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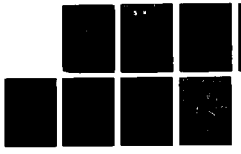

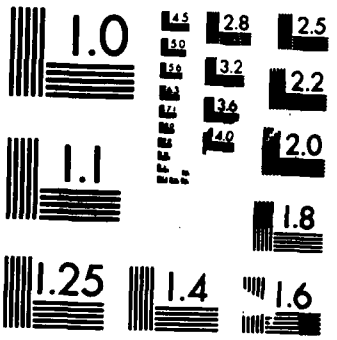

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by

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ABSTRACT

The interactions of α, β, and γ-cyclodextrins and selected napthalene derivatives as observed through fluorescence lifetime measurements are discussed in detail. These systems can be quickly characterized using the parameters obtained from experimental fluorescence decay curves. The formation of inclusion complexes can be followed with the appearance of a long-lived fluorophore which contributes to the total fluorescence according to the cyclodextrin concentration. This fluorophore is determined to be an inclusion complex between a napthalene and cyclodextrin.

Index Headings: Fluorescence Lifetime Measurements; Cyclodextrins; Spectroscopic Techniques.

INTRODUCTION

This study of cyclodextrin (CDx) complexes has been of general interest in the past several years due to their ability to form inclusion complexes with various organic solutes.[1] The unique torus shape of the CDx molecule only allows appropriately shaped guest molecules to be included in the central cavity. These cavities demonstrate hydrophobic properties which provide favorable interactions for aqueous apolar solutes.[2] The three most commonly studied members of the CDx family, α-CDx, β-CDx, and γ-CDx, have cavities of diameter 4.5-6.0 Å, 6.0-8.0 Å, and 8.0-10.0 Å, respectively.

Fluorescence lifetime measurements are especially useful in studying CDx systems.[3-9] Both the absorption and fluorescence band of included polynuclear aromatic hydrocarbons are overlapping with the bands of the free fluorophore. In these cases, physical information from steady state measurements about the interactions is not easily obtained at low CDx concentrations, where changes are subtle. Since the fluorescence lifetime is extremely sensitive to a molecule's microenvironment, information about the interaction between the included molecule and the CDx can be obtained for any CDx concentration. This is an advantage since higher fluorophore:CDx complexes are observed in concentrated CDx solutions.

This manuscript demonstrates the differences observed in the cyclodextrin complexation behavior of structural isomers of napthalene as characterized by fluorescence lifetime measurements. Considerable interest has been shown in such complexation phenomena in the past several years. In chromatography, both cyclodextrin mobile phases and stationary phases have been studied to evaluate their utility for separating structural as well as enantiomeric isomers.[10-12] Investigation of these complexation phenomena can provide useful insights into

the interactions involved in cyclodextrin inclusion of a guest molecule. The effects of substitution on the fluorescence lifetime properties of the napthalene:cyclodextrin complexes are presented and discussed.

THEORY

The data from a single photon counting fluorescence lifetime experiment can typically be fit to an exponential decay function of the form

$$\sum_{i=1}^{n} A_i e^{-t/\tau_i} ,$$

where n is the number of components. The A_i are functions of the instrument response and the emission, absorption and concentration characteristics of each component. The fluorescence lifetime of each species is given by the τ_i, which is the time required for the component to decay to 1/e of its original intensity. The experimental data may be fit by using a variety of curve fitting algorithms.[13]

The degree of interaction between the fluorophore and CDx can be judged from the A_i parameter. Since the A_i are related to concentration of the ith species, the ratio A_1/A_2 will show relative concentration of two components in a mixture of fluorophores.[14] In the case of a mixture of polynuclear aromatic hydrocarbon (PNA) and CDx, components one and two are complexed and free PNA, respectively. If this ratio increases with increasing CDx concentration, then some statement about the formation of inclusion complex can be made. Comparisons of the A_1/A_2 ratio between different PNA:CDx should be made with caution. Since the A_i are also related to the molar absorptivity and quantum yield of the fluorophore, comparisons between different PNAs must also consider these parameters.

