Polymer Swelling. 20. Sorption of Cyclic Mono- and Polyethers by Poly(styrene-*co*-divinylbenzene)

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The adsorption parameters (α, with respect to polystyrene) for 20 cyclic aliphatic ethers were established experimentally in the usual way. Among this set of ethers are members from three cyclic structural categories, namely, the polymethylene oxides [$(CH_2)_nO$; $n = 2-9$], the polymethylene formals [$(CH_2)_nOCH_2O$; $n = 2-11$], and the polyethylene oxides [$(CH_2CH_2O)_e$; $e = 1-5$], and some of the corresponding methyl or *gem*-dimethyl modifications thereof. The data obtained thereby were used to establish the log α vs N linear relationships (eq 1) for each of the subsets of homologous series contained in each of these structural categories, as described in the text. These linear relationships were then used to calculate the α-values for the many remaining members that are not yet available for experimental measurement in our laboratory. The results obtained thereby show that the α-values for the cyclic ethers in a given homologous series are uniformly greater than those for the corresponding set of acyclic ethers. They also confirm that methyl groups have a marked negative effect on α when positioned on the carbon atoms adjacent to the adsorbed ether oxygen atom, but they have the opposite effect when located one or more carbon atoms removed from adjacency. The magnitude of this positive effect appears to increase with the distance from the adsorption site. These observations parallel those observed in our earlier studies involving the corresponding acyclic aliphatic ethers.

Introduction

Earlier publications[1] 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, using a set of six $(Sty)_{1-x}(DVB)_x$ samples having known values of x, as described in considerable detail elsewhere[1−13] and recounted briefly here in the Experimental Section. These α-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. The α-values established thus far (>500 in all)[1−13] range from 0 to about 3.7, and they are reproducible to within ± 0.01.

By considering homologous series of liquids having general molecular structures (GMSs) of the types $H(CH_2)_{m+1}(CH_3)_{q'}CH_{2-q'}OCH_{2-q}(CH_3)_q(CH_2)_{n+1}H$ {in which m is an integer from 0 to 7, n is an integer from m to 7, and q' and q are integers from 0 to 2},[10−12] and the corresponding polyethers of the types $R'O(CH_2)_cOR$ {in which c is an integer from 2 to 12} or $R'O(CH_2CH_2O)_eR$ {in which e is an integer from 0 to 5},[13] it was observed that if one of the variables (m, n, q, q', c, and e) is incremented systematically within its allowable limits while the rest are kept constant, the logarithms of the α-values for the molecules that comprise that series vary linearly with N, the total number of methylene mass units (or equivalent) plus the ether oxygen atoms, i.e., [$N = 1 + m + n + q + q' + (c + 1) + 3e$], as expressed by eq 1.

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

Here N_f and N_i are the respective final and initial N values of the homologous series being considered, α_f and α_i are the corresponding α-values, and D_s is the characteristic decrementation constant (i.e., the decrease in log α per unit increase in N) for that series. The magnitude of D_s reflects not only the variable being incremented but also the proximity of that incrementation to the ether oxygen atom immobilized by liaison to the adsorption site.[12]

Since each of the subsets of homologous series within the above GMS classification can be represented by a vector of the type expressed by eq 1, it is possible to deduce, for that classification, the network of rigidly interconnected vectors in multidimensional space which includes the adsorption preference as one of the variables, i.e., which portion (R′O) of the adsorbed molecule (R′OR) is immobilized at the adsorption site and which portion (R) extends away from that site because of dynamic interaction with the mobile nonadsorbed R′OR molecules in that system at liquid-saturation. The points of intersection in this network of interconnected vectors in multidimensional space identify the α-values of all the possible permutations for the GMS being considered. Thus, after the α-values for only a relatively few members of the large set of liquids having a given GMS are determined experimentally, it is possible to deduce with reasonable confidence the α-values for the remaining members that comprise that classification, as described in considerable detail in refs 10−13.

In those cases for which the sorbed liquids are members of homologous series having the GMSs $ZCH_{2-q}(CH_3)q(CH_2)_nH$, in which Z is a univalent substituent (such as chloro, bromo, iodo, or phenyl group) that has a strong affinity for the phenyl groups in the polymer, q is an integer from 0 to 2, and n is an integer from 1 to 7,[1−8] the phenomena of adsorption are much less complicated than those for the above cases involving mono- and polyethers because the portion (Z) of the adsorbed molecule (ZR) that makes liaison with the adsorption site in a given classification is nonvariant, and therefore there are only two variables (n and q) that need to be considered in the corresponding log α vs N relationships (eq 1; in these cases $N = n + q + 1$).

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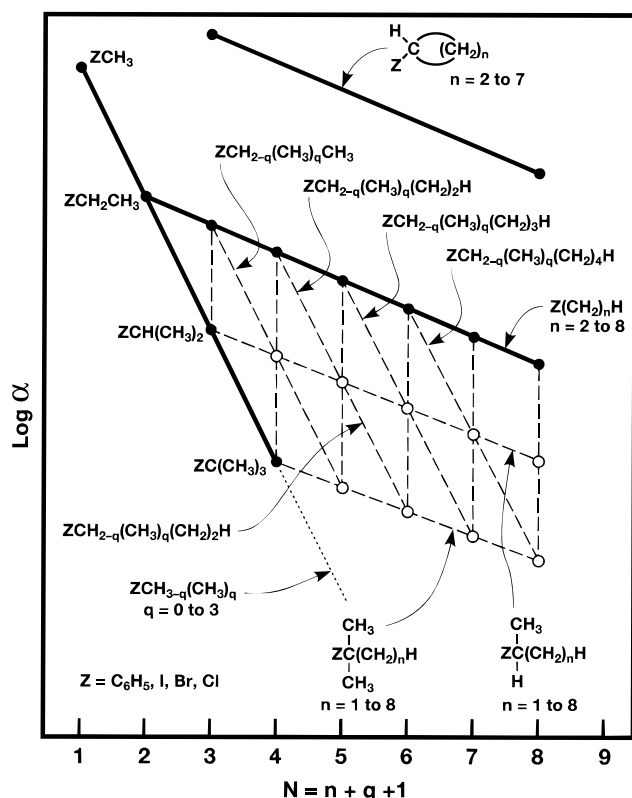
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Figure 1. Correlation of log α with the total number ($N = n + q + 1$) of aliphatic carbon atoms in the members of homologous series of liquids represented by the GMSs $ZCH_{3-q}(CH_3)_q$, $ZCH_{2-q}(CH_3)_q(CH_2)_nH$, and $ZCH(CH_2)_n$, showing the effect on log α caused by incremental increases in q while n is kept constant at $1-7$, and the corresponding effect when n is increased incrementally while q is kept constant (see also Figures $2-13$ and Tables $1-9$ in ref 7).

TABLE 1: Correlation of Z with the Corresponding $\alpha_{z,i}$- and $D_{z,s}$-Values (Eq 1) for $ZCH_{3-q}(CH_3)_q$ $\{q = 0-3\}$ and for $ZCH_{2-q}(CH_3)_q(CH_2)_nH$ $\{q = 0, 1,$ or 2 and $n = 1$ to 7 or $8\}$

Z	q	n	$\alpha_{z,i}$[f]	$D_{z,s}$[g]
I	$0-3$	0	3.45	0.127[a]
	0	$1-7$	2.64	0.087[b]
	1	$1-8$	1.91	0.087
	2	$1-8$	1.43	0.087
Br	$0-3$	0	2.72	0.096[a]
	0	$1-7$	2.26	0.070[c]
	1	$1-8$	1.83	0.070
	2	$1-8$	1.34	0.070
Cl	$0-3$	0	3.21	0.180[a]
	0	$1-7$	2.23	0.077[d]
	1	$1-8$	1.44	0.077
	2	$1-8$	0.97	0.077
Ph	$0-3$	0	1.98	0.140[a]
	0	$1-7$	1.55	0.076[e]
	1	$1-8$	1.23	0.076
	2	$1-8$	0.99	0.076

[a] Data taken from Table 3 of ref 7. [b] Calculated using the $\alpha_{z,n}$-values for $n = 2-8$, recorded in Table 1 of ref 4. [c] Calculated using the $\alpha_{z,n}$-values for $n = 2-8$, recorded in Table 1 of ref 6. [d] Calculated using the $\alpha_{z,n}$-values for $n = 2-8$, recorded in Table 1 of ref 5. [e] Calculated using the $\alpha_{z,n}$-values for $n = 2-8$, recorded in Table 3 of ref 2. [f] $\alpha_{z,i}$ is the α-value for $ZCH_{3-q}(CH_3)_q$ when $q = 0$ or for $ZCH_{2-q}(CH_3)_q(CH_2)_nH$ when $n = 1$ at $q = 0, 1,$ or 2. [g] $D_{z,s}$ is the decrementation constant established by the best straight line through the set of data points for $ZCH_{3-q}(CH_3)_q$ from $q = 0$ to 3, and for $ZCH_{2-q}(CH_3)_q(CH_2)_nH$ from $n = 1$ to 7 when q is 0 or from $n = 1$ to 8 when q is > 0.

TABLE 2: Correlation of Z with the Corresponding $\alpha_{z,i}$- and $D_{z,s}$-Values (Eq 1) for *cyclic*-$ZCH(CH_2)_n$ $\{n = 3-12\}$

Z[a]	$\alpha_{z,3}$[b]	$\alpha_{z,n}$	$D_{z,s}$[c]
I	[1.97]	$\alpha_5 = 1.43$[d]	ca. 0.07[e]
Br	[2.16]	$\alpha_4 = 1.91$[d]	0.054[f]
		$\alpha_5 = 1.62$[d]	
		$\alpha_6 = 1.49$[d]	
Cl	[2.29]	$\alpha_4 = 1.95$[d]	0.070[f]
		$\alpha_5 = 1.66$[d]	
Ph	[1.53]	$\alpha_5 = 1.11$[d]	ca. 0.07[e]

[a] Z is the functional group in the cyclic $ZCH(CH_2)_n$ liquid. [b] $\alpha_{z,3}$ is the $\alpha_{z,n}$-value for $ZCH(CH_2)_3$; the brackets indicate that it is an estimated value, established by means of eq 1. [d] $D_{z,s}$ is the decrementation constant established for the $ZCH(CH_2)_n$ series from $n = 3$ to 12. [d] Data taken from Table 9 of ref 7. [e] Estimated from Figure 13 of ref 7. [f] Calculated using the $\alpha_{z,n}$-values listed.

Thus, for a given classification based on the functional group Z, the α-values for all the permutations in the molecular structures of that classification lie in a plane in three-dimensional space that is defined by the log α vs N relationships (eq 1) established for $Z(CH_2)_nH$, in which n is $2-8$, and that for $ZCH_{3-q}(CH_3)_q$, in which q is $0-3$. The log α vs N relationships (eq 1) for the homologous series having the GMS $ZCH_{2-q}(CH_3)_q(CH_2)_nH$, in which q is 1 or 2 and n is incremented from 1 to 8, are parallel to those established for $Z(CH_2)_{n+1}H$; those for the corresponding crossover relationships from $q = 0-2$ at $n = 1-7$ are parallel to that for $ZCH_{3-q}(CH_3)_q$, as shown schematically in Figure 1. Since the mass and electronic character of Z affect the mode in which it makes liaison at the adsorption site, the paired constants $\alpha_{z,i}$ and $D_{z,s}$ in these log α vs N relationships (eq 1) vary with Z, as recorded in Table 1.

