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Complexation of Polyaromatic Hydrocarbons with Disodium 1,8-Disulfonato-3,4,5,6-Acridinetetracarboxylic Acid in Water

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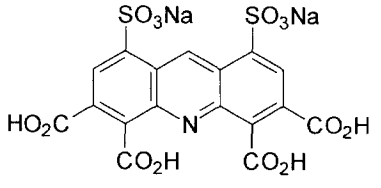
Abstract: The transport rates of seven polyaromatic hydrocarbons through water increased in the presence of disodium 1,8-disulfonato-3,4,5,6-acridinetetracarboxylic acid, **1**. The increase in rates was attributed to the inclusion of the polyaromatic hydrocarbons within the hydrophobic cavity of the dimeric form of **1**. The stability constants K of the complexes increase with the number of aromatic rings in the polyaromatic hydrocarbons. Copyright © 1996 Elsevier Science Ltd

Disodium 1,8-disulfonato-3,4,5,6-acridinetetracarboxylic acid, **1**, in its dimeric form[1] encloses a hydrophobic cavity between the two acridine walls, as shown in the CPK molecular model **2**. Since CPK molecular models indicated that the polyaromatic hydrocarbons could be included into the hydrophobic cavity of **2**, we undertook to investigate this possibility. This paper reports our study on the complexation of seven polyaromatic hydrocarbons with **1** in water using the transport method.[2]



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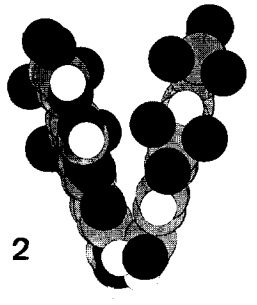

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The rate of transport of a polyaromatic hydrocarbon from one hexane phase to another through an aqueous phase in an U-tube was monitored by measuring the absorbance at a given wavelength of the polyaromatic hydrocarbon in the receiving phase.[2] Figures 1 and 2 show two typical plots, one for anthracene and the other for chrysene, of absorbance against the time taken by the polyaromatic hydrocarbon to travel from the source phase to the receiving phase.

That there is complexation between the polyaromatic hydrocarbons and **1** is shown by the increase in the transport rates of the polyaromatic hydrocarbons in the presence of **1**. Assuming that the complexes were formed from the inclusion of the polyaromatic hydrocarbons inside the cavity of the dimeric form of **1** (as shown in **3** for the case of anthracene as guest), the stability constants K of the complexes were calculated

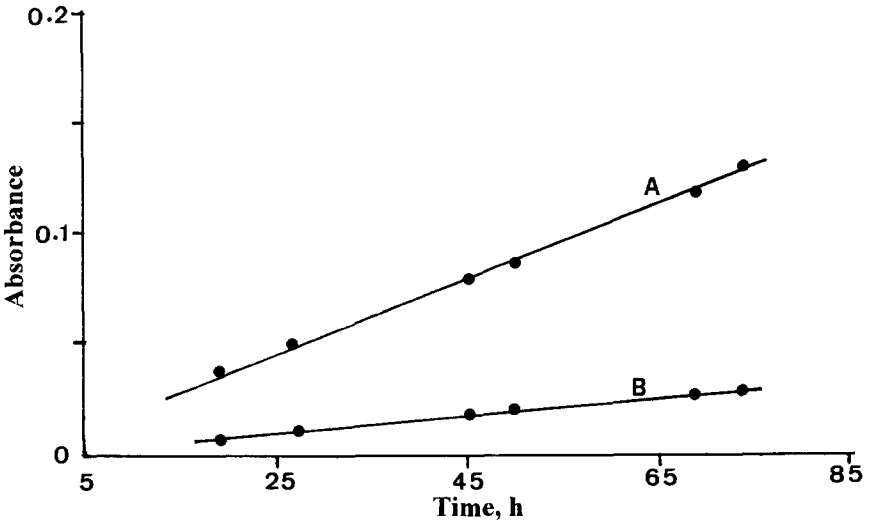


Figure 1. Relationship between absorbance at 375 nm of anthracene in the receiving phase and time. The initial concentration of anthracene in the source phase is $5x10^{-3}$ M; (**A**) $3.0x10^{-3}$ M of **1** in the aqueous phase and (**B**) no host in the aqueous phase.

