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Nonclassical Urea Oligomers. VII. Binding Specificity of Carbanilido-ethylenimine Oligomer: Absorption Behavior in Suspension

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ABSTRACT

Elementary features of the absorption behavior of oligo[1-(N-phenylcarbamoyl)aziridine] were studied. The oligomeric host shows interesting binding specificities for a variety of organic compounds. The binding process for hydrogen bond-donating compounds typified by aromatic amines is found to be related to "swelling" of the solid oligomer host, and the binding specificity may be closely related to the essentially flexible or mobile nature of the oligomer host. For polar substrates containing S=O the absorption occurs in a less swollen state, resulting in a hindrance of absorption for aromatic S=O compounds. Selective absorption from binary systems, exemplified with S=O compounds, can be attained as expected from the corresponding single-substrate systems as far as at low substrate concentrations.

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INTRODUCTION

Specific binding of small molecules or ions with a natural oligomeric compound plays an important role in biochemical processes [1-5]. Structural information has recently been accumulated for naturally occurring biologically active oligomeric compounds, inspiring organic chemists to design highly structured host molecules. A variety of crown-type host molecules for metal ion [6-17] and organic ion bindings [18-23] has been investigated, but relatively little attention [24-30] has been paid to developing new types of oligomeric host molecule in which dynamic nature is responsible for the binding specificity, though the importance of these types of natural compound has been emphasized [31-35].

We have been strongly interested in the binding behavior of the octameric oligo[1-(N-phenylcarbamoyl)-aziridine] [oligo(NPCA)], i. e., carbanilido-polyethylenimine octamer, as a candidate for this kind of new oligomeric host molecule. This oligomer, having a narrow molecular weight distribution, can be readily obtained [36]. It has the following structural features: (1) it carries a regular recurrence of eight > NCONHPh groups along each chain, which can serve as hydrogen bond-donating or -accepting site, dipolar interaction site, and π-π interaction site; (2) the molecular conformation of the oligomer is essentially nonrigid. However, the -CONHPh side groups considerably restrict the rotational freedom along the backbone chain, resulting in the molecular shapes full of cavities constructed by the phenyl groups; (3) in an extreme case, the oligomer can take a conformation in which the two alternating carbamoyl side groups produce a cavity involving two parallel aromatic planes. This structure is similar to that of crystalline poly-N-acylaziridine reported by Litt and Summers [37], in which the two alternating acyl side groups produce a spacing of 6.4-6.8 Å diameter, adequate for insertion of a benzene ring.

As reported previously, the oligo(NPCA) has unexpectedly high specificities for binding of compounds containing S=O or P=O [29] and some metal ions [30]. However, the origin of the specificity has been in question. In order to understand the elementary features of the origin of absorption specificities, the binding behavior was investigated in this work by using some types of organic molecule including hydrogen bond-donating compounds (several aromatic amines, alcohols, etc.) and hydrogen bond-accepting polar compounds (mainly S=O compounds of the aromatic series and Et_2SO_4). Some observations which are of importance in characterizing the specific absorption property of the oligo(NPCA) host were obtained. The binding behavior of binary-substrate systems were also investigated in comparison with those of the corresponding single-substrate systems. In addition, a comparison was made for the absorption specificities of the oligo(NPCA) host and a ureanized-polyethylenimine host, a branched high polymer analog of the former.

EXPERIMENTAL

Materials

Oligo[1-(N-phenylcarbamoyl)-aziridine] [oligo(NPCA)] was prepared by ring-opening polymerization of 1-(N-phenylcarbamoyl)-aziridine with Et_2SO_4 as described in the preceding paper [36]. Removal of Et_2SO_4 from the oligomer was undertaken by treating with an Amberlite-400 column, resulting in oligo(NPCA) free from Et_2SO_4; S-content, 0.09% [29, 30]. Ethyl p-toluenesulfonate and ethyl p-toluenesulfinate were the same reagents used in the previous work [29]. Aromatic amines and other substrates except for the following two compounds were commercially available and they were used after purification.

p-Tolyl ethyl sulfone ($CH_3C_6H_4SO_2Et$) was prepared by the reaction of water with a mixture of p-tolyl-SO-ONa, Et_2SO_4, and Na_2CO_3 at 50°C [38]. The resultant sulfone was extracted with benzene, then purified by recrystallization; yield, 48%; mp, 54-55°C. The structure was confirmed by IR and NMR spectroscopy.