Having established the log α vs N relationships for the liquids having the GMS $ZCH_{2-q}(CH_3)_q(CH_2)_nH$, these results (Table 1) were compared with those (Table 2) for the corresponding cyclic $ZCR(CH_2)_n$ liquids. These comparisons (Figure 1; see also Figures $11-13$ in ref 7) show that in every case the log α vs N relationship for a given cyclic series lies uniformly above the corresponding acyclic series, as shown in Figure 1. Moreover, the negative value of the decrementation constant ($D_{z,s}$; eq 1) for the cyclic series (upper bold straight line in Figure 1) is significantly less than that for the corresponding acyclic series (set of bold straight lines crossed over by a set of thin dashed straight lines at $n = 1-7$), as indicated schematically in Figure 1.

It was inferred from these observations that the cyclic molecules can self-assemble on the adsorption site much more efficiently than can the corresponding acyclic molecules, presumably owing to the greater restriction on random motion in the cyclic configuration relative to that in the corresponding acyclic configuration. That $D_{z,s}$ (eq 1) for the cyclic series (Table 2) is less negative than that for the corresponding acyclic series (Table 1) suggests that the verticality of the former with respect to the adsorption site is greater than that for the latter. Similar results were noted earlier[8,12] in the comparisons of $\alpha_{z,n}$ for the $Z(CH_2)_nZ$ liquids with those for the corresponding $Z(CH_2)_nH$ liquids, which reflects how well the substituent (Z or H) on the terminal carbon atom of the nonadsorbed portion undergoes dynamic interaction with the mobile sorbed-but-not-adsorbed molecules in the system, as described previously.[8,12] In the case of the *cyclo*-$ZCR(CH_2)_n$ liquids, however, the observed positive effect on α_n may be due solely to improved self-association in a more rigid mutually supportive vertical array on the adsorption site.

It is now of interest to determine whether or not the above difference, exhibited by the relatively simple sets of *cyclo*-ZCR-$(CH_2)_n$ and $ZCHR(CH_2)_nH$ liquids, will also be exhibited by the ethers and polyethers, which represent considerably more complicated sets of homologous series, as described above. The

TABLE 3: Sorption Data for the Cyclic Aliphatic Ethers[a]

	identification of the sorbed cyclic ether		adsorption data					
E#	name	formula	N	d	$\lambda_0^{1/3}$	C	α	χ_1
1	oxetane	$(CH_2)_3O$	4	0.893	1.71	2.07	3.31	0.24
2	tetrahydrofuran	$(CH_2)_4O$	5	0.889	1.79	2.11	2.70	0.21
3	tetrahydropyran	$(CH_2)_5O$	6	0.881	1.80	2.08	2.21	0.23
4	oxepane	$(CH_2)_6O$	7	0.890	1.74	1.94	1.79	0.32
5	furan	$(CH)_4O$	5	0.936	1.80	1.82	2.60	0.39
6	3,3-dimethyloxetane		6	0.835	1.95	1.59	1.61	0.55
7	2-methyltetrahydrofuran		6	0.860	1.71	1.74	1.81	0.44
8	3-methyltetrahydropyran		7	0.863	1.70	1.74	1.56	0.44
9	*p*-dioxane (1,4-dioxane)	$(CH_2CH_2O)_2$	6	1.034	1.75	1.72	2.10	0.45
10	12-crown-4 (1,4,7,10-tetraoxocyclodecane)	$(CH_2CH_2O)_4$	12	1.089	1.65	1.76	1.13	0.43
11	4-methylmorpholine	$CH_3N(CH_2CH_2)_2O$	7	0.920	1.92	2.07	1.95	0.24
12	1,3-dioxolane	$(CH_2)_2[OCH_2O]$	5	1.064	1.70	1.52	2.27	0.57
13	2,2-dimethyl-1,3-dioxolane		7	0.926	1.84	1.80	1.70	0.40
14	1,3-dioxane	$(CH_2)_3[OCH_2O]$	6	1.032	1.75	1.62	1.98	0.51
15	4-methyl-1,3-dioxane		7	0.976	1.78	1.60	1.59	0.52
16	5,5-dimethyl-1,3-dioxane		8	0.951	1.76	1.64	1.39	0.50
17	tetramethylene formal	$(CH_2)_4[OCH_2O]$	7	1.002	1.78	2.02	2.06	0.28
18	methyl tetrahydrofurfuryl ether (2-(methoxymethyl)tetrahydrofuran)		7	0.952	1.70	1.83	1.56	0.38
19	2-methoxy-1,3-dioxolane		7	1.092	1.71	1.40	1.52	0.65
20	methyl cyclopentyl ether	$CH_3OCH(CH_2)_4$	7	0.861	1.85	1.90	1.70	0.34

[a] E# is the numerical identification of the named ether. N is the total number of mass units; i.e., the sum of methylene groups plus oxygen atoms in the molecule. d is the density of the sorbed liquid. λ_0 is the value of λ extrapolated to $S = 0$, as defined in eq 2. C is the relative swelling power of the sorbed liquid, as defined in eq 2. α is the adsorption parameter of the sorbed liquid, as defined in eq 3. χ_1 is the Flory–Huggins interaction parameter as defined in eqs 4 and 5, i.e., $\chi_1 = 1.50 - 0.61C$.

purpose of this publication is to report the results of such investigations and 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 a test-liquid,[1–12] were used again in the present studies of swelling in cyclic aliphatic ethers. The procedure for making these composite film samples, comprised of $(Sty)_{1-x}(DVB)_x$ particles (>80% by weight) 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.[1–6] This set of samples, each containing microparticles having a known value of x (i.e., $x = 0.01, 0.02, 0.03, 0.04, 0.08,$ or 0.11), were allowed to swell to saturation in the test-liquid at 23 ± 1 °C. Reagent grade samples of these liquids were obtained from commercial sources, and they were used as such without further purification. An exception, however, is 5,5-dimethyl-1,3-dioxane (E# 14 in Table 3), which was synthesized in our laboratories and purified by distillation, as described elsewhere.[14]

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 cross-link junctions in the respective samples indicates the relative swelling power (C, in mL of adsorbed liquid per gram of particles) of the sorbed test-liquid in accordance with eq 2.

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

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.

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

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.[15]

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

Here v is the volume fraction of polymer in the polystyrene–liquid system.

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 14). Unfortunately, the usual methods for measuring χ_1 are often reproducible only to ± 1 in the first significant figure; in contrast, the polymer swelling method enables one to establish α-values that are reproducible to ± 1 in the third significant figure for liquids having α-values > 1. Thus, the α-values are ideal for correlation with molecular structure, whereas such correlations are less than satisfactory using χ_v established by the usual methods, because of the relatively poor precision in measuring the latter, as noted above. It is understood that χ_1-values, calculated by means of eqs 3 and 4, can be used in such correlations studies in lieu of the corresponding α-value. Consequently, only the χ_1-values are reported here (Table 3). The χ_v-values at any other value of v can be calculated by the interested reader using eq 5.

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

In those cases for which the α-values were not determined experimentally (i.e., those values that were established by extrapolation using eq 1), it is necessary to establish the molar volume (M/d) of that liquid before one can convert to the corresponding χ_1-value by means of eqs 3 and 4.

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TABLE 4: Sorption of Cyclic Monoethers Having the GMS $(CH_2)_nO$; $n = 2-12$; Series No. 1[a]

E#	n	N	α_N	D_1	α_4
0	2	3	[3.97][b]		
1	3	4	**3.31**	0.08879 ($r^2 = 0.9999$)	3.25
2	4	5	**2.70**		
3	5	6	**2.21**		
4	6	7	**1.79**		
4a	7	8	1.46		
4b	8	9	1.19		
4c	9	10	[0.97][c]		
4d	10	11	[0.79][c]		
4e	11	12	[0.65][c]		
4f	12	13	[0.53][c]		

[a] E# is as defined in the footnotes of Table 3. N is the total number of mass units in $(CH_2)_nO$; in this case, $N = n + 1$. D_1 is the decrementation constant for series no. 1, i.e., the negative slope of the line of best fit ($r^2 = 0.9999$) through the data points for the cyclic ethers having $n = 3, 4, 5$ and 6. Bold numerals indicate the data that were determined experimentally. [b] This is the hypothetical α-value for ethylene oxide, if it were adsorbed in the symmetrical vertical mode, characteristic for the higher members of this series. [c] These are the hypothetical α-values for 4c–4f in the absence of the unique form of steric hindrance characteristic of $(CH_2)_nO$ having $n = 9-12$.

Results and Discussion

Determination of α-Values for Cyclic Ethers. The relative swelling power (C; eq 2) for 20 cyclic ethers (E#s 1–20 in Table 3) were determined experimentally in the usual way,[1-12] and these values were then 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. These data, which contain the α-values for members from many diverse homologous series of cyclic ethers based on their GMS, can now be used to infer the α-values for the remaining members of these series by interpolation and/or extrapolation via the linear relationship expressed by eq 1, which is based on systematic incrementation of one variable that determines the molecular architecture of the alkyl portion in a given series while the rest are held constant, as described in the Introduction.

An important problem in such extrapolations, however, is in the identification of the range over which the variable can be incremented without causing deviation from the linearity expressed by eq. 1. For example, in the cases of homologous series having GMSs of the type $Z(CH_2)_nZ'$, where Z is a halogen, phenyl, or alkoxy group and Z' is Z, H, or a branched alkyl group, the limits for incrementation of n without causing deviation from linearity are from 1 to ca. 8 when Z' is H; but when Z' is Z or a branched alkyl group, the limits are from 2 to ca. 12; that is, the two terminal Z' and Z groups serve to prevent self-association of $(CH_2)_n$ chains between two molecules as long as n is less than about 13.

Cyclic Monoethers $(CH_2)_nO$ and Related Structures. In the case of the cyclic $(CH_2)_nO$, i.e., series no. 1 in Table 4, the allowable limit over which n can be extended without inducing deviation from the linearity expressed by eq 1 has not yet been established experimentally. If we assume that the upper limit is ca. 12, as is the case for the linear ethers $R'O(CH_2)_nR$ for which R is an alkoxy or nonlinear alkyl group or functional group such as ester or keto, then the set of α-values for the members that comprise this cyclic series is as given tentatively in Table 4. The α-values for the members having $n = 3-6$ (bold numerals in Table 4) were used to establish the log α vs N linear relationship (eq 1) for series no. 1 by linear regression. The decrementation constant (i.e., the negative slope of the best straight line through this set of four data points) and the square

of the correlation coefficient are respectively $D_1 = 0.0888$ and $r^2 = 0.9999$. The α-values for the remaining members of this series ($n = 2$ and 7–12 in Table 4) were determined by extrapolation via eq 1, based on the assumption that the ether oxygen atoms in the members of the $(CH_2)_nO$ series from $n = 2$ to $n = 12$ are equally accessible to the adsorption site.

Ethylene oxide, the member having $n = 2$, is a gas at room temperature and pressure, which precluded establishing its α-value under the standard conditions described in the Experimental Section, and the members having $n > 6$ are not yet available to us. Hence we were not able to test this assumption in our laboratory.

