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Polymer swelling: 22. Molecular structure–affinity correlation studies that involve poly(styrene-*co*-divinylbenzene) exposed to saturated hydrocarbons

L.A. Errede*, George V.D. Tiers

3M Corporation Research Laboratories, 3M Center Building 201-2N-22, St. Paul, MN 55144, USA

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Abstract

The adsorption parameters (α) for members of four classes of saturated hydrocarbons were compared with those observed for the corresponding ethers. The saturated hydrocarbon liquids exhibit a measurable affinity for polystyrene, as indicated by the linear relationships $\log \alpha_f = \log \alpha_i - D_s(N_f - N_i)$, each characteristic of the homologous series being considered. These values increase from the linear series $H(CH_2)_nH$ ($\alpha_i = 0.10 \pm 0.02$; $D_s = 0.00 \pm 0.02$) to those having the greatest affinity, members of the cyclic series $(CH_2)_n$, where $\alpha_i = 0.863$ and $D_s = 0.0875$. Even the latter, however, are considerably below the values for the corresponding cyclic ethers $(CH_2)_nO$ ($\alpha_i = 3.31$; $D_s = 0.0888$), demonstrating the superiority of an oxygen atom and a methylene unit in affinity for the polymer's phenyl group.

Keywords: Polystyrene; Adsorption parameter; Saturated hydrocarbons

1. 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, by means of a set of six $(Sty)_{1-x}(DVB)_x$ samples having known values of x, as described in considerable detail elsewhere [1–15] and recounted briefly here in Section 2. The α values reported thus far (> 500) range from 0 to 4, and they are reproducible to within $\pm$ 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 strong affinity for the polymer), in which one structural variable in the series is incremented systematically from 1 to its allowable limit while the others are held constant. It was observed in such studies [2–14] that the logarithms of the α values determined for a given homologous series exhibit a linear relationship with the total number (N) of methylene mass units (or equivalent) as expressed by:

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

where 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.

In this regard the studies involving sorption of ether molecules were particularly informative [10–14], especially those that are subseries of the general molecular structure (GMS) $H(CH_2)_{m+1}[(CH_3)_{q'}CH_{2-q'}OCH_{2-q}(CH_3)_q](CH_2)_{n+1}H$, where the ether oxygen is the atom having relatively strong affinity for the pendant phenyl group in the polymer; m and n are an integer from 1 to 8, and q and q' are integers from 0 to 2. Since each permutation of this GMS appears in more than one subseries, it was possible to construct a multidimensional, rigidly interconnected network of $\log \alpha$ versus N linear relationships [Eq. (1)] that represent the full set of subseries, as illustrated in Figs. 5 to 14 of [11]. Thus, after only a relatively few α values for some of the

* Corresponding author. Tel.: +1-612-733-0036; fax: +1-612-733-0648.

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key smaller molecules were established experimentally, it was possible to calculate with reasonable confidence those for the rest of the members permuted in molecular structure ($8 \times 8 \times 3 \times 3$) that comprise the GMS classification.

The above studies also demonstrated that the mode of adsorption to the pendant phenyl group of the polymer (at liquid saturation) is an important uncontrolled variable that must remain constant, if one network of $\log \alpha$ versus N linear relationships (i.e., vectors in multidimensional space) is to reproduce the experimental data. A change in the mode of adsorption within a given homologous series is signalled by a sharp change in the decrementation constant (D_s) of Eq. (1), as illustrated by examples reported in [11–15].

The understanding developed in these studies of ether sorption [10–14] enable us to interpret meaningfully the data accumulated earlier for many other functional classes of liquid that heretofore had appeared to be mutually inconsistent. The first such example was reported for sulfur-containing organic liquids, as described in our preceding publication [15]. We now report the second example, which involves sorption of saturated hydrocarbons. Since these molecules have neither a hetero atom nor a functional group, the study permits us to evaluate the lowest effective affinity between sorbable liquid molecules and the sorbent polymer, thus providing a suitable reference base for comparison with functional derivatives thereof. The purpose of this contribution is to report the data collected in this study and the conclusions derived therefrom.

2. Experimental

The set of six composite film samples, employed as polymeric sorbent in all of our previous studies of $(Sty)_{1-x}(DVB)_x$ swelling-to-saturation in hundreds of test liquids, were used again in this study of the sorption of linear, branched and cyclic saturated hydrocarbons. The greater part of these studies 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 preceding publication on sorption of sulfur-containing liquids [15]), which was done to permit us to use a 'scaled down' version of the original protocol in the evaluation of liquid samples that were available to us in only small amounts ($<$ 10 ml). The procedure for making these composite film samples, comprised of $(Sty)_{1-x}(DVB)_x$ particles ($>$ 80% by weight) enmeshed in polytetrafluoroethylene (PTFE) microfibres, and the distribution of these particles in the microporous composite films produced therefrom (see Figs. 1, 6, 7 and 20 of [1]), are described in considerable detail elsewhere [1–12]. Reagent-grade samples of test liquids were obtained from commercial sources, and most of them were used as such without further purification. Exceptions are the samples of cyclic $(CH_2)_n$ liquids, which were purified by fractional distillation, because the purities of those obtained commercially ($<$ 90%) were usually unsuitable for reliable evaluation of the relative swelling power. In contrast, the purities ($>$ 98%) of the alkyl-substituted cyclic hydrocarbons $(CH_2)_{m-1}CHR$ obtained from these sources were such that they were usable without further purification in all cases.