ANAL. Calcd for $C_9H_{12}O_2S$ (184): C, 58.26%; H, 6.57%; S, 17.40%. Found: C, 58.55%; H, 6.62%; S, 17.15%.

p-Tolyl ethyl sulfoxide ($CH_3C_6H_4SOEt$) was prepared by the reaction of EtMgBr with p-tolyl-SO-menthyl, [39, 40] then steam distilled, extracted with ether, and distilled; yield, 15%; bp, 120-125°C/Torr. The structure was identified by IR and NMR spectra.

ANAL. Calcd for $C_9H_{12}OS$ (168): C, 64.24%; H, 7.19%; S, 19.05%. Found: C, 63.92%; H, 7.28%; S, 18.83%.

Absorption of Small Molecules on the Oligo(NPCA)

A given amount of a small molecule was dissolved in ethyl acetate or ethanol. In this solution a given amount of the oligo(NPCA), finely pulverized, was suspended at a given temperature. After a specified time, the oligo(NPCA) was separated by centrifugation, and the solution was analyzed by means of GC or LC with toluene as an internal standard. The absorbed amount was determined from the difference of the initial and remaining amounts of the substrate. Toluene was used as the standard because it is not absorbed in the oligo(NPCA) at all. This was confirmed by the NMR spectrum of the oligo(NPCA) which was immersed in toluene, filtered, dried, and then dissolved in Me_2SO-d_6.

Apparatus

IR spectra were recorded with a Hitachi-EPI-2 spectrometer. Liquid chromatography was carried out by means of a Shimadzu-DuPont Model 830 apparatus equipped with a 50 cm ETH column, elution being with an equimolar mixture of methanol and water at 45°C.

RESULTS AND DISCUSSION

General Aspect of Binding of Small Molecules

The oligo(NPCA) was prepared from 1-(N-phenylcarbamoyl)-aziridine directly by ring-opening polymerization with Et_2SO_4 and purified as described before [29, 36]. Finely pulverized oligo(NPCA) was suspended in a medium containing the substrate for a given time. The hydrogen bond-donating substrates used included phenol, p-thiocresol, aniline, p-toluidine, N-methylaniline, N,N-dimethylaniline, p-phenylenediamine, and N,N-dimethyl-p-phenylenediamine. The hydrogen bond-accepting substrates included anisole, acetophenone, methyl benzoate, and some S=O-containing polar compounds.

The general trend of absorptivity of these compounds in ethyl acetate at 34.5° C, determined with GLC by using toluene as an internal standard, is shown in Table 1. The oligo(NPCA) shows higher specific affinity for phenol, methyl benzoate, aniline, and p-thiocresol than for acetophenone and p-toluidine. No affinity was observed for toluene and anisole. Since the substrate molecules are nearly of the same size, in view of the fact that they carry one benzene ring per molecule, the predominant factor for binding of these compounds is suggested as chemical interaction between CONH unit in the oligo(NPCA) and the functional groups in the substrates.

Binding of Aromatic Amines

The absorption results obtained with a series of aromatic amines under suspension in ethanol at room temperature for 3 days (second section of Table 1) indicate that the affinity depends largely upon the nature of amines. The relative absorptivity of the monoamine series (aniline > p-toluidine ~ N-methylaniline > N,N-dimethylaniline) is reasonable from their hydrogen bond-donating properties. A comparison of the IR spectrum of the free oligo(NPCA) with that of the guest-absorbed state is shown in Fig. 1, where a broadening of ν_{CONH} band of the oligo(NPCA) (1670 cm^{-1}) and a new band at 1120 cm^{-1} are observed as a result of absorption of aniline. These IR results indicate that the carbonyl oxygen atom in the oligo(NPCA) is the hydrogen bond-accepting site. The relative absorptivity of a pair of diamines, p-phenylenediamine > N,N-dimethyl-p-phenylenediamine, follows the same trend as observed for monoamine series. However, the absorptivities of the diamines are considerably higher than those of the corresponding monoamines. Time dependency in the absorption behaviors is exemplified by three amines in Fig. 2. Almost similar kinetic behavior in absorption was observed for other amines, and in all cases the amount of absorption equilibrated after 60 hr.