We have strong reasons to believe, however, that this assumption may not be valid. It is well-known[16,17] that the strain energy for medium (i.e., $n = 8-12$) sized cyclic $(CH_2)_n$ molecules is maximal at about $n = 10$. This is also true for the corresponding cyclic alcohols,[18] ketones,[18] and amines,[19] which affects adversely the usual reactivity for these functional groups toward their respective coreactants. This negative effect was attributed by the investigators[18-20] to steric hindrance imparted by the tightly compacted molecular cyclic polymethylene chain when n is 9, 10, or 11, and because the functional group is directed inward rather than outward from the composite bulk of that cyclic structure. This point of view was supported by the respective IR spectra for these cyclic molecules.[19,20]

Thus, we suspect that the ether oxygen atoms in $(CH_2)_nO$ may be more impeded from attaining the necessary proximity for association with the adsorption site when n is 9, 10, or 11 than it is when n is less than 9. Nevertheless, the linearly predicted α-values for these members are recorded in Table 4 to provide a reference base-line to indicate what the values would be in the absence of such steric impedance. When and if these liquids become available for determination of their respective α-values, the magnitude of difference between observed and hypothetical values will reflect the magnitude of the expected impedance as a function of n. These hypothetical values (E#s 4c–4f in Table 4; footnote c), however, are placed in brackets to serve as a caveat to the reader that these bracketed values may be higher than their anticipated "true" values. Hereinafter, the estimated α-values for a cyclic ether having more than nine contiguous methylene units in its ring structure will not be recorded because of the reasons described above.

A similar caveat is given in respect to the value obtained by extrapolation in the opposite direction, i.e., to $n = 2$ [bracketed value for $(CH_2)_2O$ in Table 4; footnote b]. Searles and Tamres have reported[21] that the basicities (i.e., electron-donating capacities) of oxiranes (i.e., propylene oxide and other such substituted oxides) are markedly less than those of the corresponding cyclic ethers $(CH_2)_nO$ having $n = 3, 4$, or 5. These investigators attributed this effect to "an alteration of electron distribution with ring size".[21] Moreover, in our own studies of polymer swelling in homologous series of liquids having the GMS $Z(CH_2)_nZ$, in which Z is a chloro, bromo, or methoxy group, it was observed that the α-values for the members having $n = 1$ deviate sharply from the log α vs N linear relationship (eq 1) established using the higher members (i.e., $n = 3-10$). In these cases, the compound ZCH_2Z proved to be the first member of the corresponding $Z_2CH(CH_2)_nH$ series rather than that for the $Z(CH_2)_nZ$ series, which we attributed to the electronic factors that affect the carbon atom adjacent to the adsorption site.[8,12]

Accordingly, we decided to attempt to infer the α-value for $(CH_2)_2O$ via another extrapolation using the log α vs N relationship for a second homologous series, namely, the linear α-olefin epoxides $H(CH_2)_n(CHCH_2O)$ [i.e., series no. 2; $n = 0-10$ in Table 5], the first member of which is ethylene oxide.

TABLE 5: Sorption of Epoxides Having the GMS $H(CH_2)_n(CHCH_2O)$; $n = 0-10$, Series No. 2, $\alpha_0 = 2.94$ and $D_2 = 0.0767$ in Eq 1; $r^2 = 0.999^a$

E#	n	N	d	$\lambda_0^{1/3}$	C	α	χ_1
0	0	3				$[2.94]^b$	
20	1	4	0.830	1.80	1.46	**2.17**	0.62
21	2	5	0.837	1.80	1.71	**2.07**	0.47
21a	3	6				1.73	
22	4	7	0.831	1.80	1.66	**1.43**	0.50
22a	5	8				1.21	
23	6	9	0.839	1.78	1.52	**1.04**	0.59
23a	7	10				0.85	
24	8	11	0.840	1.79	1.26	**0.71**	0.74
24a	9	12				0.60	
25	10	13	0.844	1.81	1.03	**0.49**	0.88

^{a} E#, N, d, λ_0, C, α, and χ_1 are as defined in the footnotes of Table 3. The α-values recorded in bold numerals were determined experimentally. The α-values recorded in light numerals were determined by interpolation using the calculated best straight line through the set of experimentally determined data points except that for E# 20. ^{b} This is the hypothetical α-value for ethylene oxide if it were absorbed in the tilted vertical mode, characteristic of the higher members ($n > 0$) of this series.
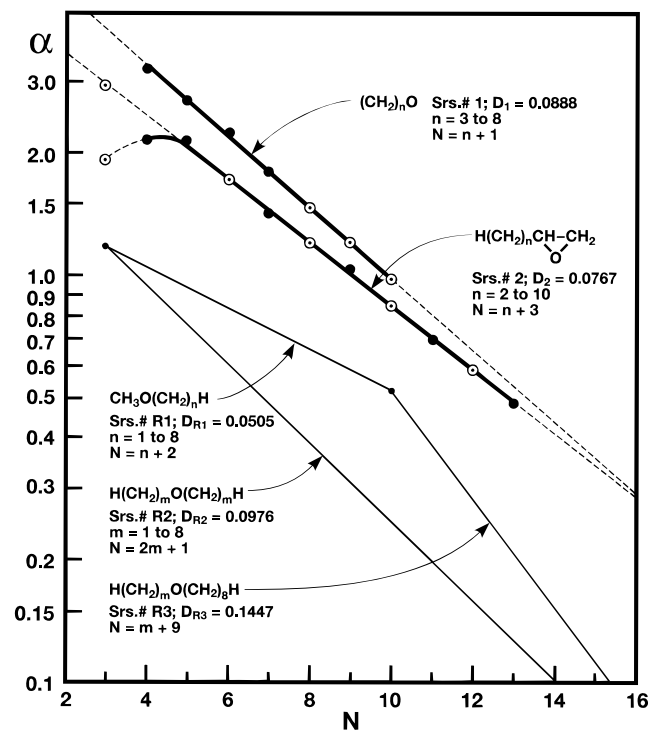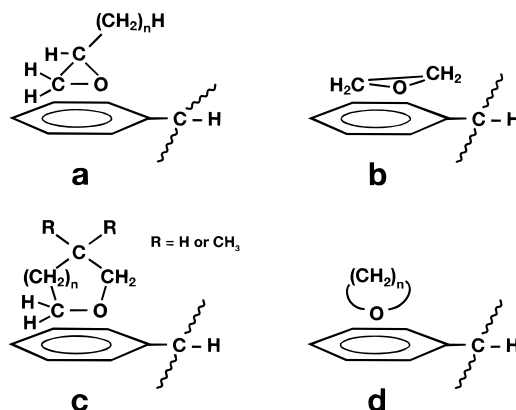

Figure 3. Schematic representations of modes for molecular adsorption of cyclic ethers to the pendent phenyl groups of polystyrene at liquid-saturation.

(dashed line extension) to $\alpha = 2.99$ at $N = 3$ rather than to 3.97, as noted for series no. 1. This proves that ethylene oxide cannot be the common first member of both series nos. 1 and 2. The negative slope ($D_1 = 0.0888$) for series no. 1 (the cyclic monoethers) is significantly greater than that ($D_2 = 0.0767$) for series no. 2 (the epoxides), which reflects the manner in which the adjacent carbon atoms affect the molecular architecture of the adsorbed molecule with respect to the "plane" of the adsorption site, i.e., the phenyl groups of the polymer at liquid-saturation. A methylene incrementation in the cyclic series affects the orientation of both methylene groups adjacent to the immobilized (adsorbed) oxygen atom, whereas a methylene incrementation in the side chain of the epoxide series affects only the molecular architecture of the nonadsorbed portion of the adsorbed molecule.

It is noticed, however, that the data point for propylene oxide ($\alpha = 2.17$: $N = 4$ in Figure 2, and E# 20 in Table 5) is significantly below that expected ($\alpha = 2.46$: $N = 4$ in Figure 2) on the basis of extrapolation using the log α vs N linear relationship established experimentally for series no. 2. This marked decrease below expectation at $N = 4$ (i.e., when $n = 1$) cannot be explained on the basis of the expected small change in electronic structure. It is, therefore, a "red flag" that signals the possible beginning of a change in the mode of adsorption from that exhibited by the higher members that comprise the epoxide series, i.e., from a rather vertical configuration (Figure 3a) to a relatively flatter configuration (Figure 3b) with respect to the plane of the adsorption site.

This point of view is supported by results, soon to be submitted for publication, dealing with sorption of linear homologous series of aliphatic ketones, esters, acetylenes, olefins, and nitriles; the lower members of these series ($n < 3$) deviate sharply from the corresponding log α vs N linear relationship established using only the data observed for the higher members ($n > 3$ but < 9). We also observed that this type of deviation from linearity exhibited by the lower members of a given homologous series is essentially erased when swelling of poly-(Sty-*co*-DVB) is allowed to occur in binary solutions comprised of equimolar amounts of the test-liquid and a second liquid that, while a nonsolvent for the polymer, has affinity for a test-liquid that when used neat exhibits the anomalous deviation.[22] Mutual association of the two components that comprise the sorbed liquid serves to suppress adsorption in the flatter mode owing to the enhanced dynamic interaction with the mobile sorbed-but-not-adsorbed molecules in the system at liquid-saturation, as discussed previously.[8,9,12]

If this sort of deviation were indeed occurring in the epoxide series (no. 2), then the α-value of ethylene oxide might be as

Figure 2. Comparisons of the log α vs N linear relationships for the cyclic ethers $(CH_2)_nO$ and the epoxides $H(CH_2)_nCHCH_2O$ with the boundaries of log α for the corresponding linear monoethers $H(CH_2)_mO-(CH_2)_nH$.

The sorption data for the members of series no. 2 that were determined experimentally ($n = 1, 2, 4, 6, 8,$ and 10; E#s 20–25, respectively) are collected in Table 5, where the observed α-values are recorded in bold numerals. These data were used to establish the log α vs N relationship (eq 1) for series no. 2 ($D_2 = 0.0767$; $r^2 = 0.999$), which was then used to deduce by interpolation the α-values for the remaining members of series 2, namely, those having $n = 0, 3, 5, 7,$ and 9. These data are also recorded in Table 5 (E#s 0, 21a, 22a, 23a, and 24a, respectively), but they are not in bold numerals to stress that they were not obtained experimentally.

The log α vs N relationships for series nos. 1 and 2 are recorded in Figure 2, which show that the two relationships *do not converge* to a common data point at $N = 3$ (i.e., $n = 0$). Moreover the log α vs N relationship for series no. 2 extrapolates

TABLE 6: Sorption of Methyl-Substituted Cyclic Aliphatic Monoethers Having the GMS *cyclo*-[CH$_2$OCH$_2$CH$_{2-q}$(CH$_3$)$_q$(CH$_2$)$_n$]; $n = 0-6$, Series Nos. 3$-$11[a]

n	$q = 0$ α:N	$q = 1$ α:N	$q = 2$ α:N		D_s	series no.
0	**3.31:4**	2.30:5	**1.61:6**	→	0.1565	3
1	**2.70:5**	1.89:6	1.33:7	→	0.1538	4
2	**2.21:6**	**1.56:7**	1.10:8	→	0.1513	5
3	**1.79:7**	1.28:8	0.91:9	→	0.1469	8
4	*1.46:8*	1.06:9	0.75:10	→	0.1449	9
5	*1.19:9*	0.87:10	0.62:11	→	0.1416	10
6	*0.97:10*	0.72:11	0.51:12	→	0.1396	11
	↓	↓	↓		↓	
	srs. no 1	srs. no 6	srs. no. 7		$D_n = D_0 + D'n$	
	$D_1 = 0.0888$	$D_6 = 0.0843$	$D_7 = 0.0827$		$D_n = 0.1563 - 0.00280n$	
	$r^2 = 0.9999$	$r^2 = 0.982$	$r^2 = 0.987$		$r^2 = 0.9960$	

[a] The bold numerals indicate the experimentally determined data points, which were used to establish the corresponding log α vs N relationships (eq 1) for series nos. 1, 3, and 5. The numerals written in italic script were established by extrapolation using eq 1, as noted in Table 4. α and N are as defined in the footnotes of Table 3. n and q are as defined in the GMS above. D_s is the negative slope (i.e., the decrementation constant) as defined in eq 1. r^2 is the square of the correlation coefficient for the relationship indicated by the vertical arrow. Each r^2 for those indicated by the horizontal arrows (series nos. 3$-$11) is >0.998.

low as 2 (dashed curved-line extension to $N = 3$ in Figure 2), which is considerably less than that ($\alpha = 3.97$; Table 4) deduced by extrapolation using the log α vs N linear relationship for series no. 1. As a partial confirmation, it was deduced[22] from the magnitude of swelling of a single poly(Sty-*co*-DVB) sample in liquid ethylene oxide at its boiling point (10.7 °C) that the α-value under these conditions is about 1.5. It is suggested, therefore, that (CH$_2$)$_2$O, if it were adsorbed in a vertical symmetrical mode, might be regarded as the first member of the cyclic ether series (no. 1; Table 4), and that if it were adsorbed in a vertical but tilted mode, might be regarded as the first member of the epoxide series (no. 2; Table 5). Extrapolation to $\alpha = 2.99$ at $N = 3$ (Figure 2) is not realized, however, because of a sharp change in mode of adsorption that begins to occur when n in the polymethylene side chain decreases to 1, as noted in Figure 3a,b. Thus, the "true" α-value for liquid ethylene oxide at 23 °C (i.e., pressurized to above atmospheric pressure) is believed to be much closer to 2.0 than it is to 3.0, which is indicative of this change in the mode of adsorption.