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 $\pm$ 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 crosslinked junctions in the respective samples, provides the relative swelling power (C, in ml of adsorbed liquid per gram of particles) of the sorbed test liquid, in accordance with:

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

where 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 the equation:

$$\alpha = 104Cd/M \tag{3}$$

where 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 [16]:

$$\chi_v = 0.49 + 1.01v - 0.61vC \tag{4}$$

where 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 Fig. 4 of [16]), only the χ_1 values are reported in Table 1. The χ_v values at any other value of v can be calculated by using:

$$\chi_v = 0.49 + v\left(\chi_1 - 0.49\right) \tag{5}$$

3. Results and discussion

3.1. Accumulation of sorption data

The sorption data accumulated in these studies using the saturated hydrocarbon liquids (Nos 1 to 20) are collected in Table 1. The relative swelling powers [C; Eq. (2)] established thereby 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 Section 2 above. The data for the saturated molecules are subdivided under four headings: the acyclic hydrocarbons, the monocyclic

Table 1
Sorption data for saturated hydrocarbons

No.	Molecular structure	N	d	$\lambda_0^{1/3}$	C	α	χ_1
(A) Acyclic hydrocarbons							
1*	n-Pentane	5	0.626	1.4	0.08	0.07	1.45
2	n-Hexane	6	0.659	0.40	0.10	0.08	1.44
3	n-Heptane	7	0.794	1.3	0.07	0.05	1.46
4*	2-Methylbutane	5	0.620	1.9	0.04	0.03	1.48
5*	2-Methylpentane	6	0.653	1.3	0.07	0.05	1.46
(B) Monocyclic hydrocarbons $(CH_2)_n$							
6	Cyclopentane $(CH_2)_5$	5	0.751	1.71	0.65	0.72	1.10
7	Cyclohexane $(CH_2)_6$	6	0.779	1.72	0.58	0.56	1.15
8	Cycloheptane $(CH_2)_7$	7	0.811	1.70	0.55	0.47	1.16
9	Cyclooctane $(CH_2)_8$	8	0.834	1.70	0.55	0.39	1.16
(C) Substituted monocyclic hydrocarbons $RCH(CH_2)_n$							
10	$CH_3CH(CH_2)_4$	6	0.749	1.80	0.42	0.39	1.24
11	$CH_3CH(CH_2)_5$	7	0.770	1.90	0.39	0.32	1.26
12	$H(CH_2)_2CH(CH_2)_5$	8	0.788	1.78	0.24	0.18	1.35
13	$H(CH_2)_3CH(CH_2)_5$	9	0.793	1.70	0.16	0.10	1.40
14	$H(CH_2)_4CH(CH_2)_5$	10	0.818	1.71	0.090	0.054	1.45
15	$(CH_3)_2CHCH(CH_2)_5$	9	0.802	1.70	0.15	0.10	1.41
16	$(CH_3)_3CCH(CH_2)_5$	10	0.831	1.70	0.086	0.053	1.45
(C) Polycyclic hydrocarbons							
17	*trans*-decalin	10	0.870	1.80	0.44	0.29	1.23
18	*cis*-decalin	10	0.897	1.85	1.00	0.68	0.89
19	1,3-dimethyladamanthane	12	0.886	1.70	0.089[a]	0.05[a]	1.45
20*	dicyclohexyl	12	0.864	1.70	0.49	0.27	1.20

N, total number of methylene mass-units or equivalent; d, density of the liquid; $\lambda_0^{1/3}$, value of $\gamma^{1/3}$ (eq. 2) extrapolated to $S = 0$; C, relative swelling power, as defined in eq. 2; α, adsorption parameter, as defined in eq. 3; χ_1, Flory–Huggins interaction parameter, calculated using eq. 4.
*indicates that these data were determined after 1996 using the 'scaled down' version of the procedure described in the Experimental Section.
[a]because of poor wetting and extremely slow rate of permeation, the procedure for this determination was modified such that the set of six composite film samples were preswelled to saturation in acetone before immersion in excess dimethyladamanthane. The presorbed 'better solvent' was then eliminated by evaporation at 23°C under a continuous stream of nitrogen for 24 h.

hydrocarbons $(CH_2)_n$, the alkyl-substituted derivatives thereof $RCH(CH_2)_{n-1}$, and the polycyclic hydrocarbons. The test liquids that were evaluated by means of 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.

3.2. Interpretation of the sorption data

3.2.1. Saturated acyclic aliphatic hydrocarbons

The results observed in our preliminary studies, involving sorption of $H(CH_2)_nH$ liquids by $(Sty)_{1-x}(DVB)_x$ as described in Section 2, were reported in Part 7 of this ongoing study [3]. We noted that these liquids wet the microporous composite film samples immediately on contact so that the interstices in the composite films were filled within seconds by capillary action. However, significant swelling of the polymer particles did not occur under the conditions described above (i.e., overnight at 23°C). In fact, only the samples having the higher-crosslink-density particles ($x > 0.03$; $\lambda^{1/3} < 3.25$) exhibited some evidence of liquid sorption, i.e., S values between 0.01 to 0.10. Even these values, however, were difficult to reproduce within $\pm$ 0.04, and varied randomly with $\lambda^{1/3}$ instead of increasing monotonically therewith. On the basis of the above preliminary results we reported that the α values for the $H(CH_2)_nH$ liquids were virtually zero (see Table 9 of [3]).