TABLE 1. Absorption of Small Molecules by Oligo(NPCA)[a]

Substrate	Medium	Substrate concn. (M)	Molar ratio, substrate/ urea unit	Temp. (°C)	Time (days)	Absorption (%)
C_6H_5–CH_3	EtOAc	0.20	0.625	34.0	5	0
C_6H_5–OCH_3	EtOAc	0.20	0.625	34.0	5	0
C_6H_5–OH	EtOAc	0.20	0.625	34.0	5	50
C_6H_5–CO_2CH_3	EtOAc	0.20	0.625	34.0	5	48
C_6H_5–$COCH_3$	EtOAc	0.20	0.625	34.0	5	38
C_6H_5–NH_2	EtOAc	0.20	0.625	34.0	5	58
p-$CH_3C_6H_4$–NH_2	EtOAc	0.20	0.625	34.0	5	34
p-$CH_3C_6H_4$–SH	EtOAc	0.20	0.625	34.0	5	52
C_6H_5–NH_2	EtOH	0.13	1.00	r. t.	3	36
C_6H_5–NHMe	EtOH	0.13	1.00	r. t.	3	24
C_6H_5–NMe_2	EtOH	0.13	1.00	r. t.	3	5
p-$CH_3C_6H_4$–NH_2	EtOH	0.13	1.00	r. t.	3	27
p-H_2N–C_6H_4–NH_2	EtOH	0.13	1.00	r. t.	3	63
p-Me_2N–C_6H_4–NH_2	EtOH	0.13	1.00	r. t.	3	43

[a]Absorption state: suspended in the medium (2 ml).

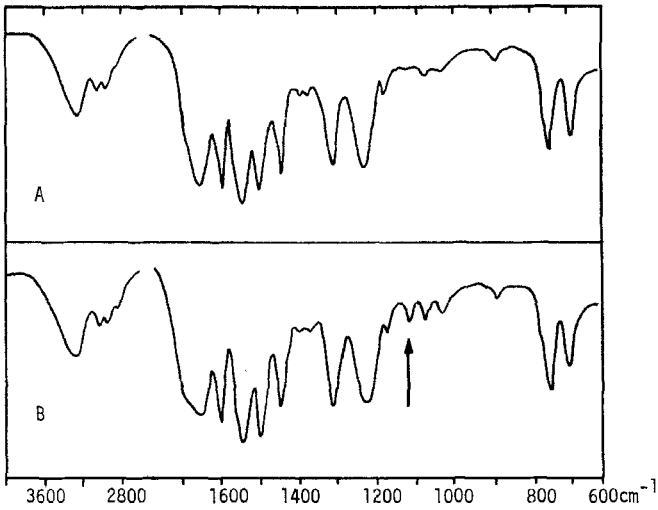

FIG. 1. IR spectra of oligo(NPCA) samples (KBr disk): (A) original sample. (B) aniline-absorbed sample. The arrow indicates a new band at 1120 cm^{-1}

The absorption-desorption equilibrium process was analyzed with the modified Langmuir equation [30]:

$$1/w = 1/K_{app}w_s c + 1/w_s$$

where w is the amount of the absorbed species, i. e., oligo(NPCA)-substrate adduct, w_s is the amount of the absorbed species at saturation, c is an equilibrium concentration of the free substrate, and K_{app} is the equilibrium constant of the process.

For the absorption of monoamines, the plots of 1/w vs. 1/c at 59.0°C in ethyl acetate gave straight lines in a relatively wide range of substrate concentration (< 0.1 M). The absorption gradually increased for all the monoamines at higher than this concentration range. The straight parts of the lines agree considerably well with the lines originated from $1/w_s = 1/8$, i. e., corresponding to one molecule of amine per monomeric unit of the oligo(NPCA), but the ideal value was not practical for all the monoamines in the concentration ranges studied. The highest absorption (w = 5, corresponding to five aniline molecules per octameric host molecule) was observed experimentally with aniline at a concentration of 0.3 M. The K_{app}