The log α vs N linear relationships for the cyclic ethers (series no. 1) and the epoxides (series no. 2) are compared in Figure 2 to those for the linear ethers H(CH$_2$)$_m$O(CH$_2$)$_n$H, which lie in a triangular plane resulting from the unsymmetrical mode of adsorption for such ethers (see Figures 3 and 4 in ref 11). This comparison shows unmistakably that the α-values for both series nos. 1 and 2 are uniformly well above those for the set of linear ethers that have the same number ($N = m + n + 1$) of equivalent mass units and that these differences exhibited in the ether series (Figure 2) are at least as great as those exhibited in any of the previous Z(CH$_2$)$_{n+1}$H vs *cyclo*-ZCH(CH$_2$)$_n$ comparisons (see Figures 11$-$13 in ref 7). This confirms the point of view expressed earlier[8] that cyclization in the alkyl portion (R) of the adsorbed molecule (RZ) fosters markedly improved self-assembly on the adsorption site, explainable by entropic considerations. This of course is consistent with the observation made earlier by Searles and Tamres[21] that the electron donor capacities of cyclic ethers (CH$_2$)$_n$O, in which n is 3$-$6, are much greater than those of the corresponding linear ethers. This may not be true, however, when n is 9$-$11 for reasons already discussed.

This comparison (Figure 2) also shows that the negative slopes for series no. 1 ($D_1 = 0.0888$) and series no. 2 ($D_2 = 0.0767$) are significantly greater than that ($D_{R1} = 0.0505$) for CH$_3$O(CH$_2$)$_n$H (reference series no. R1, in which the adsorbed portion is held constant while n in the nonadsorbed portion is incremented from 1 to 8), but significantly less than that (D_{R2}

= 0.0976) for H(CH$_2$)$_m$O(CH$_2$)$_m$H (reference series no. R2, in which m in both the adsorbed and nonadsorbed portions are incremented symmetrically from 1 to 8). It was shown[10,11] that $2D_{R2} = D_{R1} + D_{R3}$, where $D_{R3} = 0.1447$ is the decrementation constant for H(CH$_2$)$_m$O(CH$_2$)$_n$H, in which the nonadsorbed portion is held constant at 8 (or n) while the adsorbed portion is incremented from $m = 1$ to 8 (or n). It is believed, therefore, that these intermediary D_1- and D_2-values for series nos. 1 and 2, respectively, are attributable to the cyclic molecular architectures of the respective series and that each successive incrementation in the cyclic polymethylene chain affects accordingly the molecular orientation of both methylene groups adjacent to the adsorbed ether oxygen atom.

The uniform displacement to much higher α-values for the cyclic ethers relative to those of the corresponding linear moieties reflects their relative "packing" efficiencies for self-assembly at the adsorption site. This implies that here too the entropic considerations are at least as important as the enthalpic considerations.

The results observed in our studies involving sorption of linear ethers have shown that the α-value can be affected markedly by the electronic as well as steric contributions from substituents located close to the functional group that forms a liaison with the adsorption site. The same should be true for the cyclic ethers. Thus, the α-value for furan (2.60) is significantly less than that (2.70) for tetrahydrofuran (E#s 5 and 2, respectively, in Table 3), owing to the electronic contributions to the adsorbed ether oxygen atom from the two adjacent double bonds in furan. Similarly the presence of a methyl group in the cyclic structure can have a large negative effect on the α-value, owing to steric as well as electronic influences, as indicated by the α-values for 3,3-dimethyloxetane (1.61) and 3-methyltetrahydropyran (1.56; E#s 6 and 8, respectively, in Table 3) relative to those (3.31 and 2.21) for the corresponding nonsubstituted cyclic ethers (E#s 1 and 3, respectively, in Table 3).

When the α-values for the methyl-substituted cyclic monoethers (E#s 6 and 8 in Table 3) are considered along with those established for the simple cyclic monoethers (CH$_2$)$_n$O, i.e., series no. 1 in which n is 3$-$8 (Table 4), it is possible to deduce the α-values for all the 3-methyl-substituted molecules that comprise the cyclic classification having the GMS [CH$_2$OCH$_2$CH$_{2-q}$-(CH$_3$)$_q$(CH$_2$)$_n$] in which n is incremented systematically from 0 to 6 while q is held constant at 0, 1, or 2 (series nos. 1, 6, and 7 in Table 6) and the corresponding seven crossover relationships in which q is incremented from 0 to 2 while n is held constant at 0$-$6 (series nos. 3 to 5 and 8$-$11 in Table 6). The

complete 3×7 array of data points for the above set of 11 homologous series that comprise this cyclic GMS classification is shown in Table 6. The bold numerals and the italicized numerals therein indicate respectively the data points that were determined experimentally (Table 3) and those that were established by extrapolation (Table 4). The further data in Table 6 are recorded in normal print, which indicates that these were calculated by means of eq 1 using the appropriate data recorded as bold and/or italicized numerals.

This array (Table 6) was constructed stepwise as indicated below.

(1) The first four data points in series no. 1 were used to establish the decrementation constant ($D_1 = 0.0888$; eq 1) for that homologous series, which was then used to calculate the remaining three data points from $n = 4$ to 6, as noted in Tables 4 and 6.

(2) The first and third data points in series no. 3 were used to establish $D_3 = 0.1565$, which was then used to calculate the middle data point ($\alpha = 2.30$: $N = 5$) for that crossover relationship at $n = 0$.

(3) The first two data points in series no. 5 were used to establish $D_5 = 0.1513$, which was then used to calculate the last data point in that crossover relationship at $n = 2$.

(4) The first and third data points in series no. 6 were used to establish $D_6 = 0.0843$, which was then used to calculate the remaining five data points at $n = 1$ and $3-6$ in that homologous series ($q = 1$).

(5) The first and second data points in series no. 4 were used to establish $D_4 = 0.1538$, which was then used to calculate the third data point in that homologous series at $n = 1$.

(6) The first three data points in series no. 7 were used to establish $D_7 = 0.0827$, which was then used to calculate the remaining four data points at $n = 3-6$ in that homologous series ($q = 2$).

(7) The set of three data points that comprise each crossover relationship at $n = 3-6$ (i.e., series nos. $8-11$) were then used to establish the corresponding decrementation constants (i.e., D_8-D_{11}, respectively), as noted in Table 6.

The set of seven D_s-values obtained thereby (namely, D_3-D_5 and D_8-D_{11} in Table 6) confirm (see Tables 3, 4, and 9 in ref 11) that the D_s-values for the crossover relationships vary linearly with the variable (x) being incremented in the series under consideration, as expressed by eq 6.

$$D_s = D_0 + D'x \qquad (6)$$

Here D' is ($\Delta D_s/\Delta x$), i.e., the change in negative slope per unit change in x. It was observed in the earlier studies, involving sorption of the linear ethers,[11] that D' can be positive (i.e., the negative slope is becoming less negative) or negative (i.e., becoming more negative) or zero, depending on the directions of the vectorial projections that represent the respective log α vs N linear relationships (eq 1) being considered, i.e., diverging, converging, or parallel. In this case the variable being incremented is n and D' is negative, which means that the slopes of the log α vs N linear relationships that cross over (i.e., tie together) the seven series at each value of n are becoming less negative as n increases from 0 to 6. The best straight line established by linear regression through the set of seven data points ($r^2 = 0.996$) is $D_s = 0.1563 - 0.00280n$, which signifies that the three log α vs N linear relationships (series nos. 1, 6, and 7 in Table 6 and Figure 4) are converging in multidimensional space to a projected point of intersection at about $n = 50$.

The 3×7 array of data points for the above cyclic ethers (Table 6) is compared in Figure 4 with the corresponding array
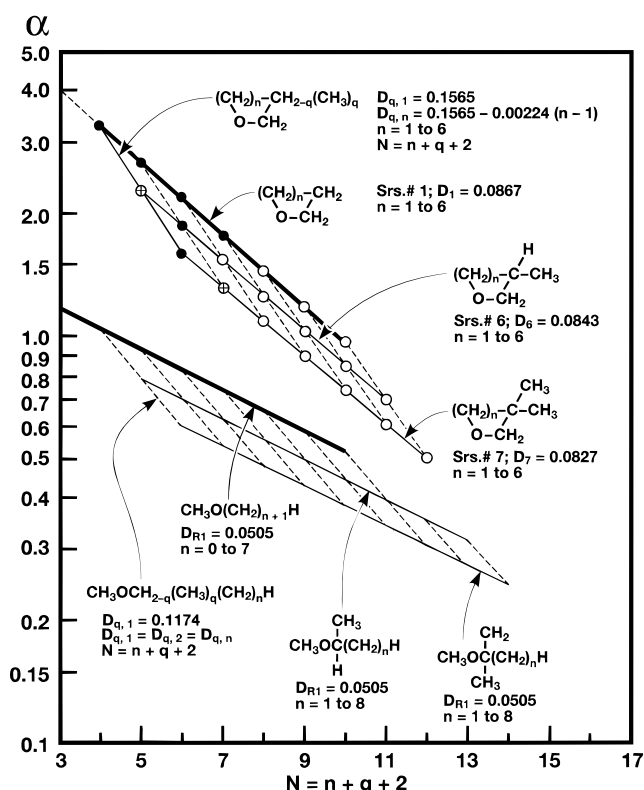

Figure 4. Comparisons of the log α vs N linear relationships for the methyl substituted cyclic monoethers with those for the corresponding linear methyl ethers $CH_3OCH_{2-q}(CH_3)_q(CH_2)_nH$.

for those (bottom portion of Figure 1; see also Figure 9 in ref 11) for the linear ethers having the GMS $CH_3OCH_{2-q}(CH_3)_q$-$(CH_2)_nH$. One sees that the set of data points for the cyclic ethers lie uniformly above that for the linear ethers; this is consistent with the comparison (Figure 2) of the log α vs N linear relationships for cyclic $(CH_2)_nO$ and the corresponding linear $CH_3O(CH_2)_nH$ ethers, and also with the comparison (Figure 1) of those for the cyclic $ZCH(CH_2)_n$ liquids and the corresponding linear $Z(CH_2)_{n+1}H$ liquids.