As part of our reconsideration of the sorption results observed earlier for saturated hydrocarbons, we decided to repeat the experiments described above, with the modification that 30 days at 23°C were allowed for the samples to attain saturation equilibrium instead of just overnight. The S versus $\lambda^{1/3}$ patterns thus obtained were more consistent with those reported for liquids having relatively poor affinity for polystyrene (i.e., those having α values < 0.05; see for example the S versus $\lambda^{1/3}$ relationships in [9] for binary solutions in which the samples are deswelled in a poor solvent after being swelled to saturation in a good solvent). The S value for each of the hydrocarbon liquids tested at 23°C for 30 days tended to increase from 0 at $\lambda^{1/3} < 2.16$ (i.e., $x > 0.11$) to about 0.5 at $\lambda^{1/3} = 3.25$ (i.e., $x = 0.03$) and then decreased sharply to $S < 0.01$ at $\lambda^{1/3} = 5.2$ (i.e., $x = 0.01$). The marked negative deviation from the linearity established using only the samples having $x > 0.02$ (the lesser

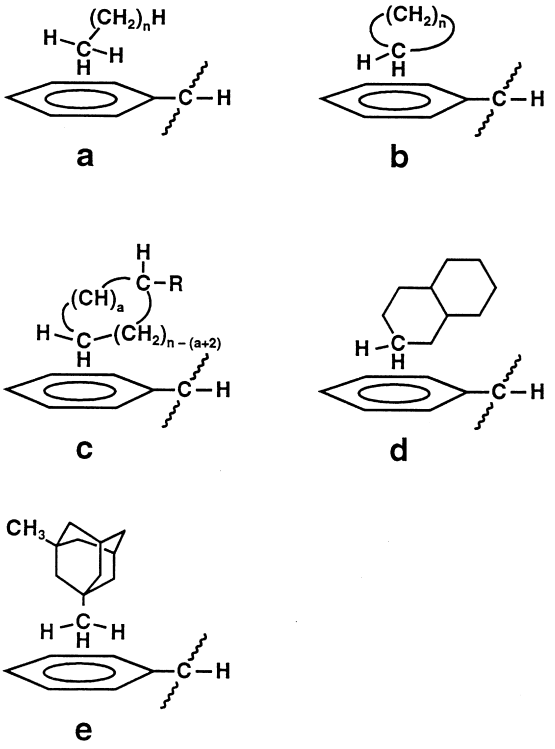

Fig. 1. Suggested modes of adsorption for various types of saturated hydrocarbon to a pendant phenyl group of polystyrene.

crosslinked samples) is caused by liquid-induced polymer–polymer association, when in the presence of a poor solvent. Such self-association is much more difficult in the higher-crosslinked polymer samples because of the greater restraints on segment mobility, which serve to suppress or preclude the requisite self-orientation of these segments needed for polymer–polymer association, as discussed earlier [9]. These physical associations are in effect 'physical crosslinks' that serve to oppose polymer swelling, as do the covalent crosslinkages, so that the degree of polymer swelling is decreased accordingly (i.e., swelling varies inversely with the sum of the two types of crosslink).

Heating the systems to about 60°C under pressure for an additional 8 h and then cooling to 23°C served only to shift $\lambda_0^{1/3}$ to lower values (i.e., to < 1.4) and to increase the S values slightly for the samples having $x = 0.01$ and 0.02, owing to the 'memory' of the system at 60°C, as discussed previously [9,15]. The slope and the maximum value attained at $x = 0.03$ or 0.04 were, however, unchanged.

The reproducibility of the S values observed for these test liquids after such exposure conditions was only somewhat better than that observed earlier by using shorter (and/or milder) exposure conditions (i.e., overnight at 23°C). The square of the correlation coefficient for the best straight line through the data points (usually less than 4) for the samples having $x > 0.02$, however, was less than $r^2 = 0.9$, which made it difficult to reproduce the slope C within $\pm$ 0.02. Hence, the logarithms of the α values calculated therefrom (Table 1) do not define a reliable $\log \alpha$ versus N linear relationship, as expressed by Eq. (1).

A semi-quantitative approximation of the 'true' $\log \alpha$ versus N relationship can be established, however, when the data for these hydrocarbons are considered in light of the results reported for similar studies involving sorption of $Z(CH_2)_nH$ liquids, in which Z is the group or atom making liaison with the adsorption site. We noted in those studies that the constants α_i and D_s for Eq. (1) depend on Z (see Table 1 of [8]). In the case of the $H(CH_2)_nH$ liquids (Series 1), it was assumed by analogy with the above that Z is a hydrogen atom on one of the two terminal methyl groups, as suggested in Fig. 1(a). This mode of adsorption should minimize steric hindrance and maximize dynamic associative interaction of the rest of the molecule with the mobile sorbed-but-not-adsorbed molecules in the polymer–liquid system at saturation.

The D_s value (characteristic of members of the series $H(CH_2)_nH$ having $n < 7$) is very small (and perhaps may even be negative; i.e., having a slightly positive slope, as indicated by the calculated value using the data points for $n = 5$ and 6). This is interpreted to mean that α_i at $N = 1$ (i.e., for CH_4) must be only about 0.1 $\pm$ 0.02. Since others have shown [17–19] that self-association owing to correlated molecular orientation of methylene units begins to be measurable in $H(CH_2)_nH$ liquids (Series 1) when $n = 6$ and thereafter increases in magnitude with the difference $n - 6$, and since we have observed that the α_n values for the member having $n = 7$ is 0.05 and those for $n = 8$ and 9 are not measurable by our method (i.e., < 0.01), it is concluded that the data points for the members having $n > 6$ must fall off sharply from the $\log \alpha$ versus N linear relationship ($\alpha_i = 0.1 \pm 0.02$ at $N = 1$; $D_s = 0.0 \pm 0.001$) established for the lower members, such that $\alpha < 0.01$ at $n \approx 9$ or 10.