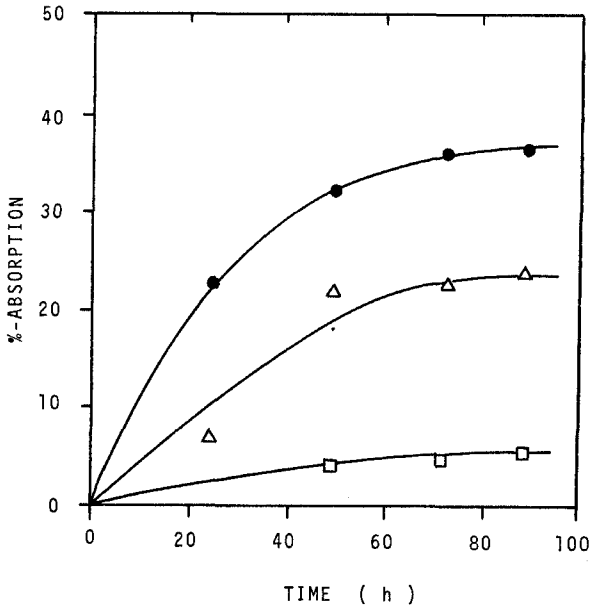

FIG. 2. Change of absorptivities in monoamine/oligo(NPCA) systems with time: (•) aniline; (△) N-methylaniline; (□) N,N-dimethylaniline. Absorption conditions: see the lower section of Table 1.

values together with free energy changes of the process calculated from $\Delta G = -RT \ln K_{app}$ are listed in Table 2 for the three monoamines.

Figure 3 shows a plot of 1/w vs. 1/c for the absorption of p-phenylenediamine at 59.0°C in ethanol. In the lower concentration range the absorption of the diamine can be represented by a linear relation, but a significant enhancement of absorption occurs at a concentration range higher than 0.03 M, which is much lower than the case of monoamines. The experimental points at the linear part of the plot can be approximated by a line crossing at $1/w_s = 1/8$, and this value was practical at a concentration of 0.1 M. Hence, at higher than this substrate concentration, it is plausible to assume that the oligo(NPCA) absorbs one p-phenylenediamine molecule per urea unit in the oligomer. It is concluded that only one of the amino groups in p-phenylenediamine is absorbed to the host molecule and the other amino group remains unabsorbed.

The temperature dependence for absorption of p-phenylenediamine was examined at 5.5, 29.5, 44.5, and 59.0°C. The K_{app} values, together

TABLE 2. K_{app} and ΔG Values for Absorption of Monoamines[a]

Substrate	K_{app} (liter/mole)	ΔG (kcal/mole)
$C_6H_5-NH_2$	4.03	-0.92
$p\text{-}CH_3C_6H_4-NH_2$	3.05	-0.74
$C_6H_5-NHCH_3$	2.04	-0.58

[a]Absorption conditions: oligo(NPCA), 0.0032 mole, suspended in 1 ml of ethyl acetate at 59.0°C for 5 days. The number of significant figures in the K_{app} value is two, and in ΔG values one place of decimals.

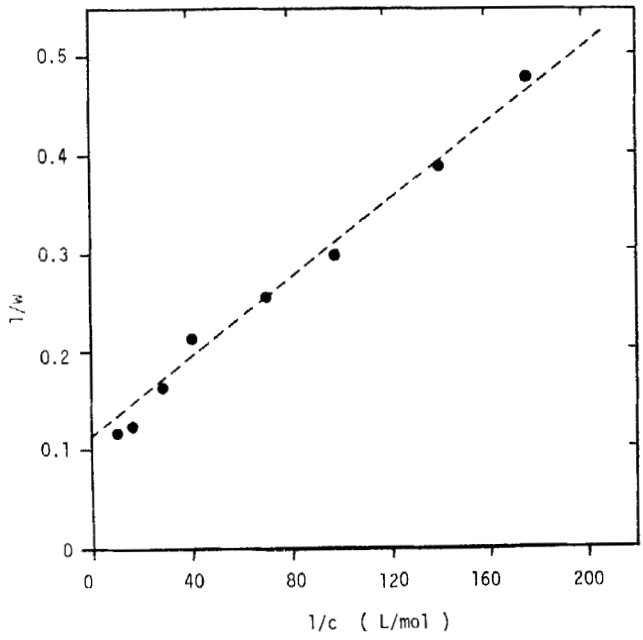

FIG. 3. Plot of 1/w vs. 1/c for absorption of p-phenylenediamine to oligo(NPCA). Absorption conditions: oligo(NPCA), 1.62×10^{-5} mole. Suspended in 1 ml of EtOH for 3 days at 59.0°C. The broken line is drawn from the 1/w equals to 1/8.