Thus, the value of $D' = \Delta D_s/\Delta n$ in the crossover relationships for the cyclic ethers relative to those for the linear ethers gives added insight into the mode of adsorption of the cyclic ethers to the pendent phenyl groups of the polymer at liquid-saturation. Our earlier studies, involving sorption of linear monoethers,[10-13] have shown that D' for the crossover relationships of the ethers, in which the adsorbed portion (R'O) of the adsorbed ethers $R'OCH_{2-q}(CH_3)_q(CH_2)_nH$ and n in the nonadsorbed portion are kept constant while q in the nonadsorbed portion is incremented from 0 to 2, is in every case equal to 0; that is, the value of D_s for each crossover relationship at all values of n that comprise the given homologous series is equal to that ($D_{R1} = 0.0505$) at $n = 1$. This means that the array of data points that represent a GMS of the type $R'OCH_{2-q}(CH_3)_q(CH_2)_nH$ can be represented by two sets of mutually parallel log α vs N linear relationships, as indicated by the example (where R' is CH_3) recorded in Figure 4.

On the other hand, the log α vs N linear relationships for the homologous series in which the nonadsorbed portion (R) of the adsorbed ether having the GMS $H(CH_2)_mCH_{2-q'}(CH_3)_{q'}OR$ is held constant, while one of the variables (in this case m) in the adsorbed portion is incremented between its allowable limits [or of the symmetrical ethers of the type $H(CH_2)_m$-$CH_{2-q'}(CH_3)_{q'}OCH_{2-q}(CH_3)_q(CH_2)_mH$ in which m in both the adsorbed and nonadsorbed portions are incremented symmetrically], diverge sharply (as shown in Figure 7 of ref 11;

TABLE 7: Sorption of Methyl-Substituted Cyclic Aliphatic Monoethers Having the GMS *cyclo*-[CH$_2$OCH$_{2-q}$(CH$_3$)$_q$(CH$_2$)$_n$]; Series Nos. 12−20[a]

n	$q = 0$ $\alpha{:}N$	$q = 1$ $\alpha{:}N$	$q = 2$ $\alpha{:}N$		D_s	series no.
0	**3.31:4**	2.23:5	1.49:6	→	0.1737	13
1	**2.70:5**	**1.81:6**	1.27:7	→	**0.1737**	12
2	**2.21:6**	1.48:7	0.99:8	→	0.1737	14
3	**1.79:7**	1.20:8	0.80:9	→	0.1737	15
4	*1.46:8*	0.98:9	0.66:10	→	0.1737	16
5	*1.19:9*	0.80:10	0.53:11	→	0.1737	17
6	*0.97:10*	0.65:11	0.44:12	→	0.1737	18
	↓	↓	↓		↓	
	srs. no. 1	srs. no. 19	srs. no. 20		$D_s = D_0 + D'n$	
	$D_1 = 0.0888$	$D_{19} = 0.0882$	$D_{20} = 0.0891$		$D_0 = 0.1737$ and $D' = 0$	
					$D_s = 0.1737 = D_{12}$	
	$r^2 = 0.9999$	$r^2 = 0.9999$	$r^2 = 0.9994$			

[a] α, N, n, q, D_s, and r^2 are as defined in the footnotes of Table 6.

series nos. R2, 11 and 12), such that the negative slopes (D_s) for the crossover relationships (series no. 5 and 21−25 in Figure 7 of ref 11) increase sharply ($D' = 0.39$) with each unit increase in m. This large value of D' when the adsorbed portion is incremented while the nonadsorbed portion is kept constant, relative to that ($D' = 0$) observed when the nonadsorbed portion is incremented while the adsorbed portion is kept constant, demonstrates the crowding (steric) effect and its extreme dependence on the location along the molecule.

In contrast to the marked divergence exhibited by the three log α vs N linear relationships for the symmetrical ethers having the above GMS as m is incremented from 1 to its allowable limit at constant q and q', the corresponding three relationships for the linear ethers having the GMS (CH$_3$)$_{q'}$CH$_{2-q'}$-[(CH$_2$)$_m$O(CH$_2$)$_m$]CH$_{2-q}$(CH$_3$)$_q$ are actually converging as m is incremented from 1 to its allowable limit (see Figure 7 in ref 11; series nos. R2, 13, and 14), such that D_s for the corresponding crossover relationships becomes less negative as expressed by $D_s = 0.258 - 0.00421m$ (i.e., eq 12 in ref 11). In the former case the dominant factor is the cumulative steric hindrance to further adsorption imparted by the CH$_{2-q}$(CH$_3$)$_q$(CH$_2$)$_m$H groups adjacent to the adsorbed ether oxygen atom, but in the latter case this is attenuated by distance and by the resulting enhancement of dynamic interaction of the terminal CH$_{2-q}$(CH$_3$)$_q$ groups (relative to CH$_2$CH$_3$) with the mobile sorbed-but-not-adsorbed ether molecules in the gel system at liquid-saturation.[8,15] Since both attenuation and interaction increase with q and q', the three log α vs N linear relationships having the above GMS converge with m instead of diverge.

Similar interaction effects were noted in studies involving sorption of Z(CH$_2$)$_n$R liquids in which Z is a chloro or bromo substituent[8] or methoxy group[15] and R is Z or H. In each case the negative slope (D_s; eq 1) of the respective log α vs N linear relationship became significantly less negative when the terminal H atom was replaced by a Z substituent, owing to enhanced dynamic interaction with the mobile sorbed-but-not-adsorbed molecules in the gel system at liquid-saturation, as described previously.[8,15]

Evidence that branching in the polymethylene chain also enhances dynamic interaction with sorbed-but-not-adsorbed molecules has already been observed in studies involving sorption of unsymmetrical ethers R′OR.[11] In every case in which the mass of the two alkyl groups are the same, the alkyl group having the greater number of branched methyl groups becomes the nonadsorbed portion (R) and the other is the adsorbed portion (R′O).[11] Reasoning by analogy with these observations, it follows that unless the position of the methyl substituent(s) is symmetrical with respect to the ether oxygen

atom, the dynamic (averaged) molecular orientation of the adsorbed cyclic ether will be, as shown in Figure 3c, tilted in a "vertical" orientation toward the side having the greater number of methylene units between the adsorption site and branched carbon atom in the cyclic polymethylene chain. If the cyclic structure is symmetrical with respect to the adsorbed ether atom, however, then the (averaged) molecular orientation in the adsorbed state will extend symmetrically away from that site, as shown in Figure 3d for (CH$_2$)$_4$O.

The data collected in Table 3 show that the α-value for only a single member of the homologous series having the cyclic GMS [CH$_2$OCH$_{2-q}$(CH$_3$)$_q$(CH$_2$)$_n$] has been determined experimentally, namely that for 2-methyltetrahydrofuran (E# 7 in Table 3). Normally the α-value for at least two methyl substituted members for such a cyclic homologous series is required to establish a crossover array of log α vs N linear relationships of the type shown in the lower part of Figure 4. This may not be necessary in the present case, however, because for the corresponding acyclic series having the GMS ROCH$_{2-q}$(CH$_3$)$_q$(CH$_2$)$_n$H, in which the adsorbed portion (RO) of the adsorbed ether is kept constant while n in the nonadsorbed portion is incremented from 1 to its allowable limit, the decrementation constants (D_s) for the crossover relationships do not vary with n [that is, D' in eq 6 is 0 and therefore the 3 × 8 array of data points for such series define two sets of mutually parallel lines, as shown in Figure 9 of ref 11 and also by the example for CH$_3$OCH$_{2-q}$(CH$_3$)$_q$(CH$_2$)$_n$H) recorded here in the lower portion of Figure 4]. If one assumes tentatively that this is true for the cyclic monoethers, then a 3 × 7 array of data points for the series *cyclo*-CH$_2$OCH$_{2-q}$(CH$_3$)$_q$(CH$_2$)$_n$, in which n is 1−6, can also be established in the manner described for the series *cyclo*-CH$_2$OCH$_2$CH$_{2-q}$(CH$_3$)$_q$(CH$_2$)$_n$, in which n is 0−6, using only the α-values for (CH$_2$)$_n$O (i.e., series no. 1 in which n is 3−8; Table 4) and that for 2-methyltetrahydrofuran (E# 7 in Table 3), via a stepwise consideration similar to that described for deducing the array recorded in Table 6.

Thus, the first two data points in series no. 12 (Table 7) were used to establish $D_{12} = 0.1737$ for the crossover relationship at $n = 1$. In this case, D' in eq 6 is assumed to be 0 for reasons described above, which implies that D_s for all the other crossover relationships must also be equal to 0.1737, and therefore the α-values for all the members of the crossover relationship at $n = 0$ and 2−6 (series nos. 13−18, respectively, in Table 7) can be calculated by means of eq 1 using for α_i the appropriate α-values that comprise series no. 1 ($q = 0$). The calculated best straight lines through the two columns of data points that comprise series nos. 19 and 20 (Table 7) represent the log α vs N linear relationships for the ethers having the GMS *cyclo*-

TABLE 8: Sorption of Methyl-Substituted Cyclic Aliphatic Ethers Having the GMS *cyclo*-[(CH$_2$)$_{p+2}$O(CH$_2$)$_p$CH$_{2-q}$(CH$_3$)$_q$]; Series Nos. 21−23[a]

p	$q = 0$ α:N	$q = 1$ α:N	$q = 2$ α:N		D_s	series no.
0	3.31:4	2.23:5	1.49:6	→	0.1737	13
1	2.21:6	1.56:7	1.10:8	→	0.1513	5
2	1.46:8	1.09:9	0.81:10	→	0.1279	23
	↓	↓	↓		↓	
	srs. no. 1	srs. no. 21	srs. no. 22		$D_s = D_0 + D'p$	
	$D_1 = 0.0888$	$D_{21} = 0.0776$	$D_{22} = 0.0659$		$D_s = 0.1737 - 0.0225p$	
		$D_s = 0.0.0889 - 0.01145q$			$r^2 = 0.9991$	
		$r^2 = 0.9998$				

[a] α, N, n, q, D_s, and r^2 are as defined in the footnotes of Table 6.

CH$_2$OCH$_{2-q}$(CH$_3$)$_q$[(CH$_2$)$_n$, in which q is 1 and 2, respectively. The decrementation constants for these two relationships (D_{19} = 0.0882 and D_{20} = 0.0891) confirm as expected that they are essentially parallel to that (D_1 = 0.0888) for series no. 1, which indicates that the calculated α-values are consistent with expectation. It is hoped, however, that one or more of the ethers in this array will become available to us to permit an experimental test of these questionable predictions.