The very low α values exhibited by the $H(CH_2)_nH$ liquids suggest that the affinity of these liquids for polystyrene is comparable to that for molecules of its own kind (owing to correlated molecular orientation when $n > 6$), as described above. This implies that the mode of adsorption of $H(CH_2)_nH$ to polystyrene may involve association of methylene units with the backbone of the polymer as well as with pendant phenyl groups. In fact, the very small α values observed for these liquids might be attributed to simultaneous adsorption to both the backbone and a pendant phenyl group. This in effect is a multidentate mode of adsorption that differs markedly from the monodentate mode shown in Fig. 1(a); i.e., the entire $H(CH_2)_nH$ molecule would make contact with the polymer making further adsorption sterically more difficult.

That the $\log \alpha$ versus N linear relationship for the $H(CH_2)_nH$ liquids is qualitatively different from those exhibited by both the $Z(CH_2)_nH$ and $(CH_2)_n$ series (i.e., D_s of Eq. (1) is 0 or > 0 instead of < 0) is consistent with the view that the mode of adsorption may be unique to the $H(CH_2)_nH$ series, as described above.

The α value for 2-methylbutane (0.03 $\pm$ 0.02 at $N = 5$)

was less than that for n-pentane (0.07 ± 0.02), and that for 2-methylpentane (0.05 ± 0.02 at $N = 6$) was less than that for n-hexane (0.08 ± 0.02). These observations are consistent with expectation regardless of the mode of adsorption, because in either case a branched methyl group will serve to increase steric hindrance to further adsorption.

It should be noted here that because an experimental means (spectrometric or otherwise) for characterizing the molecular architecture of the adsorbed molecule in the presence of a much greater amount of mobile sorbed-but-not-adsorbed molecules of its own kind in the gel system at liquid saturation is unknown, it is not possible to obtain hard physical evidence that can support or refute the validity of the suggested modes of adsorption shown in Fig. 1 (and in similar figures recorded in earlier publications). These schematic representations, therefore, represent imaginary models that have been inferred from earlier results and by intuitive reasoning. They are offered to serve as useful visual aids to the understanding of association between molecules. Until an experimental means is found that would enable one to 'see' the true architecture of molecules in their adsorbed state, these models will continue to be used as working hypotheses, but only so long as they remain consistent with the observed results and have predictive value.

3.2.2. Saturated cyclic aliphatic hydrocarbons

Pure samples of the liquids having the GMS $(CH_2)_n$ were more difficult to obtain commercially. Even the samples labelled 'spectro' and 'reagent' grade contain significant quantities of related hydrocarbons as impurities, which do not affect adversely the intended applications. These samples were unsuitable for our purposes, however, and had to be fractionally distilled to increase the purity to at least 95% (preferably $> 99\%$) before they were acceptable for determination of their respective adsorption parameters (Nos 6 to 9 in Table 1). Compared with the results observed for the acyclic hydrocarbons (described above), the volumes (S) of sorbed liquid per gram of polymer in each of the six composite film samples were considerably greater and more easily reproducible. Moreover, the full set of six S values obtained thereby fell on a straight line, as given by Eq. (2), so that the relative swelling power (C) and adsorption parameter (α) for these test liquids could be established within the usual range of ± 0.01.

The negative slope of the best straight line ($r^2 = 0.933$) through the set of four log α data points for the members having $n = 5$ to 8 (filled circles on the middle straight line in Fig. 2) was used to establish the decrementation constant [Eq. (1); $D_2 = 0.0875$] for this homologous series (Series 2