with ΔG values obtained from the linear parts of the plots of $1/w$ vs. $1/c$ at each temperature, are tabulated in Table 3. The results show a trend that the absorption is promoted by increasing temperature. The nautre of the process for three temperature ranges can be deduced from the following relation: $\log K_{app} = -\Delta H/2.303R(1/T_2 - 1/T_1)$. The ΔH values thus obtained for the temperature changes between 5.5 and 29.5, between 29.5 and 44.5, and between 44.5 and 59.0°C are found to be +5.5, +9.6, and +17.7 kcal/mole, respectively. The corresponding ΔS values are calculated as +23, +29, and +62 cal/degree-mole, respectively. The positive values of the ΔH suggest that the absorption process involves dissociation of interactions of the oligomer host prior to absorption of the substrate diamine.

Since the oligo(NPCA) used here is an amorphous powder and every oligomer molecule is short, containing only ca. 25 atoms along its backbone chain, it is feasible to change the structure of the oligomeric host by dissociating hydrogen bonding and semipolar interactions, even in the solid state, and as a result expansion and/or increase of the surface area occurs. A significant increase of ΔS along with ΔH values at higher temperatures indicates that the absorption process is one somewhat like that accompanied by swelling of a polymer system. Thus, the flexibility or mobility of the oligomeric compound seems to play a crucial role for binding a given substrate in a specific manner.

Variation of the K_{app} values and the thermodynamic parameters with temperature obtained for absorption of aniline in ethanol is also shown in Table 3 for comparison. The absorption behavior of aniline seems rather straightforward, in view of the fact that the surface absorption takes place at the lowest temperature, followed by weakening of this interaction due to elevation of temperature up to ca. 15°C (maximum ΔG and almost zero ΔH); then with elevation of temperature, absorption accompanied by "swelling" of the oligo(NPCA) occurs as in the case of p-phenylenediamine (increase of positive ΔH and positive ΔS).

Hence it is apparent that the absorption of p-phenylenediamine differs from that of aniline in that the former is able to dissociate the oligo(NPCA) aggregates much more readily. The characteristic feature that only one of the two NH_2 groups in p-phenylenediamine is absorbed in the oligomer host can be applied to a site-selective reaction to synthesize monobenzylated product in the matrix of the oligo(NPCA) [41].

Binding of Polar Compounds

Among the aromatic hydrogen-bond accepting compounds, i. e., anisole, acetophenone, and methyl benzoate, the latter two compounds are shown to be strongly absorbed (Table 1). This appears to be due

TABLE 3. Temperature Dependences of K_{app} and Thermodynamic Parameters for Absorption of Aniline and p-Phenylenediamine[a]

	Temp. (°C)	K_{app} (liter/mole)	ΔG (kcal/mole)	ΔH (kcal/mole)	ΔS (cal/degree-mole)
Aniline[b]	3.0	2.51	-0.50		
				-3.7	-12
	17.0	1.81	-0.34		
				+0.4	+2.5
	43.0	1.91	-0.41		
				+3.2	+12
	61.0	2.52	-0.61		
p-Phenylenediamine[c]	5.5	4.26	-0.8		
				+5.5	+23
	29.5	9.35	-1.3		
				+9.6	+29
	44.5	19.8	-1.9		
				+17.7	+62
	59.0	67.6	-2.8		

[a]Suspended in 1 ml of EtOH for 3 days. The number of significant figures in the K_{app} and ΔG values is estimated as two.

[b]Oligo(NPCA), 18 mg (1.37×10^{-5} mole); concentration range of aniline, from 17.5 to 70 mmole/liter, i. e., linear part of the plot of 1/w vs. 1/c.

[c]Oligo(NPCA), 21 mg (1.62×10^{-5} mole); concentration range of p-phenylenediamine, from 5.6 to 28.6 mmole/liter, i. e., linear part of Fig. 3.