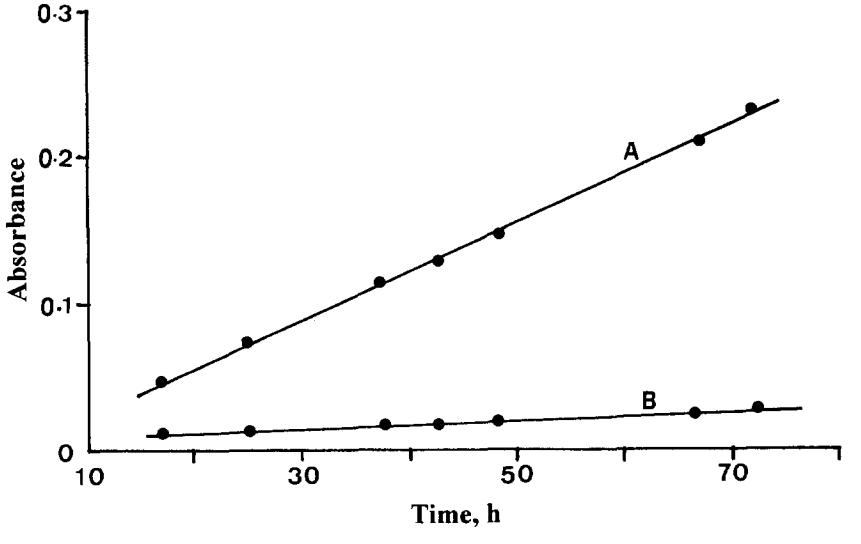
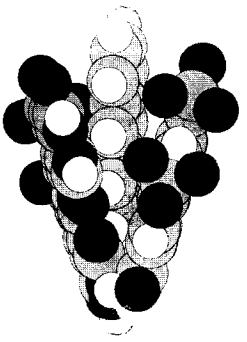


Figure 2. Relationship between absorbance at 266 nm of chrysene in the receiving phase and time. The initial concentration of chrysene in the source phase is $5x10^{-3}$ M; (**A**) $3.0x10^{-3}$ M of **1** in the aqueous phase and (**B**) no host in the aqueous phase.



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from the slopes of such plots given in Figures 1 and 2, using the equations given earlier.[2,3] The calculated K values are given in Table 1.

Table 1. Stability Constants K of Complexes Formed from Polyaromatic Hydrocarbons and Dimeric **1** in Water[a]

Hydrocarbon	**K (M^{-1})**	**K (M^{-1})[b]**	**N[c]**
Naphthalene	$(0.9\pm0.1)\times10^{2}$	4.5×10^{2}	2
Acenaphthene	$(9.9\pm0.2)\times10^{2}$	1.6×10^{3}	2.5
Fluorene	$(1.3\pm0.1)\times10^{3}$	3.6×10^{3}	2.5
Phenanthrene	$(5.8\pm0.3)\times10^{3}$	1.4×10^{4}	3
Anthracene	$(5.3\pm0.3)\times10^{3}$	2.3×10^{4}	3
Pyrene	$(2.0\pm0.1)\times10^{4}$	4.3×10^{4}	4
Chrysene	$(1.8\pm0.1)\times10^{4}$	7.0×10^{4}	4

[a]Determined by transport method[2,3] at room temperature (about 29^{0}C); concentration of polyaromatic hydrocarbons in source phase 5×10^{-4} to 5×10^{-3} M; concentration of **1** 3.0×10^{-3} M; **1** prepared according to ref.1 and the polyaromatic hydrocarbons were recrystallized commercial samples. [b]K values for cyclotetrachromotropylene as host.[2] [c]Number of aromatic rings in the polyaromatic hydrocarbon; a non-aromatic ring containing double bonds is counted as half.[2]

The dimeric form of **1** is a poorer host for the polyaromatic hydrocarbons, compared with the macrocycles as hosts reported by us earlier.[2,4] For example, the K values are about three times smaller than those given by cyclotetrachromotropylene (a macrocycle consisting of four naphthalene units).[2] A plot of log K versus N (the number of aromatic rings in the guest[2]) gives a satisfactory straight line (correlation coefficient 0.938, slope 1.01 and intercept 0.42). The slope of 1.01 is close to those obtained for cyclotetrachromtropylene (0.92)[2], cyclophane (0.98)[2], and H-acid-formaldehyde macrocycle (1.10)[4]. This is not surprising because the magnitude of the slope is a measure of the interaction energy between an aromatic ring of the guest molecule and the aromatic walls of the host molecule. A slope of 1.0 corresponds to an aromatic π-π interaction energy of -1.4 Kcal mol^{-1}(slope multiplied by -2.303RT where R is the gas constant and T the absolute temperature) which is close to the values of -1 to -2 Kcal mol^{-1} calculated by Burley and Petsko[5] for the interaction between two phenyl rings in several proteins.

ACKNOWLEDGEMENT

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