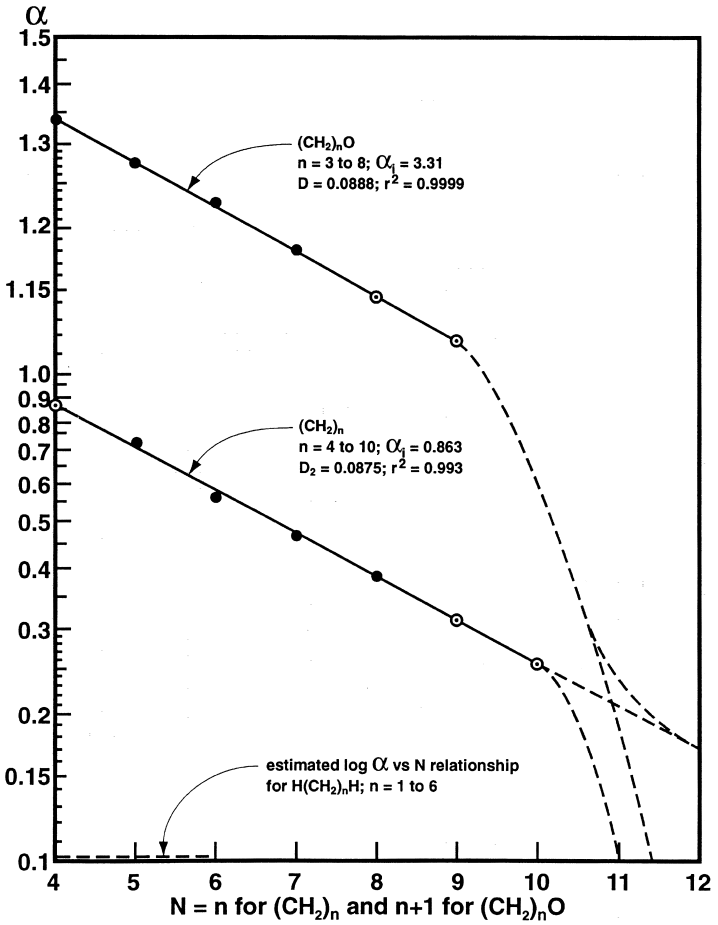

Fig. 2. Comparison of the log α versus N linear relationships for $H(CH_2)_nH$ and $(CH_2)_n$ with that for $(CH_2)_nO$.

Table 2
Log $\alpha_f = \log \alpha_i - D_s(N_f - N_i)$ relationships for subseries of hydrocarbons having the GMS $(CH_2)_{m-1}CH(CH_2)_nH$

m	n	Series no.	α_i:N_i	D_s	α_f:N_f	r^2
4 to 10	0	2	0.863:4	0.0875	0.258:10	← 0.993
4 to 10	1	2a	0.481:5		0.143:11	
4 to 10	2	2b	0.268:6		0.0800:12	
4 to 10	3	2c	0.150:7		0.0448:13	
4 to 10	4	2d	0.0834:8		0.0248:14	
4 to 10	5	2e	0.0465:9		0.0139:15	
4 to 10	6	2f	0.0259:10		0.00773:16	
4 to 10	7	2g	0.0145:11		0.00433:17	
4 to 10	8	2h	0.00806:12		0.00241:18	
			↑		↑	
			Series 3a		Series 3f	
4	0 to 8	3a	0.863:4		0.00806:12	
5	0 to 8	3b	0.706:5		0.00606:13	
6	0 to 8	3	0.577:6	0.2537	0.00539:14	← 0.9997
7	0 to 8	3c	0.472:7		0.00441:15	
8	0 to 8	3d	0.386:8		0.00361:16	
9	0 to 8	3e	0.315:9		0.00294:17	
10	0 to 8	3f	0.258:10		0.00241:18	
			↑		↑	
			Series 2		Series 2h	

r^2 is the square of the correlation coefficient determined by linear regression for the homologous series being considered, as indicated by the arrow.

in Table 2). The α values for three other members of $(CH_2)_n$ were deduced (with reasonable confidence) by extrapolation downwards to $n = 4$ and upwards to $n = 10$ (empty circles on that straight line). Extrapolation to higher members of this series was deemed unwarranted. The melting points reported [20] for the members having $n = 11$ ($-$ 7.6°C) and $n = 12$ (61°C) suggest that significant self-association would occur owing to correlated molecular orientation of polymethylene segments, which would result in the α values for the members having $n > 10$ deviating markedly below the linear relationship, as shown in Fig. 2 by the hypothetical lower curved dashed line.

Comparison of this set of data points ($\alpha = 0.863$ at $N = 4$ to $\alpha = 0.258$ at $N = 10$) for the members of $(CH_2)_n$ with those for the members of $H(CH_2)_nH$ (i.e., all less than $\alpha \approx 0.10$) shows clearly that the α values for the cyclic molecules are well above those for the corresponding acyclic molecules. This observation is consistent with the results observed in similar comparative studies, which involved sorption of iodo-, bromo-, chloro- or phenyl-substituted alkanes [7] also those involving hydrocarbon ethers [14] or thioethers [15]. This is interpreted to mean that the cyclic moiety can self-assemble on the adsorption site more efficiently than the corresponding acyclic moeity, and that the differences in the respective $\log \alpha$ versus N relationships reflect the difference in the relative steric hindrance to additional adsorption. It is suggested that the mode of adsorption of the $(CH_2)_n$ molecules to the pendant phenyl groups of the polymer is between a hydrogen on the cycloalkane and the π electrons of the phenyl group (rather than with the backbone of the polymer) while the rest of the adsorbed molecule extends away from the adsorption site, as shown in Fig. 1(b). Although local polarity of the C–H bond (and thus of the CH_2 group) may be invoked here, the cycloalkanes are markedly denser than the acyclics and therefore have higher polarizability, which in turn implies stronger van der Waals' interaction with the polarizable phenyl group.

In this respect it is interesting to note that the $\log \alpha$ versus N linear relationship for the members of $(CH_2)_nO$ having $n = 3$ to 8 [Eq. (1); $\alpha_i = 3.25$; $D_s = 0.0888$; upper straight line in Fig. 2] is uniformly above and virtually parallel to that for the members of $(CH_2)_n$ having $n = 4$ to 10 [Eq. (1); $\alpha_i = 0.863$; $D_s = 0.0875$; middle straight line in Fig. 2]. This parallelism implies that the decreases in $\log \alpha$ per unit change in n is virtually the same for these two series. This supports the point of view that association is predominantly with the phenyl groups, and further suggests that the angles at which the non-adsorbed portions of the cyclic structures project away from the adsorption site in these two series [Fig. 2(b)] are about the same. The magnitude of the displacement of the former relationship above the latter reflects the affinity of the heterocyclic oxygen atom for the adsorption site relative to that of a cyclic methylene unit.