TABLE 4. Absorption of S=O Compounds by Oligo(NPCA)[a]

Compound	Absorption (%)
CH_3–C_6H_4–SO–Et	19.3
CH_3–C_6H_4–SO_2–OEt	18.1
CH_3–C_6H_4–SO–OEt	7.0
CH_3–C_6H_4–SO_2–Et	6.6

[a]Absorption conditions: oligo(NPCA), 6.5 mg (5×10^{-6} mole); substrate concentration, 0.02 M; molar ratio of the urea unit of oligo(NPCA) to the substrate, 1.00. Suspended in 2 ml of ethyl acetate at 60°C for 8 days.

to high polarity of the C=O groups involved in the substrates. The effect of polarity is essentially similar to the cases of compounds containing S=O and P=O reported previously [29]. Since the previous work was concerned only with the affinity at saturation, we have examined some detailed behavior by using a series of the following aromatic S=O compounds as typical of polar substrates, in comparing with those of aromatic hydrogen bond-donating amines: i. e., sulfonate ($CH_3C_6H_4SO_2OEt$), sulfinate ($CH_3C_6H_4SO$–OEt), sulfone ($CH_3C_6H_4SO_2Et$), and sulfoxide ($CH_3C_6H_4SOEt$). For comparison, the results for absorption of Et_2SO_4 are also included.

The amounts of these S=O compounds absorbed at 60°C in ethyl acetate for 8 days depend upon the S=O bond character of the guest compounds, i. e., sulfoxide > sulfonate ≫ sulfinate > sulfone (Table 4). The plots of 1/w vs. 1/c for these aromatic S=O compounds and for Et_2SO_4 are shown in Figs. 4A and 4B, respectively. The experimental plots can be approximated by the lines having an intercept of 1/w = 0.25, corresponding to 4 guest molecules per single oligomer chain. However, this ideal value is attained only for Et_2SO_4.

The K_{app} values determined for the absorption of a series of aromatic S=O compounds (Table 5 are found to decrease in the following order: $CH_3C_6H_4SOEt$ > $CH_3C_6H_4SO_2$–OEt > $CH_3C_6H_4SO$–OEt > $CH_3C_6H_4SO_2Et$. If the absorption of the S=O compounds to the oligo(NPCA) is due totally to hydrogen bonding, the K_{app} values would be: $CH_3C_6H_4SOEt$ > $CH_3C_6H_4SO_2Et$ > $CH_3C_6H_4SO$–OEt > $CH_3C_6H_4$-SO_2–OEt [42]. A considerable deviation in the observed order of K_{app} values from this expectation shows that hydrogen-bonding interaction is not the only factor for absorption of the S=O compounds

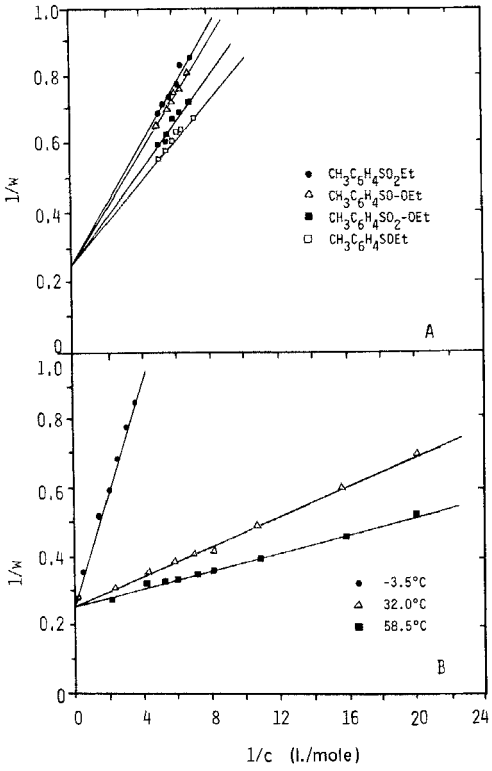

FIG. 4. Plots of 1/w vs. 1/c for absorption of (A) aromatic S=O compounds at 32.0°C for 5 days and (B) Et_2SO_4 for 5 days. Absorption conditions: oligo(NPCA), 0.0032 mole. Suspended in 1 ml of ethyl acetate.

and that semipolar interaction must be important in addition to the hydrogen-bonding interaction.

