which is the member common to both series.

From the standpoint of adsorption, cyclohexene (**2** in Table 1) is not the first member of the 2- $[\text{H}(\text{CH}_2)_n]$ -substituted cyclohexenes, because the former is a dialkyl-substituted ethylene and the latter are trialkyl-substituted ethylenes, which have different modes of adsorption.¹⁷ In the case of *cis*-dialkyl-substituted ethylenes the modes of adsorption involve both double-bonded carbon atoms, as shown in Figures 2a and b, whereas only one double bonded carbon atom can be involved in the case of trialkyl-substituted ethylenes. The remainder of the molecular structure extends away from the adsorption site, as shown in Figure 2c. Hence, the first member of the 2- $[\text{H}(\text{CH}_2)_n]$ -substituted cyclohexene series is 1-ethylcyclohexene and consequently the α value for at least one more member ($n = 2–8$) of this series is needed in order to establish its decrementation constant, before one can make meaningful comparisons with the corresponding 3- and 4-substituted cyclohexenes.

The effect on α caused by a change in molecular structure at constant N from that for 4-methylcyclohexene to that for 1-methylcyclohexene can be appreciated by comparison of their α values at $N = 7$, i.e., $\alpha = 1.20$ and 1.15 (**6** and **7**, respectively, in Table 1). A decrease in α of about the same magnitude is caused by an analogous molecular transformation at constant N in the acyclic series. Thus, the α value for *cis*-2-pentene is 0.43, whereas that for 2-methyl-2-butene is 0.37 (**25** and **28**, respectively, in Table 3 of ref 17). Both of these results, caused by similar methyl group transpositions at constant N , are attributed to the change in the mode of adsorption owing to replacement of one of the two hydrogen atoms attached to the double bond by a methyl substituent, as shown in Figure 2a–c.

Comparison of the α -value for 1-methylcyclohexene (1.15) with that (0.37) for *cis*-2-heptene (**26** in Table 3 of ref 17)

confirms that ring closure of an acyclic olefin to the corresponding cyclic olefin causes a marked improvement in the entropic factors that favor adsorption. It is assumed that this may also be true for the tri- and tetrasubstituted olefins, but unfortunately we have not been able to obtain such samples, which would have enabled us to test this assumption.

Although sufficient experimental data has not yet been accumulated to permit one to establish the $\log \alpha$ vs N linear relationships for the homologous series, in which 4-vinyl-1-cyclohexenes (**8** and **9** in Table 1) are members, when these data are compared with the large reference base already accumulated for related series, it is possible in each case to adjudicate which of the two double bonds (external or internal) is actually involved in liaison with the adsorption site, in the manner described previously in Table 6 of ref 17. The α value (1.22) for 4-vinyl-1-cyclohexene (**8** in Table 1) is much closer to that (0.954, series **11** in Table 2) for 4-ethyl-1-cyclohexene than it is to that (0.23, see Table 1 in ref 17) for $\text{H}(\text{CH}_2)_6\text{CH}=\text{CH}_2$, or that ($< \text{ca. } 0.4$) estimated for cyclohexyl ethylene. Hence, in this case it can be asserted that the double bond in the ring is the one that makes liaison with the adsorption site, while the external olefin remains in the nonadsorbed portion of the molecule that extends away from the adsorption site, where it is involved in dynamic associative interactions with the mobile sorbed-but-not-adsorbed molecules in the polymer-liquid system at saturation, and that the mode of adsorption is akin to that for a cis-disubstituted olefin, as shown in Figure 2d.

In the case of (\pm)limonene (**9** in Table 1, Figure 2e) the consideration is more complicated because one is trying to adjudicate between an external gem-disubstituted ethylene structure and an internal trisubstituted cyclic ethylene structure in a molecule that is chiral owing to an asymmetric carbon atom. We found that the chirality affects the α value only slightly. Duplicate determinations of an approximately 50:50 mixture of the chiral isomers showed that $\alpha = 0.64$, whereas those for duplicate determinations of dextro- and levo-rotatory samples ($>97\%$ pure) showed that $\alpha = 0.65$ (**9a** and **9b**, respectively, in Table 1), which assured us that this difference was at most only a minor complicating factor. Thus we could establish the mode of adsorption by the usual method of comparison with related structures belonging to series whose modes of adsorption had already been established. To this end, we noted that the α value (0.64) for (\pm)limonene is much closer to that ($> \text{ca. } 0.5$) anticipated for 4-isopropyl-1-methylcyclohexene than it is to that ($< \text{ca. } 0.2$) anticipated for *gem*-methyl-4-methylcyclohexyl-ethylene (i.e., ring hydrogenated limonene). We concluded, therefore, that the double bond internal in the ring structure is the one that is a liaison with the adsorption site, as shown in Figure 2e, and that the mode of adsorption is akin to that of a trialkyl-substituted olefin (See Figure 2g in ref 17).