In like manner a 3 × 3 array of data points for the cyclic ethers having the GMS *cyclo*-(CH$_{2+p}$)O(CH$_2$)$_p$CH$_{2-q}$(CH$_3$)$_q$ can be constructed from the data recorded for series no. 1 (N = 4, 6, and 8 in Table 4), series no. 5 (N = 6, 7, and 8 in Table 6), and series no. 13 (N = 4, 5, and 6 in Table 7), as shown in Table 8. In this construction, the data for the first two members (p = 0 and 1) of series no. 21 (q = 1) were used to calculate its decrementation constant (D_{21} = 0.0776), which was then used to calculate by means of eq 1 the α-value (1.09) for the third member (p = 2) of that series. In like fashion the decrementation constant for series no. 22 (q = 2) and the α-value for the third member of that series were deduced respectively to be D_{22} = 0.0659 and α = 0.81. The decrementation constant for the crossover relationship at p = 2 (i.e., series no. 23 in Table 8) was given by the negative slope of the best straight line (D_{23} = 0.1279; r^2 = 0.99998) through the three data points that comprise this relationship. This array was not extended to include the members of series nos. 1, 21, and 22 having $p > 2$ because of the uncertainty regarding the validity of such extrapolation owing to the special effect of steric hindrance that is exhibited by cyclic polymethylenes when the ring size is 9−11 members, as discussed earlier.[16−20]

The effect on α caused by incrementation of the number (n) of units in the polymethylene chain and by the number (q) of methyl substituents on the ring structure, with respect to proximity to the adsorption site, can be understood more readily by the diagrammatic correlation of the α-values (reported in Tables 3, 4, 6, and 7) with their respective molecular structures, as displayed in Figure 5. The α-values recorded in bold numerals were determined experimentally. The rest of these values and the decrementation constants (D_s) for the homologous series that comprise the array shown in Figure 5 were deduced by means of eq 1, as described above. The comparisons of the relative D_s-values for the eight homologous series (i.e., nos. 3 with 13, 4 with 12, 5 with 14, and 8 with 15; rightmost column in Figure 5), in which the ring size (n) was held constant while the number (q) of methyl groups on a given methylene group was incremented from 0 to 2, show that the negative effect on α, owing to such incrementations, decreases as expected with distance from the oxygen atom; that is, the negative effect on α caused by methyl substitution is greater when it occurs at the methylene unit adjacent to the adsorbed oxygen atom than it is when it occurs at the methylene unit once removed from that site; presumably it will be even less when the substitution occurs
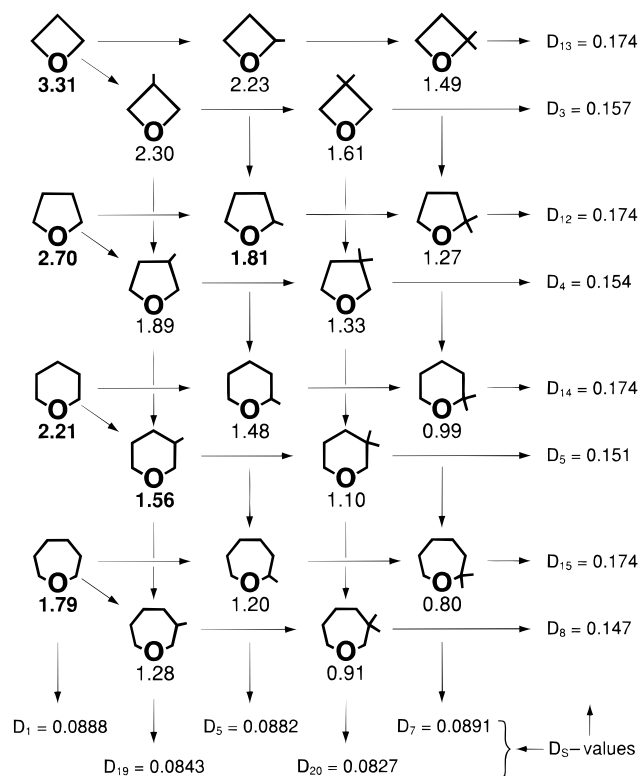
Figure 5. Effect of ring size and methyl substitution thereto on the α- and D_s-values for the homologous series of cyclic monoethers.

at the methylene unit twice removed from that site and be rapidly attenuated to zero thereafter.

The comparisons of the relative D_s-values for the five homologous series (i.e., nos. 1, 5, 7, 19, and 20; bottom row in Figure 5), in which q is held constant at 0, 1, and 2, while the ring size (n) is incremented from 4 to 7, show that the negative effect on α, owing to such incrementations, decreases as expected with increase in the number of methylene units away from the ether oxygen atom. It is interesting to note, however, that in the series (nos. 1, 19, and 20) involving methyl substituents at the methylene unit once removed from the adjacent carbon atom, the diminishing effect is greater when there are two methyl substituents (series no. 20; D_{20} = 0.0827) than when there is only one methyl substituent (series no. 19; D_{19} = 0.0843). This "beneficial" effect that increases with q is similar to that observed in the study of sorption involving linear ethers, in which D_s for incrementation of m in the monoethers having the GMS (CH$_3$)$_q$CH$_{2-q}$[(CH$_2$)$_m$O(CH$_2$)$_m$]-CH$_{2-q}$(CH$_3$)$_q$ [D = 0.0928 for q = 1 and D = 0.0888 for q = 2 in Table 3 of ref 11] was compared to the corresponding values for those having the GMS H(CH$_2$)$_m$CH$_{2-q}$(CH$_3$)$_q$OCH$_{2-q}$(CH$_3$)$_q$-(CH$_2$)$_m$H [D = 0.272 for q = 1 and D = 0.486 for q = 2 in Table 4 of ref 11], which implies that the negative effect on α
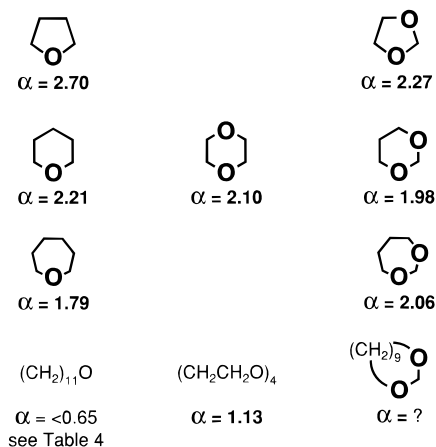
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Figure 6. Comparison of the α-values for the cyclic monoethers with those for the corresponding cyclic polyethers.

Figure 7. Diagrammatic correlation of the α- and D_s-values with the molecular structures of cyclic diethers, showing the effect thereto caused by progressive methyl substitution.

caused by increase in mass units is mitigated considerably when due to branched methyl groups not located on the carbon atom adjacent to the oxygen atom at the adsorption site. This mitigating effect will be discussed more fully in future publications dealing with acyclic branched aliphatic alkyl ethers.

Cyclic Diethers and Related Structures. The α-values for five cyclic polyethers (E#s 9, 10, 12, 14, and 17; Table 3) are compared diagrammatically in Figure 6 with the corresponding cyclic monoethers [(CH$_2$)$_n$O]; it is evident that the α-values do not vary linearly with the number (*e*) of ether oxygen atoms in molecules of the same ring size. These results are similar to those observed in the earlier studies that correlated α with *e* in the molecular structures of the corresponding linear aliphatic ethers and therefore consistent with the point of view that adsorption of polyethers to the phenyl group of polystyrene at liquid-saturation involves monodentate liaison. The nonadsorbed ether oxygen atoms, however, can affect α electronically or sterically or via dynamic associative interactions with mobile molecules (or combinations thereof), as discussed in the study of sorption of acyclic aliphatic polyethers.[12] These factors that operate on the acyclic ethers should affect α for the cyclic ethers in the same qualitative way; but the net result will be affected further by the cyclic structure; ring formation of hydrocarbons has a strong positive effect on α.

We were surprised, however, to observe that the α-values for the cyclic formals (CH$_2$)$_n$[OCH$_2$O] having *n* = 2, 3, and 4 (E#s 12, 14, and 17, respectively, in Table 3 and the rightmost column in Figure 6) did not decrease monotonically with *n*. The α-value for 1,3-dioxane (*n* = 3; α = 1.98) is indeed less than that (α = 2.27) for 1,3-dioxolane (*n* = 2), and the difference in the respective log α-values [Δ log α = (log α$_1$ − log α$_2$) = 0.0594] is reasonable, relative to the decrementation values (D_s = ca. 0.09; series nos. 1, 6, 7, 19, and 20 in Tables 6 and 7 of ref 11) observed for the cyclic monoether series; but the α-value (2.06) observed for tetramethylene formal (*n* = 4, E# 17 in Table 3) is considerably higher than that (1.73) expected on the basis of linearity expressed by eq 1 using the observed Δ log α for 1,3-dioxolane and 1,3-dioxane noted above.

In view of this anomalous observation, it was important to question the purities of the samples, *n* = 2 and 3 (Aldrich Chem. Co.), and 4 (GAF Co.). The analytical results (NMR and GC) showed that the samples were correctly labeled and that the purity of each was better than the 97% claimed by the vendor. Accordingly, we accepted that the observed α-values for these three liquids are valid measurements.

We have reported[8,12] two cases of similar apparently anomalous results exhibited by the lower members of a given series,
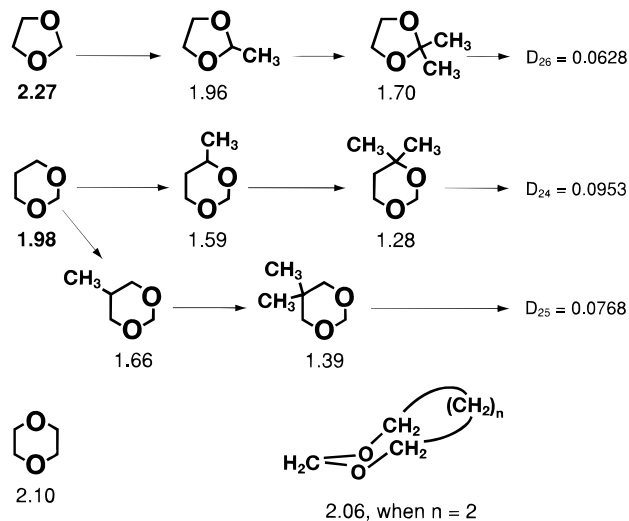
and in each case the cause of the apparent anomaly proved to be a change in the mode of adsorption, as described above in the discussion of the cyclic (CH$_2$)$_n$O ethers. Presumably this apparently anomalous result indicates that the mode of adsorption to the pendent phenyl groups of the polymer at liquid-saturation in the case of the (CH$_2$)$_n$OCH$_2$O liquids changes when *n* is >3. Examination of molecular models of such structures having *n* = 2−11, made using HPK Harvard Atomic Models, tends to support a change in the molecular architecture of the adsorbed state, which occurs when *n* becomes greater than 3. The model for 1,3-dioxolane (*n* = 2) is planar with the two oxygen atoms facing in directions differing by about 150°. This means that the mode of adsorption should resemble that for 1,4-dioxane, i.e., in a vertical-but-tilted mode (Figure 3c) owing to one ether oxygen atom being anchored to the adsorption site while the other is in dynamic associative interaction with the mobile sorbed-but-not-adsorbed molecules in the system at liquid-saturation. The attraction of an oxygen atom to a phenyl group is of course the interaction of a local dipole with a polarizable electron cloud. The model for 1,3-dioxane (*n* = 3) has a rigid chair conformation with the two oxygen atoms rotated slightly out of plane and toward one other, such that they face in directions differing by about 120°. This means that the mode of adsorption should be similar to that just described for 1,3-dioxolane. This is shown in Figure 7, which is a diagrammatical correlation of the α-values for the cyclic diethers with their respective molecular structures.

The model for tetramethylene formal (*n* = 4) has a somewhat looser chairlike conformation, so that the two oxygen atoms can rotate considerably more toward one another, such that they face in directions differing only by about 70°. This angle of rotation decreases only slightly with further increases in *n*, the difference between the directions that the oxygen atoms face when *n* is 11 (ca. 65°) being essentially unchanged from that at *n* = 4. This means that when *n* is greater than 3, the mode of adsorption can involve simultaneous attraction of both oxygen atoms to the adsorption site, while the polymethylene chain on the other side of the imaginary line between the two oxygen atoms is in dynamic associative interaction with the mobile molecules. This affords a "torque" about the imaginary line between the two adsorbed oxygen atoms, which causes the methylene unit between the oxygen atoms to become the third leg of a tripod on the adsorption site, while the rest of the molecule extends outward, as shown in Figure 7.

This is a bidentate mode of adsorption, but since it occurs at the same site, the number of available adsorption sites is not decreased thereby. Consequently the negative effect on α is markedly less than it would be if the bidentate mode of adsorption involved two separate adsorption sites, for example two different phenyl groups in the polymer at liquid-saturation.