The ΔH values obtained for absorption of Et_2SO_4 at temperature ranges of -3.5 to 32 and 32 to 58.5°C are ca. +10.4 and +6.3 kcal/mole, respectively. The ΔS values calculated from these ΔH and ΔG values (Table 5) corresponding to these temperature changes are ca. +39 and +26 cal/degree·mole, respectively. The net behavior for the absorption is essentially similar to that described above. However, it is important that the Et_2SO_4-absorption proceeds with smaller increment of ΔH and ΔS than in the case of diamine absorption. Further, the increments of ΔH and ΔS are considerably higher at the lower temperature range than at the higher temperature range. These

TABLE 5. K_{app} and Thermodynamic Parameters for Absorption of S=O Compounds[a]

Substrate	Temp. (°C)	K_{app} (liter/mole)	ΔG (kcal/mole)	ΔH (kcal/mole)	ΔS (cal/degree·mole)
$CH_3C_6H_4SO$–Et	32.0	4.35	-0.89		
$CH_3C_6H_4SO_2$–OEt	32.0	3.85	-0.82		
$CH_3C_6H_4SO$–OEt	32.0	3.23	-0.71		
$CH_3C_6H_4SO_2$–Et	32.0	2.94	-0.65		
Et_2SO_4	-3.5	1.47	-0.21		
				+10.4	+39
Et_2SO_4	32.0	13.9	-1.60		
				+ 6.3	+26
Et_2SO_4	58.5	23.8	-2.09		

[a]Absorption conditions: see Fig. 4.

results indicate that Et_2SO_4 can be absorbed in a less swollen state of the oligo(NPCA) than in the case of diamine absorption.

This effect seems to be due to a combination of at least two factors: that the Et_2SO_4 molecule is small and that the semipolar interaction is relatively readily attainable. No significant change of host structure is needed. The previous observation that the saturate absorption of Et_2SO_4 is almost independent of the nature of the substituent groups in the carbamoyl side chain in the oligomer host [36] and is affected to some extent by introduction of methyl groups in the main chain [43] can be directly understood by the effect that the absorption of Et_2SO_4 occurs at a less swollen state of the oligomer. The lower absorptivities for the phenyl-substituted S=O compounds relative to Et_2SO_4 are probably due to steric hindrance of the phenyl group and to weaker semipolar nature of the S=O groups through conjugation. In this respect, there exists a significant difference between absorptions of aromatic amines and of aromatic S=O compounds.

Selectivity in Absorption for Binary S=O Compound Systems

The absorption selectivity of the S=O compounds to the oligo(NPCA) is applied to the following binary systems containing equal amounts of two kinds of S=O compounds, i. e., $CH_3C_6H_4SO_2Et$—$CH_3C_6H_4SO$–OEt (system 1) and $CH_3C_6H_4SOEt$—$CH_3C_6H_4SO$–OEt (system 2) binary

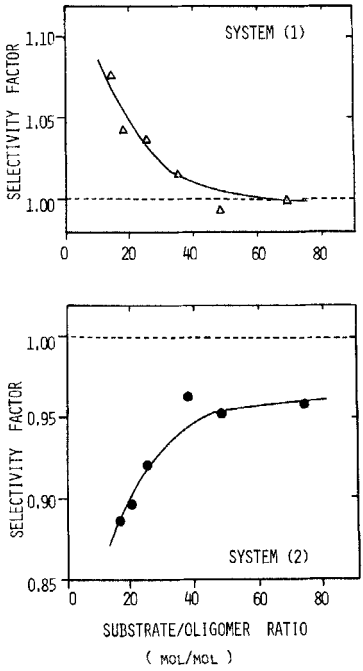

FIG. 5. Selective absorption of binary systems in relation to the change of substrate concentration for system 1): $CH_3C_6H_4SO_2Et$—$CH_3C_6H_4SO$–OEt, 1:1 mole/mole, and system (2): $CH_3C_6H_4SOEt$—$CH_3C_6H_4SO$–OEt, 1:1 mole/mole. The selectivity factor is defined for system 1 as the molar ratio of $CH_3C_6H_4SO_2Et$ to $CH_3C_6H_4SO$–OEt remained unabsorbed, and for system 2 as that of $CH_3C_6H_4SOEt$ to $CH_3C_6H_4SO$–OEt remained unabsorbed. Absorbed under suspension of oligo(NPCA) (0.0064 mole) in 2 ml of ethyl acetate at 32.0°C for 5 days. Dashed lines indicate the nonselective value.

systems. In these experiments, the oligo(NPCA) was suspended in ethyl acetate and absorption was undertaken at 32°C for 5 days. The absorption selectivity was determined by means of liquid chromatography by observing the relative concentration of each compound remained in the ethyl acetate phase. The effects of substrate concentration on the selectivity which is represented by molar ratio of the two S=O compounds unabsorbed are given in Fig. 5.