The mode of adsorption for vinylcyclohexane (**10** in Table 1) is less clear. Comparison of its α -value (0.79) with that (0.23) for 1-*n*-octene (see **4** in Table 1 of ref 17) and with that (0.18) for ethylcyclohexane (**12** in Table 1 in ref 16), does not allow one to differentiate easily and unambiguously between the two alternatives. The possibility that the vinyl group is the one making liaison with the adsorption site leaving the cyclohexyl group in the "nonadsorbed" portion of the molecule where it is free to be involved in dynamic associative interactions to alleviate steric hindrance to further adsorption (i.e., exhibit a "desteric" effect), is about as probable as the alternative, namely, that the cyclohexyl group is the one that is a liaison with the adsorption site, leaving the vinyl group in the "nonadsorbed portion" where it is free to interact with the mobile molecules

of its own kind. Earlier comparisons of this type (see Table 6 in ref 17 and Table 4 in ref 15), however, have shown that the affinity of cyclohexyl and $-\text{CH}=\text{CH}_2$ groups for a pendent phenyl group on polystyrene are comparable, but the ability of the latter to contribute "desteric" influences owing to dynamic associative interactions is much greater than that of the former. On the basis of this consideration it is believed tentatively that it is the cyclohexyl group of vinyl cyclohexane that is making liaison with the adsorption site, as shown in Figure 2f, leaving $-\text{CH}=\text{CH}_2$ in the nonadsorbed portion where it can exert a stronger "desteric" influence than can a nonadsorbed cyclohexyl group.

Polyunsaturated Cyclic Hydrocarbons. *cyclo*- $[(\text{CH}_2)_{n-2q}(\text{CH}=\text{CH})_q]$ -. The $\log \alpha$ vs N plots (Figure 1) for $(\text{CH}_2)_n$ and for *cyclo*- $[(\text{CH}_2)_{n-2}\text{CH}=\text{CH}]$ -, series **2** and **3**, respectively, in Tables 2 and 3, show that deviation from the linearities established by the best straight line through the data points for the lower members ($n = 4$ to $n' < 11$) begins even sooner in the case of the latter series (at $n' = \text{ca. } 8$) than it does in the former series (at $n' = \text{ca. } 10$), as shown in Figure 1. One suggestion is that this difference might be attributed to a progressive increase in the ratio of trans to cis configurations in the analyte samples as n increases above 8, which serves to exacerbate the negative effect caused by the "sequestering" phenomenon described previously. This exacerbation may be responsible for the very low α -value (0.09 at $N = 12$) observed for cyclododecene (**10** in Table 1), which is about 63% trans.

If the above suggested causes were responsible for the observed deviation, then the addition of one or more olefinic double bonds (at least one of which would have a cis configuration) should produce a marked positive effect on the α values for the members in each cyclic series being considered. As on steric grounds a trans-double bond should be more readily sequestered, it is assumed that the cis-double bond would be available for liaison via the cis-mode of adsorption, even when $n > 8$, and that the other(s) might be available for dynamic associative interactions with the mobile sorbed-but-not-adsorbed molecules of its own kind, which serves to exert a "desteric" effect, as described earlier.¹⁷ That this is indeed the case is shown by the data points for the set of seven cyclic olefins having more than one double bond (**11–17**) recorded in Table 1, all of which lie considerably above the $\log \alpha$ vs N plot in Figure 1 for the corresponding members of *cyclo*- $[(\text{CH}_2)_{n-2}\text{CH}=\text{CH}]$ -. This is especially true for the members having $n > 8$, as shown by the comparison of the α value (1.08, **17** in Table 1) for 1,5,9-*trans,trans,cis*-cyclododecatriene with that (0.09) for cyclododecene. The latter has its double bond "sequestered" within the polymethylene chain, where it is precluded from making contact with the adsorption site, whereas one of the three double bonds in the former makes contact with the adsorption site, probably via the cis-double bond, leaving at least one of the two trans-double bonds free to contribute a "desteric effect".

