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# TRANSPORT OF AROMATIC HYDROCARBONS BY CYCLOTETRACHROMOTROPYLENE IN WATER

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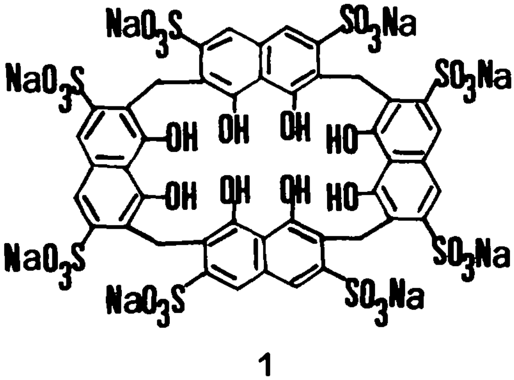
Abstract: The transport rates of eight aromatic hydrocarbons through an aqueous phase increase in the presence of cyclotetrachromotropylene. An equation relating the transport rates and host-guest association constants is given.

The transport of ions and molecules from one liquid phase to another liquid phase using synthetic macrocycles as carriers is of great interest because it gives an understanding of the important life process of transporting electrolytes and non-electrolytes in the biological system. A considerable amount of work has been done on the transport of cations through an organic phase using the macrocyclic crown ethers and cryptands as carriers.[1] However, few data are available on the macrocycle-mediated transport of non-electrolytes through an aqueous phase.[2] Diederich and Dick,[3] in their study on the transport of five aromatic hydrocarbons through an aqueous phase using a cyclophane type of macrocycle as the carrier, found that host-guest complexation in the aqueous phase was essential for the acceleration of transport. But they were unable to relate the transport rates to the host-guest association constants.

The macrocycle, cyclotetrachromotropylene (1),[4,5] was found to form strong 1:1 complexes with aromatic hydrocarbons in aqueous solutions.[6] We used it as the carrier to study its transport of eight aromatic hydrocarbons through an aqueous phase using the U-tube method[3] in this work. This paper reports the results of our study and our proposed equation relating the transport rates to the host-guest association constants.



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Results and Discussion. The aromatic hydrocarbon dissolved in *n*-hexane in one arm of the U-tube (source phase) was transported through an aqueous phase (bottom of the U-tube) to the other arm of the U-tube containing pure *n*-hexane (receiving phase). The concentration of the aromatic hydrocarbon in the receiving phase was plotted against the time taken by the aromatic hydrocarbon to travel from the source phase to the receiving phase. The slope of the linear part of the plot gives the transport rate[3] (Figure 1 shows the plots for anthracene in the presence and absence of **1**). The transport rates in the presence of **1** (r) were found to be greater than in the absence of **1** ($r_o$) for all the eight aromatic hydrocarbons. The relative rates, $^r/r_o$, are given in Table 1.