Since samples of the members of the cyclic $(CH_2)_n$ series having $n > 8$ are rare, we were not able to establish the upper allowable limit for n. Although samples of the lower members ($n < 4$) are indeed available, they are gases at room temperature, and therefore the α values for these members could not be established by our experimental procedure. Moreover, they could not be estimated with confidence by extrapolation of the $\log \alpha$ versus N linear relationships established using the higher members because of the uncertainty concerning the mode of adsorption when $n = 3$. Our studies with the cyclic ethers, $(CH_2)_nO$ (see

Table 4 in [14]), have shown that a change in the mode of adsorption occurs in the ether series at $n = 2$ — from the vertical mode characteristic of the members having $n > 2$ to the horizontal mode unique to $(CH_2)_2O$ (see Figs. 3d and 2d respectively in [14]) — which manifests itself in an α value for ethylene oxide that is about half that expected on the basis of extrapolation, as discussed in [14].

In addition, the above study called attention to a change in adsorption mode that can occur in the $(CH_2)_nO$ series when n is 8 to 10. Others had reported [21–26] that members of cyclic homologous series of the type $(CH_2)_nA$, in which A is a functional group such as CHOH, $CHNH_2$ and C=O, react normally with chemical reagents with $n < 9$, but are insensitive towards these reagents when $n = 9$ to 12. The earlier investigators of this phenomenon attributed the observed anomalous chemical behaviour to steric hindrance owing to the tightly compacted cyclic polymethylene chain, which causes the functional group to be directed inwards rather than outwards, thereby rendering the normally reactive group inaccessible to the reagent even when dissolved. Reasoning by analogy with the above observations, we suggested that the ether oxygen atom in the members of the $(CH_2)_nO$ series having $n > 8$ might also be directed inwards instead of outwards, thereby preventing that atom, which has the relatively strong affinity for the adsorption sites (i.e., the pendant phenyl groups), from actually making contact therewith. Consequently the data points for the members having $n > 8$ should deviate negatively and sharply from the $\log \alpha$ versus N linear relationship exhibited by those for the cyclic ethers having $n = 3$ to 8. This is indicated in Fig. 2 by the hypothetical curved dashed line extending downwards from the upper line, for $(CH_2)_nO$ at $N = 9$, towards the dashed linear extension of the lower line, for $(CH_2)_n$ at about $N = 11$.

3.2.3. Substituted saturated cyclic hydrocarbons $(CH_2)_{m-1}CHR$, m = 4 to 10

It was suggested in the preceding section that the enormous differences observed in adsorptivity between the cyclic and acyclic polymethylene molecules having the same number of carbon atoms is attributable to entropic considerations; i.e., self-assembly of the cyclic molecular architecture (which has an additional favourable statistical factor) can be accommodated more efficiently than that of the acyclic moieties, which offer greater steric hindrance to additional adsorption owing to unrestrained motion of the linear segments not attached to the adsorption site. If this were indeed the case then the decrementation constant of the $\log \alpha$ versus N linear relationship for a subseries of $[(CH_2)_{m-1}CH](CH_2)_nH$, in which m is held constant while n is incremented from 0 to 8, should be considerably greater than that for those in which n is held constant while m is incremented from 4 to 10. This is because the higher cyclic polarizability, the statistical factor and the markedly improved packing efficiency in the case of cyclic $(CH_2)_m$, owing to severe restraints on segment flexibility, will be negated progressively as n in the $(CH_2)_nH$ segment is incremented from 0 to 8.

This is indeed the case, as shown in Fig. 3, which compares the $\log \alpha$ versus N linear relationship for members of the $[(CH_2)_{m-1}CH](CH_2)_nH$ series, in which m is incremented from 4 to 10 while n is kept constant at 0 (i.e., $\alpha_i = 0.863$ at $N = 4$; $D_2 = 0.0875$ and $r^2 = 0.993$ for Series 2 in Table 2), with the $\log \alpha$ versus N linear relationship for the series in which m is kept constant at 6 while n is incremented from 0 to 8 (i.e., $\alpha_i = 0.577$ at $N = 6$; $D_3 = 0.2537$ and $r^2 = 0.9997$ for Series 3 in Table 2, which was deduced in the usual way using the data for hydrocarbons Nos 11 to 14 in Table 1). This comparison (Table 2) shows that the decrementation constant for Series 3 ($D_3 = 0.2537$) is about three times greater than that ($D_2 = 0.0875$) for Series 2, which reflects among other effects the respective magnitudes of increased steric hindrance to adsorption caused by incrementation of methylene units in the cyclic structure relative to that for the corresponding incrementation in the attached linear segment, owing to the disruptive effect on packing efficiency by the protruding $(CH_2)_nH$ substituent, as suggested in Fig. 1(c).

The set of six subseries of $[(CH_2)_{m-1}CH](CH_2)_nH$, in which m is held constant at 4 to 10 while n is incremented from 0 to 8, or the set of eight subseries in which m is incremented from 4 to 10 while n is held constant at 0 to 8 (Table 2), bear formal resemblance to the corresponding subsets of the homologous series having the GMS $ZCH_{2-q}(CH_3)_q(CH_2)_nH$, in which Z is a chloro, bromo, iodo, phenyl or RO group. Sorption studies of the Z classifications showed that the sets of $\log \alpha$ versus N linear relationships for each subseries of a given Z fall on a well-defined plane in multidimensional space such that the vectorial relationships, obtained when q is held constant at 1 or 2 while n is incremented from 0 to 8, are parallel to those obtained when q is held constant at 0. Similarly, the corresponding cross-over relationships obtained when n is held constant at 1 to 8 while q is incremented from 0 to 2 are parallel to those obtained when n is held constant at 0. Thus, the intersections of these two sets of mutually parallel lines identify the α values for all the permutations in molecular structures of each Z classification (for examples, see Figs. 7 to 10 in [7] and Figs. 9 to 12 in [11]).