The above observations are consistent with the view that tetramethylene formal (E# 17 in Table 3) is the first "true" member of the $(CH_2)_nOCH_2O$ series ($n > 3$) and that the cyclic formals with $n = 2$ and 3 are adsorbed differently from those of the higher members, the lower members being adsorbed in the monodentate mode whereas the higher members are adsorbed in the bidentate mode. This should have a significant effect on the decrementation constant (D_s; eq 1) for the log α vs N relationships of the respective homologous series having a ring-attached polymethylene side chain $(CH_2)_mH$ which is incremented from $m = 1$ to 8, such that the negative slopes (D_s) for the series having the two smaller cyclic ether structures ($n = 2$ and 3) should be essentially parallel, and those attached to the larger cyclic ether structures ($n = 4-11$) should also be essentially parallel, but the two sets of relationships will not be parallel to one another. On the basis of molecular model studies, it is suspected that the average D_s-value for the smaller set should be significantly less than that for the larger set.

These models also show that, unlike the case in the *cyclo*-$(CH_2)_nO$ series (Table 4), the accessibility of the adsorption site to the two ether oxygen atoms should not decrease with n in the $(CH_2)_nOCH_2O$ series. This implies that perhaps the range over which the log α vs N relationship (eq 1) remains linear in the $(CH_2)_nOCH_2O$ series may extend from $n = 4$ to >11 We are hopeful that we may someday obtain one or more of the higher members in each of these series to permit us to test the above hypotheses.

Meanwhile, it must be mentioned here that computer modeling studies of these cyclic 1,3-diethers by Dr. John Stevens of the Computational Science Center of 3M Corporate Technical Planning and Coordination, who utilized a Tripos Associates SYBYL 6.2 program running on a Silicon Graphics 340D computer, showed that in the liquid state the most probable lowest energy state configurations for the OCH_2O portion of these (isolated) molecules are indeed independent of n, because of anomeric effects,[23,24] but that the two oxygen atoms in this set of cyclic molecular structures both remain in the positive synclinal orientation ($+sc$), even when n is increased to 11. This implies that formation of bidentate liaison with a given pendent phenyl group via bimolecular collision is not favored.

It can be argued, however, that bidentate liaison can occur stepwise when the force of attraction with the adsorption site is sufficiently great, which is indeed the case as evidenced by the strong affinity (α-values from 1 to 3; Table 4) of the cyclic monoethers $(CH_2)_nO$ for polystyrene. Thus, monodentate collisional liaison of the phenyl group with one of the two ether oxygen atoms occurs first. Induced rotation of the other from $+sc$ to $-sc$ can occur subsequently to form a second liaison on the same adsorption site, provided that the flexibility of the $(CH_2)_n$ chain between the oxygen atoms is sufficiently great to allow such rotation. Our consideration of the molecular models suggests that this occurs only when n is >3.

If one accepts the hypothesis that the first two members of this series of cyclic ethers (1,3-dioxolane and 1,3-dioxane; E#s 12 and 14, respectively, in Table 3) are adsorbed in the monodentate mode, as shown in Figure 7, then it follows that it should be possible to establish the corresponding log α vs N linear relationships for the methyl-substituted modifications thereof in the manner described for cyclic monoethers, such as

TABLE 9: Sorption of Methyl-Substituted 1,3-Dioxanes and 1,3-Dioxolanes[a]

cyclic diether	$q = 0$ α:N	$q = 1$ α:N	$q = 2$ α:N		D_s	series no.
4-$(CH_3)_q$-1,3-dioxane	**1.98:6**	**1.59:7**	1.28:8	→	0.0953	24
5-$(CH_3)_q$-1,3-dioxane	**1.98:6**	1.66:7	**1.39:8**	→	0.0768	25
2-$(CH_3)_q$-1,3-dioxolane	**2.27:5**	1.96:6	**1.70:7**	→	0.0628	26

[a] α, N, q, and D_s are as defined in the footnotes of Table 8.

tetrahydrofuran and tetrahydropyran) or for a cyclic diether, such as *p*-dioxane (E#s 2, 4, and 9, respectively, in Table 3), which are also adsorbed in the monodentate mode.

The α-values for the three methyl-substituted cyclic diethers and those for the two parent cyclic diethers are collected in Table 9. The experimentally determined α-values for these five ethers are recorded as bold numerals that are distributed over the three columns having the headings $q = 0$, $q = 1$, and $q = 2$ (which indicate respectively the number of methyl groups in the position of the molecular structure defined in the leftmost column). The α-values for the $q = 0$ and 1 members of series no. 24 were used to calculate the decrementation constant ($D_{24} = 0.0953$) for that series, and the $q = 0$ and 2 members of series nos. 25 and 26 were used to establish their respective D_s-values, namely, $D_{25} = 0.0768$ and $D_{26} = 0.0628$. These three D_s-values were used in turn to calculate the α-values for the corresponding remaining third member of each series by means of eq 1, using for constant α_i the appropriate value listed in the $q = 0$ column.

The α- and D_s-values for these cyclic diethers are correlated diagrammatically in Figure 7 with their respective monodentate modes of adsorption (relative to the bidentate mode illustrated there for the $(CH_2)_nOCH_2O$ ethers that have $n > 3$). Comparison of this diagrammatic layout with that for the cyclic monoethers (Figure 6) shows that replacement of a ring methylene unit by an oxygen atom causes a decrease in the corresponding α-value when there are no methyl substituents (leftmost columns in Figures 6 and 7), but the effect of this replacement is reversed in the presence of methyl substitutents. Moreover, the magnitude of the reversal effect is greater when there are *gem*-dimethyl substituents than when there is a single methyl substituent at the position being considered. This is not presently understood.

Cyclic Polyoxyethylenes $(CH_2CH_2O)_e$. The data collected in Table 3 show that the α-values for only two members of this series have been determined experimentally, namely, *p*-dioxane and 12-crown-4 (E#s 9 and 10). By analogy with the observations made in the study involving sorption of linear α,ω-dialkyl ethers of polyoxyethylenes,[13] however, it is possible to deduce with reasonable confidence the α-values for at least three additional members of the cyclic polyoxyethylene series, namely those having $e = 1$, 3, and 5.

We inferred from the results observed in our earlier studies[13] that the mode of adsorption of the linear polyethers having the GMS $H(CH_2)_mO(CH_2CH_2O)_e(CH_2)_nH$ depends on the number of ethylene oxide spacer units (e) between the two external polymethylene segments (i.e, m and n, where m is $1-8$ and n is $m-8$). When e is <2 the mode of adsorption is lopsided, as shown in Figure 4a of ref 13; but when e is >1, the mode of adsorption is more symmetrical, as shown in Figure 4b of ref 13, one of the inner oxygen atoms attached to ethylene oxide units being immobilized by liaison with the adsorption site while the two adjacent ethylene oxide segments (and the polymethylene segments, m and n, attached thereto) extend away from that site. Thus, the mode of adsorption for the linear series having $e > 1$ is analogous to that described here for the cyclic ethers.
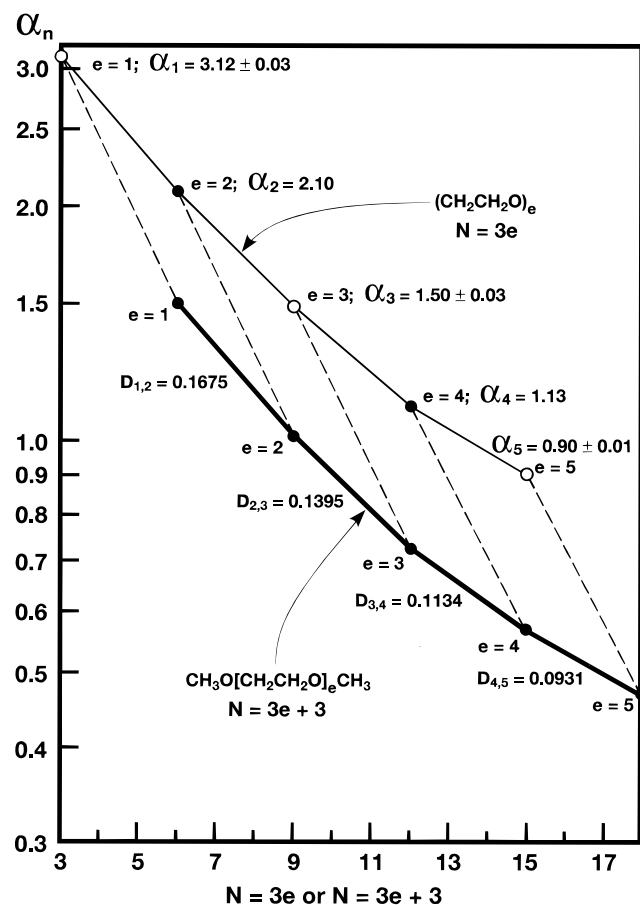
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Figure 8. Correlation of log α with the total number (N) of mass units for the cyclic polyethylene oxides $(CH_2CH_2O)_e$ ($N = 3e$) and for the corresponding linear methyl-terminated polyethylene oxides $CH_3O(CH_2CH_2O)_eCH_3$, where $N = 3e + 3$.

Our earlier study[13] showed that the log α vs N relationship for the series having the GMS $CH_3O(CH_2CH_2O)_eCH_3$ does not decrease linearly with N, presumably owing to the mitigating effect of additional ether oxygen atoms, which increases with e. Instead log α appears to approach an asymptotic limit attained at about $N = 30$. Thus the slopes ($-D_{e,e+1} = -3D_s$) of the set of contiguous bold-line segments (Figure 8) that connect log α_e to log α_{e+1} become less negative with increase in e. The data collected in Table 10 (see also Table 5 and Figure 5 in ref 13) show that the difference ($D_{e,e+1} = \log \alpha_e - \log \alpha_{e+1}$) for the $CH_3O(CH_2CH_2O)_eCH_3$ ethers decreases linearly with e (i.e., $D_{e,e+1} = 0.1926 - 0.0260e$, for $e = 0-5$).

This stepwise decrease in negative slope reflects the net contributions to α from the two methylene units and the ether oxygen atom of each added ethylene oxide unit. A similar pattern of stepwise decrease in negative slope per unit increase in e should also be exhibited by the cyclic $(CH_2CH_2O)_e$ series because the molecular architecture adjacent to the adsorbed ether oxygen is the same as that in the linear series when e is >1. The differences ($D_{s,e} = \log \alpha_e - \log \alpha_{1,e,1}$) in these crossovers should be considerable, however, not only because cyclization without change in mass units ($\Delta N = 0$) results in a large decrease in steric hindrance but also because this cyclization results in a decrease of three mass units owing to elimination of dimethyl ether as indicated below.

$$CH_3O(CH_2CH_2O)_eCH_3 \rightarrow (CH_2CH_2O)_e + CH_3OCH_3$$
$$\alpha_{1,e,1} \qquad\qquad \alpha_e \qquad \alpha_{1,0,1}$$
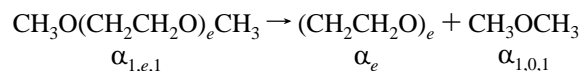
Thus, one can anticipate that the log α_e-values for the set of cyclic $(CH_2CH_2O)_e$ ethers should lie uniformly above the set

of bold reference lines that join the α_e-values for the corresponding linear $CH_3O(CH_2CH_2O)_eCH_3$ ethers. The locations of the data points (two filled circles at $N = 6$ and 12 in Figure 8) for $(CH_2CH_2O)_2$ and $(CH_2CH_2O)_4$ [E#s 9 and 10, respectively, in Table 3] are consistent with this expectation.