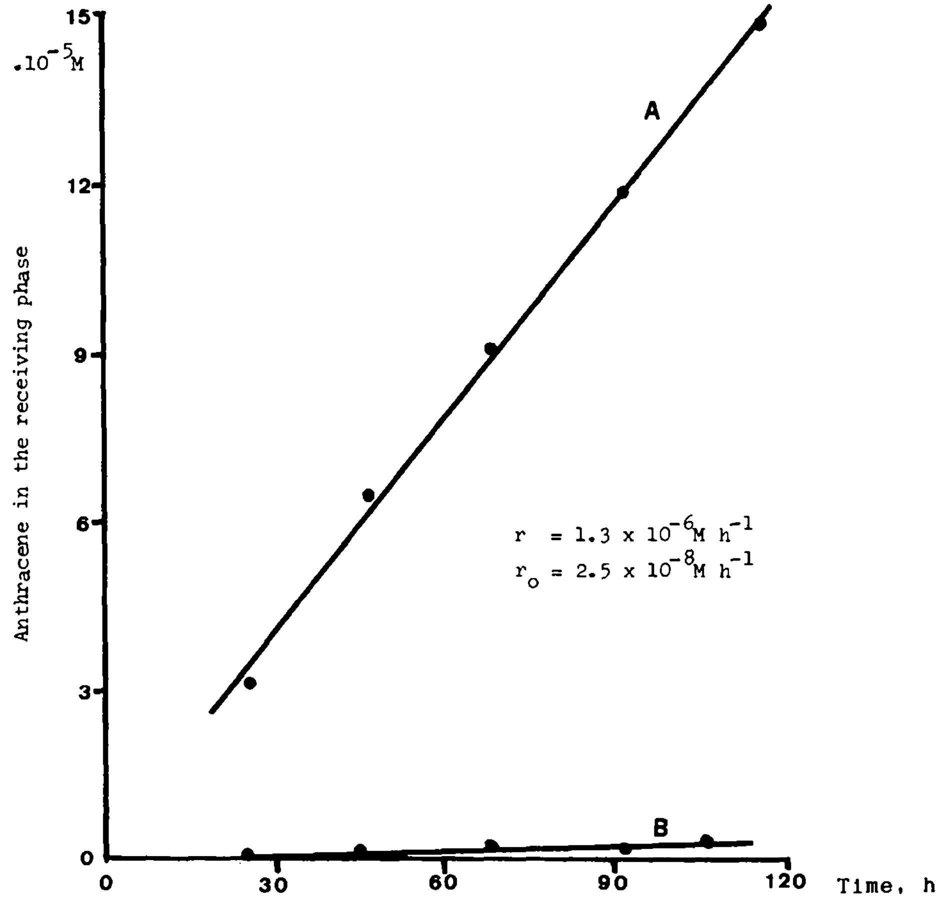


Figure 1. Transport of anthracene through (A) 5.0 x $10^{-3}$M of **1** in water and (B) water. The initial concentration of anthracene in the source phase is 3.0 x $10^{-3}$M; 27 - 29°; medium stirring speed.

Table 1. Relative Rates[a] of Transport of Aromatic Hydrocarbons through the Aqueous Phase and 1-Aromatic Hydrocarbon Association Constants, 27-29°

| No. | Hydrocarbon[b] | $r/r_o$[c] | $(M/M_o)^{1/2}$ | $K_a$, L mol$^{-1}$ Eq. 7 | $K_a$, L mol$^{-1}$ SL[d] |
|---|---|---|---|---|---|
| 1 | chrysene | 170 | 2.61 | $8.8 \times 10^4$ | $7.0 \times 10^4$ |
| 2 | pyrene | 99 | 2.74 | $5.4 \times 10^4$ | $4.3 \times 10^4$ |
| 3 | anthracene | 48 | 2.90 | $2.7 \times 10^4$ | $2.3 \times 10^4$ |
| 4 | phenanthrene | 14 | 2.90 | $0.8 \times 10^4$ | $1.4 \times 10^4$ |
| 5 | fluorene | 5.8 | 2.99 | $2.9 \times 10^3$ | $3.6 \times 10^3$ |
| 6 | acenaphthene | 2.5 | 3.09 | $0.9 \times 10^3$ | $1.6 \times 10^3$ |
| 7 | naphthalene | 2.0 | 3.36 | $6.7 \times 10^2$ | $4.5 \times 10^2$ |
| 8 | durene | 1.7 | 3.06 | $4.3 \times 10^2$ $(1.4 \times 10^2)$[e] | $1.2 \times 10^2$ |

[a] Concentration of 1 = $5.0 \times 10^{-3}$M; medium stirring speed with a Gallenkamp magnetic stirrer. [b] Initial aromatic hydrocarbon concentration in source phase: $3.0 \times 10^{-2}$M(No.4-8); $3.0 \times 10^{-3}$M (No.2,3); $3.0 \times 10^{-4}$M (No. 1). [c] Reproducible within 10%. [d] Solid-liquid extraction method, ref. 6. [e] Assuming the complexed durene diffuses as a free durene, see text.

Diederich and Dick[3] attributed the increase in the transport rate of an aromatic hydrocarbon to the formation of a host-guest complex in the aqueous phase. However, they were not able to relate the transport rate to the host-guest association constant. We propose here a relationship between the transport rate and the association constant.