The methylene group in the cyclic structure of $[(CH_2)_{m-1}CH](CH_2)_nH$ that presumably makes liaison with the adsorption site in this series corresponds to Z in the original series. The rest of the cyclic structure in this series corresponds to the middle portion $CH_{2-q}(CH_3)_q$ that is adjacent to Z. Although the quantitative effect on the electronic and steric considerations at the adsorption site caused by incrementation of q while n is kept constant in the case of the $ZCH_{2-q}(CH_3)_q(CH_2)_nH$ series is much greater than that caused by incrementation of m while n is kept constant in a series having the GMS $[(CH_2)_{m-1}CH](CH_2)_nH$, the qualitative considerations are unchanged. Hence, the set of six $\log \alpha$ versus N linear relationship for the $[(CH_2)_3(CH_2)_{m-4}]CH(CH_2)_nH$ subseries in

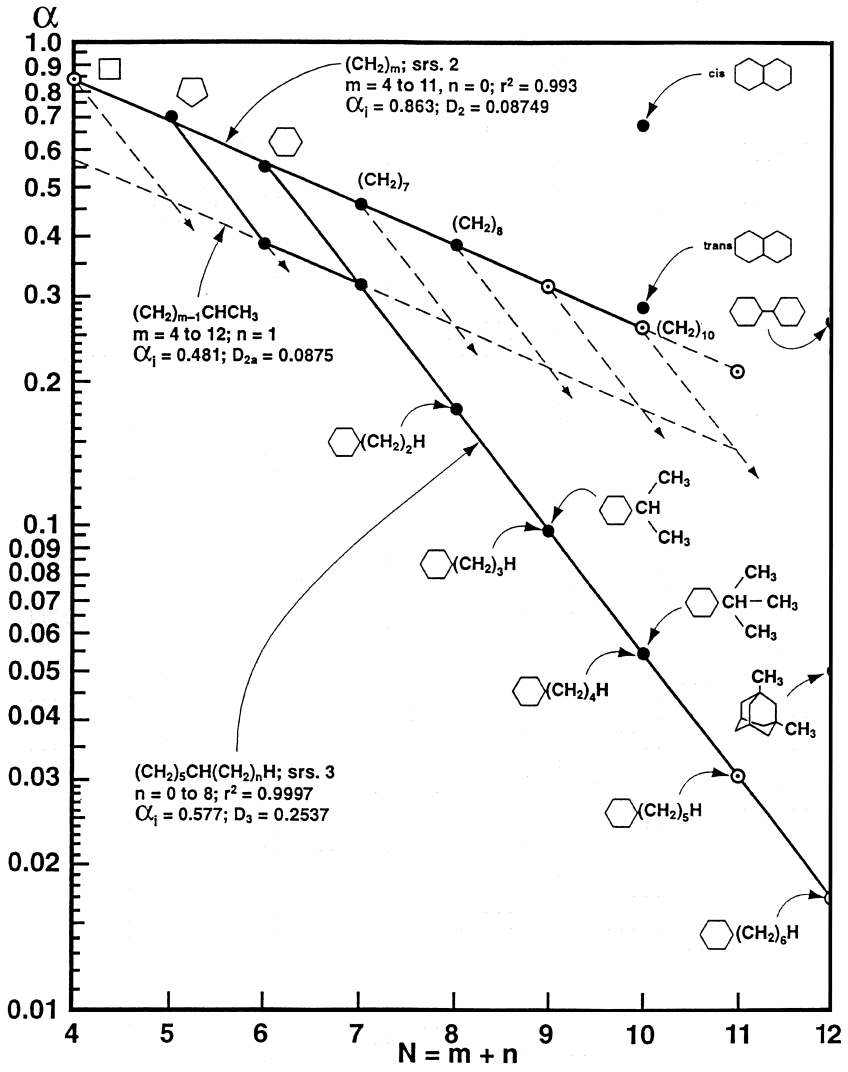

Fig. 3. Log α versus N linear relationships for $[(CH_2)_{m-1}CH](CH_2)_nH$ and related structures.

which m is held constant at 4, 5 and 7 to 10 while n is incremented from 0 to 8 (Series 3a to 3f in Table 2) should be parallel to that ($D_3 = 0.2537$) when m is held constant at 6 (Series 3 in Table 2), and the set of corresponding cross-over relationships (Series 2a to 2h in Table 2), obtained when m is incremented from 4 to 10 while n is held constant at 1 to 8, should be parallel to that ($D_2 = 0.0875$) when n is constant at 0 (Series 2 in Table 2).

Experimental support for this point of view results from the observations that the value for the decrementation constant for Series 3b (i.e., $m = 5$; n incremented from 0 to 8), calculated using the α values for only the first two members of that series (Nos. 6 and 10 in Table 1), is $D = 0.266$, and that for Series 2a (i.e., m incremented from 4 to 10; $n = 1$) calculated using the α values for only the second and third members of that series (Nos. 10 and 11 in Table 1) is $D = 0.0859$. These determinations of the decrementation constants for Series 2a and 3b are within reasonable reproducibility of the respective D_2 and D_3 values determined by linear regression using experimental α values for four or five members, as indicated by the filled circles in Fig. 3.