It was also observed in our study of adsorption involving the linear poly(oxyethylene) ethers $H(CH_2)_mO(CH_2CH_2O)_e-(CH_2)_mH$ that the segments representing the differences ($D_{e,e+1} = \log \alpha_e - \log \alpha_{e+1}$) for crossovers from e to $e + 1$ (for values of $e = 2-5$) at $m = 2-8$ are parallel to the corresponding crossovers at $m = 1$, as shown in Figure 5 of ref 13. It is reasonable to expect, therefore, that the same will be true for $cyclo$-$(CH_2CH_2O)_e$ because cyclization via elimination of the polymethylene groups at the extremities of the linear ethers will not alter the molecular architecture at the adsorption site, which involves liaison with one of the inner oxygen atoms.

If the two segments from point ($\alpha_2 = 2.10$: $N = 6$) to point ($\alpha_3 = u$: $N = 9$) and from there to point ($\alpha_4 = 1.13$: $N = 12$) are indeed parallel to the corresponding two bold-line reference segments in Figure 8 (the negative slopes of which are respectively $D_{2,3} = 0.1395$ and $D_{3,4} = 0.1134$; Table 10), then it is possible to estimate the value of u for α_3 in two ways by means of the appropriate log α vs e relationship, namely by the summations (log $\alpha_2 - D_{2,3}$) and (log $\alpha_4 + D_{3,4}$). These estimations of α_3 have the numerical values of 1.52 and 1.47, respectively (Table 10). In like fashion $\alpha_1 = 3.09$ and $\alpha_5 = 0.91$ were deduced for ethylene oxide and $(CH_2CH_2O)_5$, respectively, i.e, log $\alpha_1 = (\log \alpha_2 + D_{1,2})$ and log $\alpha_5 = (\log \alpha_4 - D_{4,5})$, using the appropriate values of α_2, α_4, $D_{1,2}$, and $D_{4,5}$, recorded in Table 10.

It is also possible to obtain second estimates for α_1 and α_5 by a more circuitous route, namely, by first establishing the linear $D_{s,e}$ vs e relationship (rightmost column in Table 10) and then calculating α_1 and α_5 via eq 1 using the appropriate $\alpha_{1,e,1}$- and $D_{s,e}$-values (rows 2, 3, and 4 under e, the leftmost column in Table 10). As explained above in the discussion of the cyclic polymethylene oxides, the value of the decrementation constant (the negative slope D_s) of the line that crosses over from one log α vs N linear relationship to another that increments systematically to the same variable (x) varies linearly with x, as expressed by eq 6.

In this case the variable x common to both the linear and the cyclic polyoxyethylene series is e; thus the value of $D_{s,e}$ for crossover from the cyclic to the linear series at each value of e can be calculated from eq 1 [i.e., $D_{s,e} = (\log \alpha_e - \log \alpha_{1,e,1})/(N_e - N_{1,e,1})$]. Table 10 shows that the values of $D_{s,e}$ at $e = 2$ and 4 are respectively 0.1045 and 0.0991, which were calculated using the experimentally determined values recorded for the corresponding pairs of α_e- and $\alpha_{1,e,1}$-values (bold numerals in Table 10). Similarly, the value for $D_{s,e}$ at $e = 3$ was calculated to be 0.1013 (italic numerals; rightmost column in Table 10), using the experimentally determined value for $\alpha_{1,3,1}$ and the average of the two estimated values for α_3. The best straight line through these three data points for $D_{s,e}$ was calculated by linear regression ($r^2 = 0.989$) to be $D_{s,e} = 0.1098 - 0.0027e$ for $e = 0-5$. This line was then used to extrapolate to the corresponding $D_{s,e}$-values at $e = 1$ and 5, as recorded in the rightmost column in Table 10. These values of $D_{s,e}$ were then used to calculate the corresponding α_e-values at $e = 1$ and 5, by means of eq 1 using the appropriate experimentally determined $\alpha_{1,e,1}$-values (bold numerals in Table 10). The numerical value established for α_5 (0.89) via this circuitous route is very close to that ($\alpha_5 = 0.91$) established via the direct route. The corresponding pair of values established for α_1 [3.09 and 3.14] are as close to one another as those for α_3 (1.52 and 1.47), which

TABLE 10: Comparison of the α-Values for the Linear and Cyclic Polyethylene Oxides Having the GMSs $CH_3O(CH_2CH_2O)_eCH_3$ and $(CH_2CH_2O)_e{}^a$

e	$\alpha_{1,e,1}$	D_e	α_e		$D_{s,e}$
1	**1.50**	0.1675	$[3.09, 3.14]^b$		0.1071
2	**1.02**	0.1395	**2.10**	→	**0.1045**
3	**0.74**	0.1134	1.52, 1.47	→	*0.1013*
4	**0.57**	0.0894	**1.13**	→	**0.0991**
5	0.464		0.91, 0.89		0.0962

$$\downarrow \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow$$

$$D_e = 0.1926 - 0.02604e \qquad\qquad D_{s,e} = 0.1098 - 0.00271e$$
$$r^2 = 0.9988 \qquad\qquad\qquad\qquad r^2 = 0.989$$

^{a} $\alpha_{1,e,1}$ is the α-value for $CH_3O(CH_2CH_2O)_eCH_3$ from Table 4 of ref 13. D_e is (log $\alpha_{1,e,1}$ − log $\alpha_{1,e+1,1}$). α_e is the α-value for $(CH_2CH_2O)_e$. $D_{s,e}$ is (log α_e − log $\alpha_{1,e,1}$)/ΔN, where ΔN is 3. ^{b} This α-value for ethylene oxide (3.12 ± 0.03), established via extrapolation of $(CH_2CH_2O)_e$ to $e = 1$, is much closer to that (2.94; Table 5) established via extrapolation of the epoxides $H(CH_2)_n(CH_2CH_2O)$ to $n = 0$ than it is to that (3.97; Table 4) established via extrapolation of $(CH_2)_nO$ to $n = 0$.

were both established by the more direct route as described above. These values for α_1 are placed in brackets because they must be higher than the "true" values, owing to the change in adsorption mode from tilted but "vertical", characteristic of the higher members of this series, to the almost flat orientation unique for ethylene oxide, as discussed earlier.

It is interesting to note that the average α-value for ethylene oxide (3.12 ± 0.03; Table 10) deduced by extrapolation to $e = 1$ in the $(CH_2CH_2O)_e$ series is much closer to that (2.94; Table 5) deduced by extrapolation to $n = 0$ in the $H(CH_2)_n(CHCH_2O)$ series than it is to that (3.97; Table 4) deduced by extrapolation to $n = 1$ in the $(CH_2)_nO$ series. It is inferred from these observations that the mode of adsorption for the cyclic polyethylene oxides is similar to that characteristic of the epoxide series, i.e., tilted to one side as shown in Figure 3a,c, rather than similar to that characteristic of nonsubstituted cyclic monoethers, such as tetrahydrofuran (Figure 3d), which is not tilted with respect to the adsorption site.

It is also interesting to compare the α-values for tetrahydropyran (2.21), *p*-dioxane (2.10), and 4-methyl morpholine (1.95; E#s 4, 9, and 11, respectively, in Table 3), which decrease in the order mentioned. This is in sharp contrast to the large increases in α caused by such replacements of methylene units by an oxygen atom exhibited by the corresponding linear series.

Polyethers Comprised of Acyclic and Cyclic Units; RO-$(CH_2)_m[CH(CH_2)_{n-1}O]$. When alkyl substituents are present on the ring structures of cyclic polyethers, it can no longer be assumed that the ether oxygen atoms therein are equivalent with respect to the adsorption site. Our studies of acyclic polyethers have shown[10−13] that adsorption selectively favors the oxygen atom having the lesser number of substituents on the adjacent methylene units. The same is true for the cyclic polyethers. Thus, it is easy to see that adsorption selectivity in the cases of the 4-methyl and 4,4-dimethyl-1,3-dioxolanes favors the oxygen atom farther away from the position of methyl substitution. It is more difficult, however, to make the correct assignment of adsorption preference in the case of 2-methoxymethyltetrahydrofuran (E# 18 in Table 3). Here it is possible to form liaison with the phenyl group via the external methyl ether oxygen atom or the nearby internal cyclic ether atom, as shown in parts a and b of Figure 9, respectively. It may be possible to adjudicate between these two possibilities, however, by comparing the α-value observed for this diether (α = 1.56; E# 18 in Table 3) with those observed for related structures.

If one assumes that the adsorption preference favors the ether oxygen in the ring, then the proper comparison is with that (α =1.81) for 2-methyltetrahydrofuran (E# 7). This comparison, however, indicates a decrease in α that is much greater than expected owing to insertion of two additional mass units in the side chain. If instead one assumes that the adsorption preference
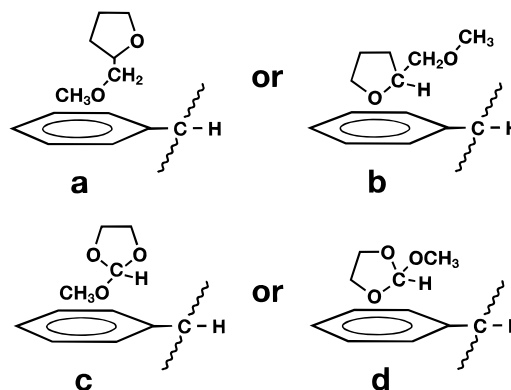

Figure 9. Schematic representations of alternative modes for molecular adsorption to the pendent phenyl groups of polystyrene at liquid-saturation that may be exhibited by molecules having ether oxygen atoms in both cyclic and acyclic locations.

favors the methoxy ether atom, then the best comparison is with that (α =1.70) for methylcyclopentyl ether (E# 20). This difference is closer to that expected for incrementation of a single mass unit in the side chain of a homologous series of this type. Hence, it is judged (tentatively) that the adsorption preference in this case favors the methoxy ether over the cyclic ether oxygen atom, i.e., the mode shown in Figure 9a over that shown in Figure 9b.

The assignment of the adsorption preference in the case of 2-methoxy-1,3,-dioxolane (α =1.52, E# 19 in Table 3) is even more uncertain. Here, the choice is between the methoxy oxygen atom (Figure 9c) or one of two cyclic oxygen atoms (Figure 9d) that are covalently bonded to the same carbon atom. Here again the comparison of the α-value (1.52) for E# 19 with that (α =1.96; q = 1;Table 10) for 2-methyl-1,3-dioxolane and with that (1.70) for methyl cyclopentyl ether (E# 20 in Table 3) shows that decrease in α is closer to that expected for incrementation in the side chain of methyl cyclopentyl ether by one mass unit than it is for the corresponding incrementation in the side chain of 2-methyl-1,3-dioxolane. Thus it is believed, tentatively, that the adsorption preference favors the methoxy oxygen atom (Figure 9c) over the cyclic ether atom (Figure 9d). It is obvious, however, that the (averaged) mode of adsorption to crosslinked polymer at liquid-saturation will not be established unequivocally until an analytical tool can be created that permits one to characterize the architecture of dynamically immobilized adsorbed molecules in the presence of much larger numbers of the mobile nonadsorbed moecules that comprise such liquid−polymer gel systems.

Meanwhile we will continue to test the conclusions inferred from our ongoing study of adsorption to polymer at liquid-saturation as a function of molecular structure, by comparing

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predicted α-values for molecules not yet available to us with the experimental values that will be determined when they do become available. If the observed values continue to agree with the predicted values as well as they have in the past, then the confidence in the predictive value of the relationships developed in this ongoing study will be increased; but if the observed values do not agree with prediction, then our inferences regarding molecular adsorption will have to be altered accordingly until a completely self-consistent hypothesis is developed.

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