The lifetime of the complexed and free PNA is an indicator of the fluorophore's environment. Differences in τ_i can generally be attributed to changes in the deactiviation pathways of the excited state or changes in the interaction of the excited state with the surrounding. Since the interior of the CDx cavity differs significantly from the bulk solvent, changes in the fluorescence lifetime of the complex would be expected to occur by one or all of the cited interactions.

EXPERIMENTAL

All napthalene derivatives were obtained from Aldrich and used as received. Cyclodextrins were obtained from Advanced Separation Technologies, Inc. Aqueous solutions of the napthalenes were prepared by sonicating an excess of the crystalline napthalene compound in deionized water and allowing the solution to stand until needed. Saturated solutions were necessary in order to obtain fluorescence intensities suitable for lifetime measurements. Aliquots of these solutions were taken and sonicated with solid α, β, and γ-CDx to give the desired cyclodextrin concentrations.

Fluorescence lifetimes were measured using Photochemical Research Associates System 3000 Fluorescence Lifetime Instrumentation. The data were taken at 10 degrees celsius. The excitation/emission wavelengths were determined by measuring the absorbance and fluorescence maxima on a Perkin-Elmer 650-10S Fluorescence Spectrophotometer. The pulse lamp was filled with hydrogen, which gave an excitation pulse of less than 2 nanoseconds at full width-half maximum. This pulse width was negligible compared to the smallest measured lifetime of 20 nanoseconds, so deconvolution of the lamp-instrument response function was not necessary. The lifetime data were analyzed using least-squares curve fitting and the Marquardt gradient search method.[15]

RESULTS AND DISCUSSION

The results of the fluorescence lifetime measurements on systems of substituted napthalenes and α, β, and γ-CDx are shown in Table I, II, and III, respectively. For each napthalene compound, the change in lifetimes and A_1/A_2 ratio with increasing CDx concentration is presented. Notice that all the data are well fit as judged by the X_r^2 statistic, which should fall close to unity.[15] The experimental procedure prevents comparison between different napthalenes and the observed A_1/A_2 dependence on CDx concentration. The initial napthalene concentrations were not equivalent, so no valid comparisons between compounds can be made. However, the effects of α, β, and γ-CDx on each napthalene compound can be deduced, since the same napthalene stock solution was characterized with each CDx.

The lifetimes of both the free and complexed compounds are fairly constant within the experimental and curve-fitting error for all of the observed data. This demonstrates the validity of the conclusions drawn from the data. The appearance of a longer lived component with a well defined lifetime provides evidence that the inclusion complex is formed and experimentally observable. It is important to note that the lifetime of the inclusion complex in no way indicates the strength of the equilibrium between the fluorophore and CDx. Longer lifetimes of the complex cannot necessarily be associated with larger equilibrium constants.

The results of the α-CDx experiments presented in Table I indicate that an inclusion complex is formed with napthalene, 2-methylnapthalene and 2-ethylnapthalene. In each case, a long lived component is observed upon the addition of α-CDx. The magnitude of the lifetime of the included napthalenes is a strong indication that an inclusion complex is formed. For

such a change in lifetime, a substantial change in the environment of the fluorophore is implied. The only reasonable mechanism for this environmental change is inclusion in the α-CDx cavity. From the value of A_1/A_2, it is evident that the relative ratio of the included to free napthalene increases with increasing α-CDx concentrations, as expected.

Substituents in the 1- position on the napthalene ring seem to have a blocking effect on the formation of the complex. Complexes with the 1-substituted napthalenes that were studied were not observed within the α-CDx concentration ranges examined. Since the fit of the napthalene into the small α-CDx cavity is tight, substituents in the 1- position could block the entrance of one end the molecule into the cavity. This is supported by the experimental data. On the other hand, 2-substitution would not block entrance to the cavity, so inclusion complexes could be formed, as the data indicates.