The set of α_i values for those that are parallel to Series 2 ($D_2 = 0.0875$) are given respectively by the set of α values for the members that comprise Series 3a (i.e., $m = 4$; $n = 0$ to 8), and the set of α_i values for those that are parallel to Series 3 ($D_3 = 0.2537$) are given respectively by the set of α values for the members that comprise Series 2 (i.e., m incremented from 4 to 10; $n = 0$).

Thus the α values for all the permutations of $[(CH_2)_{m-1}CH](CH_2)_nH$ are given by the intersections of these two sets of mutually parallel lines, which are contained in a parallelogram bounded at the top by the log α versus N linear relationship for Series 2, at the bottom by that for Series 2h, on the left by that for Series 3a and on the right by that for Series 3f (Table 2). Although only the top portion of this parallelogram (dashed lines that intersect the log α versus N linear relationship for Series 2 and 3) is indicated in Fig. 3, the exact α values for the rest of the

48 possible permutations of the above GMS can be calculated by means of the appropriate log α versus N linear relationship listed in Table 2.

That the decrementation constants for the series in which m is incremented from 4 to 10 while n is held constant at 0 to 8 (Series 2a to 2f in Table 2) have the same value (D_2 = 0.0875) is interpreted to mean that the adsorption mode for these series is the same, which implies that in each subseries the attached extension $(CH_2)_nH$ to the cyclic structure is not located on, or adjacent to, the portion of the molecule making liaison with the adsorption site. It is most probably located on the ring carbon atom furthest from the adsorption site, as shown in Fig. 1(c). Hence, the series having the GMS $[(CH_2)_{m-1}CH](CH_2)_nH$ might be represented more usefully if written in the form $[(CH_2)_3(CH_2)_{m-4}CH](CH_2)_nH$, where the segment $(CH_2)_3$ in the ring structure calls attention to this important conclusion.

That this may be general for all monosubstituted monocyclic hydrocarbons can be inferred from the observations that the α values for n-propyl- and isopropylcyclohexane (Nos 13 and 15 in Table 1) are the same (0.10), and those for the n-butylcyclohexane (Nos 14 and 16 in Table 1) also have essentially the same value (0.054 and 0.053 respectively), as shown in Fig. 3.

This is not true, however, in the cases that R in the $(CH_2)_nCHR$ molecule is itself a cyclic substituent. Thus, α for bicyclohexyl (No. 20 in Table 1) is about 0.27, whereas the α value calculated for n-hexylcyclohexane (Fig. 3, Series 3b in Table 2) is only 0.017. It was difficult to establish α for bicyclohexyl precisely because the viscosity of this liquid is so high that more than a month of immersion in this test liquid was required to attain apparent saturation at 23°C. This determination was repeated with the modification that the six composite film samples were swollen to saturation overnight in the test liquid at about 60°C, and then allowed to cool to room temperature for 24 h before initial gravimetric determination of the amounts of liquid sorbed. These amounts, however, were about twice those expected, presumably owing to the 'memory' of the molecular architecture of the system at 60°C. The samples were monitored periodically thereafter, which indicated that at least three weeks were required to return to an apparent equilibrium at 23°C. At this point the system exhibited essentially the same linear relationship [Eq. (2)] observed via swelling the set of dry samples to saturation in the test liquid at 23°C, thereby confirming equilibrium. Similar marked differences are noted when the α values observed for n-butylcyclohexane (0.054; No. 14 in Table 1) and that calculated for cyclodecane (0.26; Series 2 in Table 2) are compared with those (0.68 and 0.29) for *cis*- and *trans*-decalin, respectively (Nos 17 and 18 in Table 1).

All of the above comparisons reflect the relative improvement in 'packing density' onto the pendant phenyl group of the polymer at liquid saturation caused by progressive rigidization owing to cyclization of the molecular structures having the same mass, as noted in Fig. 1(c) and Fig. 1(d). In this respect, the denser *cis* configuration of decalin might be more easily accommodated by the pendant phenyl group than the *trans*, the latter being only slightly better than that anticipated for the monocylic moiety having the same number of carbon atoms [i.e., 0.26 for $(CH_2)_{10}$; Series 2 in Table 2] but considerably greater than that (0.054) observed for n-butylcyclohexane (No. 14 in Table 1). The argument based on polarizability, as established by refractive index [20], is strongly supported by the virtual identity of that for cyclodecane (n_D^{20} = 1.4710) and that for *trans*-decalin (n_D^{20} = 1.4690), whereas that for *cis*-decalin is n_D^{20} = 1.4800.

It is of interest to note that the α value for 1,3-dimethyladamantane (0.05 at N = 12; No. 19 and footnote a in Table 1) is about three times greater than that (0.017 at N = 12) anticipated for $(CH_2)_5CH(CH_2)_6H$ (see Series 3 in Table 2). This difference reflects the relative steric hindrance to further adsorption of the 12-carbon rigidly bulky 1,3-dimethyladamantane, as compared with the extended but much less rigid n-hexylcyclohexane. The mode of adsorption for 1,3-dimethyladamantane (n_D^{20} = 1.4780) may involve liaison of a methyl substituent with the adsorption site (owing to steric considerations), as shown in Fig. 1(e), whereas n-hexylcyclohexane utilizes one of the ring methylene units, as shown in Fig. 1(c).

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