In the sulfone-sulfinate system (1) sulfinate is more strongly absorbed, and in the sulfoxide-sulfinate system (2), the sulfinate is less strongly absorbed. The absorption selectivities in the binary systems at lower substrate concentrations are parallel to the absorption specificities observed for the individual systems, but as increasing

in the substrate concentration the selectivities decreased gradually. The selectivities expected from the K_{app} values of each component are 1.10 for system 1 and 0.74 for system 2. The observed maximum selectivities are 1.08 and 0.89, respectively. On taking into account the fact that these observed values were obtained for systems with rather small differences in K_{app} and ΔG in the presence of still a large excess of substrate (ca. 18 mole excess to the oligomer), the observed selectivities in the binary systems are satisfactory.

It is apparent that absorption in a binary system involves competition of two substrate components, together with exchange of the absorbed species. The fact that the observed selectivities in the binary systems resemble the values expected from the single-component systems suggests these factors are small, at least at a considerably low substrate concentration. However, at higher concentrations, these factors become quite important.

Comparison of Specificities of Oligo(NPCA) with Ureanized-Polyethylenimine for Binding of Compounds Containing S=O

In the preceeding work [30] it has been shown that absorption specificity of the oligo(NPCA) for divalent metal ions is largely different from that of the ureanized polyethylenimine (ureanized-PEI), a branched high polymer analog of IR spectroscopically similar. Such a difference in absorption specificities for S=O compounds between oligo(NPCA) and the ureanized-PEI was also observed, as shown in Table 6. The ureanized-PEI also has an affinity for a various type of S=O compounds, but the specificity is considerably lower than that of oligo(NPCA). For example, the relative affinities standardized from the absorption of Me_2SO lie in a range of 0.9 to 2.8 for the ureanized-PEI, whereas they are in the range of 0.5 to 4.4 for oligo-(NPCA). Among these, the absorption behavior for Et_2SO_4 and Ph_2SO_2 differs most significantly for the two kinds of host compound.

CONCLUSION

In order to understand some elementary features of the origin of absorption specificity, absorption behavior of the oligo (NPCA) host for a variety of aromatic substrates having hydrogen bond-donating or -accepting properties was studied. The absorption specificity was found to relate to the nature of functional groups of the substrates. For a series of amine substrates, "swelling" of the host by a given substrate seems to be the key problem. In this case, steric factors of the substrate containing a phenyl group can be overcome

TABLE 6. Comparison of Binding Specificities of Oligo(NPCA) and Ureanized Polyethylenimine Hosts for S=O Substrates[a]

Substrate	Relative absorptivity[b]	
	Oligo(NPCA)	Ureanized-PEI[c]
Me_2SO	1.0	1.0
Me_2SO_2	1.0	0.9
Ph_2SO_2	0.5	1.2
$\overline{CH_2-CH_2-CH_2-CH_2-SO_2}$	1.2	2.2
Et_2SO_4	4.4	2.0
$p\text{-}CH_3C_6H_4SO_2\text{-}OEt$	4.0	2.8

[a]Absorption conditions: absorbent, 0.328 g; molar ratio, substrate/urea unit, 1.0; suspended in 10 ml of ethyl acetate at 60°C for 8 days.

[b]Standardized from absorption of Me_2SO as 1.0.

[c]PEI denotes commercial polyethylenimine which is a branched high polymer (tertiary N:secondary N = 1:2, molecular weight = 30,000-100,000). Preparation of the ureanized-PEI as described previously [30].

by temperature elevation. In the "swelling" of the host material the flexible or mobile nature of the relatively short oligomer chain seems to play a crucial role. On the other hand, absorption of S=O substrates seems to occur at a less swollen state of the oligomeric host, so that the aromatic S=O compounds are less absorbed. Thus, the dual nature of the > NCONHPh group in the oligomeric host, i. e., hydrogen bond-accepting or donating property, behaves in a different manner for given substrates to produce significant specificity in absorption.

The absorption selectivity for two binary systems containing S=O compounds is shown to be satisfactory, at least at a low substrate concentration. In addition, the absorption specificity for some S=O compounds is considerably higher with the oligo(NPCA) host than with the corresponding ureanized-PEI host.

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