Inclusion complexes between β-CDx and all of the napthalenes are experimentally observed, as presented in Table II. The presence of a second, long-lived component again indicates the formation of the inclusion complex. Also the A_1/A_2 ratios for all the napthalenes show the predicted increase with cyclodextrin concentration. Comparison of the β-CDx results to those of α- and γ-CDx indicate that β-CDx is the most versatile cyclodextrin for studying napthalene compounds.

Notice that the β-CDx cavity is able to accommodate substitution in the 1-position. However, the lifetimes of these complexes are shorter than the 2-substituted napthalenes. This could indicate that the β-CDx can only include part of the 1- substituted napthalene molecules, while the 2- substituted napthalene can completely enter the cavity. When more of the napthalene ring resides in the interior of the β-CDx, it is likely that more protection from deactivation pathways is offered. This possible explanation is also

demonstrated in the cases of 1-methylnapthalene and 1-ethylnapthalene. The methyl group is less bulky, so the molecule can better fit into the β-CDx cavity and exhibits a longer lifetime.

The longer lifetimes of the β-CDx complexes of 2-substituted napthalenes with respect to napthalene indicate that the substituent may offer some additional protection from deactivation. A reasonable explanation is that the 2-substituent could likely be projecting from one end of the β-CDx cavity. This would effectively block one end of the complex from interaction with the aqueous solvent and quenchers, enhancing the lifetime.

The interaction of γ-CDx with the napthalene derivatives, presented in Table III, show some interesting differences from α-CDx and β-CDx. First, an inclusion complex between napthalene and γ-CDx is not indicated by the data. However, the observed substituted napthalenes form inclusion complexes which exhibit the lifetime and A_1/A_2 properties shown by α-CDx and β-CDx complexes. This observation may be rationalized by noting that the molecular dimensions of napthalene are approximately 9.5 Å x 5 Å. The tightest fit of napthalene in the γ-CDx cavity would occur with the long axis across the diameter of the cavity. This configuration would reduce the area of interaction between the napthalene and γ-CDx, causing the inclusion complex to be less favorable due to a poor fit. Substituents in either the one or two position make the napthalene molecule bulkier along the short and long axis, possibly producing a tighter fit in the γ-CDx cavity.

The lifetime data demonstrates that γ-CDx produces the greatest lifetime enhancement, followed by β-CDx and α-CDx. For each of the substituted napthalenes, the lifetime of the complex becomes longer as the progression from α-CDx to β-CDx to γ-CDx is made. This result is reasonable, since the larger cyclodextrins would reduce the interaction of the napthalene with the aqueous

solvent, decreasing the chances for deactivation of the excited state. Yet, this result demonstrates that the lifetime enhancement is not necessarily linked to the strength of the inclusion complex.

CONCLUSIONS

The results presented in this manuscript demonstrate that fluorescence lifetime measurement is a useful and sensitive method for studying inclusion complexes of cyclodextrins and PNAs. Verification of the presence of inclusion complexes and physical characterization of the interactions can be made with relative ease. The changes in the experimentally observed parameters are large with respect to the changes observed in steady state measurements. This allows the experimenter to measure the properties of one or two samples and determine if a given cyclodextrin-PNA pair are of interest. This can reduce the development time involved in devising experimental schemes involving cyclodextrins.

ACKNOWLEDGMENTS

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TABLE I. Variation of Lifetime Parameters of Napthalenes With [α-CDx]