A remaining problem is to establish how the α values for homologous series having the GMS *cyclo*- $[(\text{CH}_2)_{n-2q}(\text{CH}=\text{CH})_q]$ - vary quantitatively with both n and q . The results observed in similar studies involving homologous series having the GMS $\text{H}(\text{CH}_2)_n\text{CH}_3$ - $q\text{Z}_q$ -, in which Z is Cl, Br, OCH_3 , or OCH_2CH_3 , showed that α at constant n exhibit maximal values at $q = 2$ or 3, depending on the value of n , as described in the Introduction (for examples see Figures 6 and 9 in ref 12). The observed maxima reflect the net results of the electronic, steric and associative contributions, which affect the mode of adsorption differently as q is incremented from 0 to 3 at constant n . It

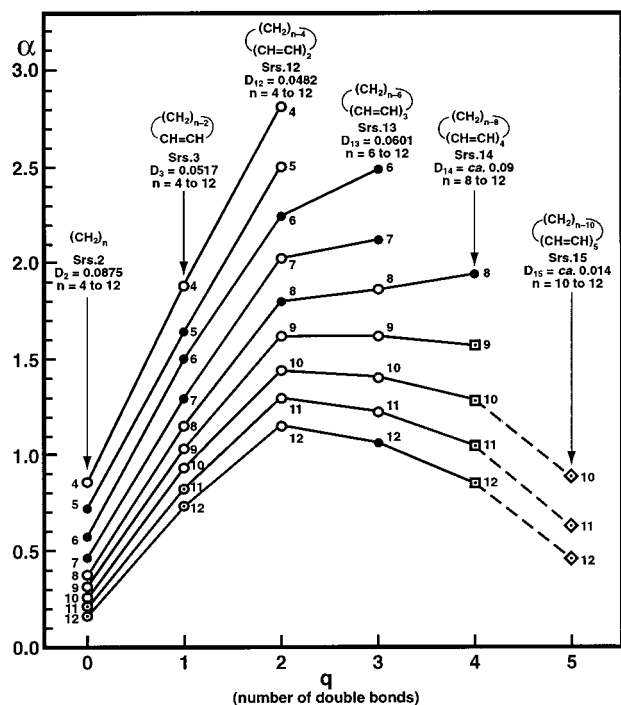


Figure 3. The effect on α for the cyclic polyethylenes $[(CH_2)_{n-2q}(CH=CH)_q]$ caused by increasing ring size (n) and progressive unsaturation (q).

was reasoned by analogy with these results that similar relationships might be exhibited by subseries of *cyclo*- $[(CH_2)_{n-2q}(CH=CH)_q]$ -, which could be revealed by creating a map that scales from 0.1 to 4.0 on the vertical coordinate the α values for each subseries in which n is incremented from its initial n' to its allowable limit at $q = 0, 1, 2, 3$, and 4 scaled from 1 to 6 on the horizontal coordinate, as shown in Figure 3.

To this end, the α values deduced for the nine members of the two subseries in which q is kept constant at 0 and 1 while n is incremented from 4 to 12 (Series **2** and **3** respectively in Table 3) are recorded in the column of data over the horizontal coordinates $q = 0$ and 1 in Figure 3. The experimental data points used to establish $D_2 = 0.0875$ and $D_3 = 0.0518$ are indicated by filled circles. The data established by extrapolation by means of eq 1 are indicated by empty circles, and those of these sets that are "phantom values" are indicated by the dot-in-a-circle symbols. The column of α values for the nine members of the subseries in which $q = 2$ (series **12** in Table 3) were calculated by means of eq 1 using the data points determined experimentally for members $n = 6$ and 8 [filled circles in Figure 3, **11** and **14** in Table 1, $D_{12} = (\log \alpha_6 - \log \alpha_8)/2 = 0.0487$].

The $\log \alpha$ vs N linear relationship for the subseries in which q is kept constant at 3 while n is incremented from 6 to 12 (series **13** in Table 3) was determined by linear regression ($r^2 = 0.9991$; $\alpha_i = 2.47$ at $N = 6$; $D_{13} = 0.06005$), using the data points established experimentally for members $n = 6, 7$, and 12 (filled circles in Figure 3, **12**, **13**, and **17** in Table 1). The α values for the rest of the members in this series (indicated by empty circles) were determined therefrom by interpolation, using $\alpha_i = 2.47$ at $N = 6$ and $D_{13} = 0.06005$.

Since only the first member (cyclooctatetraene, **16** in Table 1) of series **14** ($q = 4$; $n = 8-12$ in Table 3) was determined experimentally, it was not possible to establish D_{14} for its $\log \alpha$ vs N linear relationship unequivocally. Its approximate value, however, can be estimated by analogy with the results observed in similar studies involving sorption of $H(CH_2)_nCH_3-qZ_q$ liquids, as described above. These studies showed that D_s for the

homologous series in such comparisons that follow after the q series of maximal values is about 1.5 that of the preceding series. In this case, D_s for the maximal series (i.e., $q = 3$, series **13** in Table 3) is $D_{13} = 0.060$. Hence, D_s for series **14** should be about $D_{14} = 0.09$, which enables one to estimate accordingly the α values for the remaining members of series **14**, as indicated in Table 3. These estimated values for the four remaining members of series **14** are indicated in the data column at $q = 4$ of Figure 3 by the dot-in-a-square symbols, the placement of which is meant only to show qualitatively how the magnitude of negative slope in going from $q = 3$ to 4 at constant n will increase linearly with n , in the manner shown in Figures 7 and 9 of ref 12.

The above results show clearly that progressive unsaturation (incrementation of q) at constant ring size (n) causes α to increase accordingly to a maximal value attained at a value of q that depends on n . In every case the positive effect on α over the first two incrementations of q causes a sharp and almost linear increase, but thereafter the net results are relatively small positive contributions, which even become negative contributions owing to the steric factors that negate the entropic factors that favor self-assembly at the adsorption site, such that the α values for the first and last members of series **15** ($q = 5$, $n = 10-12$, Table 3) are estimated to be below 0.9 and 0.5 respectively (indicated in Figure 3 by the empty diamond symbols at the end of the dashed lines), and that the α -value for the first member of series **16** ($q = 6$, $n = 12$) is estimated to be below 0.1 .

In this respect it is interesting to compare the effect on α caused by incrementation of q from 0 to its maximum possible value in the rings having $n = 4, 6$, and 8 . When n is 6 , the observed increase in α caused by incrementation of q from 2 to 3 is about a third of that caused by incrementation of q from 1 to 2 , despite that the end product is an aromatic structure (i.e., benzene, $\alpha = 2.50$). The comparison is even more pronounced when n is 8 ; the increase in α caused by incrementation of q from 2 to 4 is about a seventh of that from 1 to 2 . In this case the end product is cyclooctatetraene, the α -value of which (1.96) is comparable to that (1.91) for styrene (**15** and **16**, respectively, in Table 1). These values in turn are significantly greater than that (1.55) for ethyl benzene. These results reflect the complicated (and not yet fully understood) manner in which the electronic, steric, and "desteric" factors interact to influence the value of α .

When one or more samples of a $H(CH_2)_n$ -*cyclo*- $[CH(CH_2)_{n-1-2q}(CH=CH)_q]$ - series having $n = 1$ to 8 become available, it will then be possible to establish the characteristic $\log \alpha$ vs N linear relationship for those subseries representing substitution on a ring-methylene unit at least once removed from the $CH=CH$ units. Those subseries in which the substituent is on one of the ring double bonds will require at least one additional sample to establish its characteristic $\log \alpha$ vs N linear relationship, because substituents in such positions cause a change in the mode of adsorption from that characteristic of the parent *cyclo*- $[(CH_2)_{n-2q}(CH=CH)_q]$ - molecule, thereby eliminating the possibility that it is the first member of the corresponding $H(CH_2)_n$ -substituted series.

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