Compound	[α-CDx](mM)	τ_1(ns)	τ_2(ns)	A_1/A_2	X_r^2
napthalene	0.00	*	38.1	*	1.07
	0.53	-	37.9	-	1.08
	1.46	99.0	38.1	0.027	0.94
	2.84	92.6	37.7	0.108	1.00
	4.84	90.4	35.9	0.335	1.14
1-methylnapthalene	0.00	*	33.3	*	1.08
	0.60	-	33.3	-	1.18
	1.64	-	33.3	-	1.20
	3.25	-	33.3	-	1.22
	5.27	-	33.9	-	1.11
1-ethynapthalene	0.00	*	31.1	*	1.00
	0.65	-	30.6	-	1.12
	1.62	-	31.0	-	0.87
	3.05	-	31.7	-	1.03
	5.22	-	32.1	-	1.18
2-methylnapthalene	0.00	*	30.3	*	1.08
	1.02	65.3	30.5	0.040	1.09
	2.66	59.8	30.5	0.272	1.20
	4.14	61.0	32.2	0.493	1.01
	5.69	57.2	29.4	1.308	1.03
2-ethylnapthalene	0.00	*	29.5	*	1.25
	0.69	-	29.4	-	1.09
	1.82	-	30.5	-	1.16
	3.60	56.7	30.9	0.183	1.04
	5.87	53.9	31.7	0.441	1.20

(*) Second component not present

(-) Second component not observed

TABLE II. Variation of Lifetime Parameters of Napthalenes with [β-CDx]

Compound	[β-CDx](mM)	τ_1(ns)	τ_2(ns)	A_1/A_2	X_r^2
napthalene	0.00	*	38.1	*	1.07
	0.74	60.0	36.1	0.647	1.11
	1.73	59.8	34.1	1.747	1.03
	3.02	59.4	26.9	3.855	1.10
	4.68	60.9	26.6	5.128	1.02
1-methylnapthalene	0.00	*	33.3	*	1.08
	0.82	58.9	30.5	1.261	1.07
	1.47	60.2	28.6	4.329	1.07
	2.88	60.0	25.8	5.512	0.84
	4.65	58.6	24.0	5.893	1.05
1-ethylnapthalene	0.00	*	31.1	*	1.00
	0.65	52.2	30.2	0.300	1.01
	1.62	50.7	31.0	0.630	0.76
	3.05	48.4	29.5	1.534	1.01
	5.22	49.2	28.2	2.291	1.27
2-methylnapthalene	0.00	*	30.3	*	1.08
	0.94	71.9	30.1	0.218	1.25
	2.31	76.6	31.0	0.243	1.13
	3.86	72.0	29.3	0.335	1.13
	5.25	77.1	30.8	0.270	1.20
2-ethylnapthalene	0.00	*	29.5	*	1.25
	0.72	63.7	33.8	0.213	0.93
	1.87	69.4	36.2	0.551	0.99
	3.62	68.1	35.0	0.959	0.99
	5.48	65.4	31.4	1.657	1.08

(*) Second component not present

TABLE III. Variation of Lifetime Parameters of Napthalenes with [γ-CDx]

Compound	[γ-CDx](mM)	τ_1(ns)	τ_2(ns)	A_1/A_2	X_r^2
napthalene	0.00	*	38.1	*	1.07
	0.60	-	38.8	-	1.08
	1.37	-	39.5	-	1.16
	2.56	-	40.5	-	1.45
	4.20	-	41.7	-	1.35
1-methylnapthalene	0.00	*	33.3	*	1.08
	0.62	83.7	33.3	0.030	1.01
	1.71	85.5	33.2	0.159	1.03
	4.19	82.7	32.4	0.382	1.23
1-ethylnapthalene	0.00	*	31.1	*	1.00
	0.46	63.0	31.3	0.017	1.04
	1.18	67.8	31.9	0.022	1.03
	2.22	65.6	32.0	0.053	0.96
	4.03	71.6	33.4	0.055	1.02
2-methylnapthalene	0.00	*	30.3	*	1.08
	0.98	80.0	29.8	0.041	1.15
	2.28	84.9	29.7	0.146	0.94
	3.85	88.9	30.3	0.240	1.00
	5.23	85.9	29.5	0.336	1.06
2-ethylnapthalene	0.00	*	29.5	*	1.25
	0.80	-	29.2	-	0.98
	1.85	86.4	29.6	0.046	1.05
	3.65	84.1	30.0	0.199	1.09
	5.40	92.1	31.0	0.264	1.02

(*) Second component not present

(-) Second component not observed

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