Two equilibria are involved. First, there is the distribution equilibrium of the free aromatic hydrocarbon guest G in the hexane source phase and in the aqueous phase as follows

$$G(\text{hexane}) \overset{K_d}{\rightleftharpoons} G(H_2O) \qquad (1)$$

where $K_d$ is the distribution coefficient defined as

$$K_d = [G]_{H_2O}/[G]_{\text{hexane}} \qquad (2)$$

Second, there is an equilibrium involving the formation of a 1:1 complex HG from the host H and guest in the aqueous phase as follows

$$H(H_2O) + G(H_2O) \overset{K_a}{\rightleftharpoons} HG(H_2O) \qquad (3)$$

where the association constant $K_a$ is given by

$$K_a = [HG]_{H_2O}/[H]_{H_2O}[G]_{H_2O} \qquad (4)$$

Since the transport rate of the guest aromatic hydrocarbon is determined by its solubility in the aqueous phase[3], we have $r_o \alpha [G]_{H_2O}$ and $(r - r_o) \alpha [HG]_{H_2O}$. The diffusion coefficient of the free guest G differs from that of the complexed guest HG because the diffusion coefficient of a molecule is inversely proportional to its size, the viscosity of the medium ($r_o$ is measured in water whereas r is measured in water containing the host), and the square root of the mass of the molecule.[7] Taking these three factors into account, the ratio of $(r - r_o)/r_o$ can be expressed in terms of $[HG]_{H_2O}/[G]_{H_2O}$ as follows

$$[HG]_{H_2O}/[G]_{H_2O} = \frac{(r - r_o)}{r_o}\left(\frac{M}{M_o}\right)^{1/2}\left(\frac{S}{S_o}\right)\left(\frac{V}{V_o}\right) \qquad (5)$$

where M and S respectively refer to the mass and size of HG, $M_o$ and $S_o$ the mass and size of G, $V_o$ is the viscosity of water and V the viscosity of water containing the host. Equation 5 implicitly assumes that the complexed guest diffuses as a complexed guest, that is, the dynamic equilibrium between the complexed and free guests can be ignored. This assumption is valid when $[HG]_{H_2O} \gg [G]_{H_2O}$. Two further assumptions are made to enable us to obtain an equation to calculate $K_a$. First, we assume that $V = V_o$ since the host solutions were dilute. Second, we assume that $S = S_o$ (an assumption regarding the relative magnitude of S and $S_o$ is necessary since it is not possible to know what magnitude of S and $S_o$ to use in the case of non-spherical molecules.[7] The results in Tables 1 and 2 seem to justify our assumption).

Thus, equation 5 becomes

$$[HG]_{H_2O}/[G]_{H_2O} = \left(\frac{r - r_o}{r_o}\right)\left(\frac{M}{M_o}\right)^{1/2} \qquad (6)$$

and equation 4 then becomes

$$K_a = \frac{1}{[H]_{H_2O}}\left(\frac{r}{r_o} - 1\right)\left(\frac{M}{M_o}\right)^{1/2} \qquad (7)$$

where $[H]_{H_2O}$ is the initial concentration of <u>1</u> used in the aqueous phase since $[H]_{H_2O} \gg [HG]_{H_2O}$ and H and HG are only present in the aqueous phase.

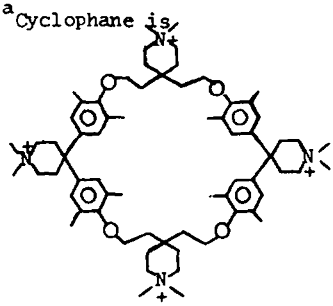
We calculated the $K_a$ values from the $r/r_o$ values using equation 7 and found them to be close to those obtained by the solid-liquid extraction method[6] (Table 1). However, the calculated $K_a$ value of $4.3 \times 10^2$ L mol$^{-1}$ for durene is much higher than the value of $1.2 \times 10^2$ L mol$^{-1}$ obtained by the solid-liquid extraction method. A possible reason is that the dynamic equilibrium between the complexed and free guests cannot be ignored in this case since the condition of $[HG]_{H_2O} \gg [G]_{H_2O}$ is not fulfilled (for $[H]_{H_2O} = 5.0 \times 10^{-3}$ M and $K_a = 1.2 \times 10^2$ L mol$^{-1}$ we have $[G]_{H_2O}:[HG]_{H_2O} = 3:2$). The effect of this dynamic equilibrium is to convert the slower diffusing complexed durene into the faster diffusing free durene. As a result, the $K_a$ value calculated from equation 7 is higher than the true value because of the $\left(\frac{M}{M_o}\right)^{1/2}$ term. The $K_a$ value of $1.4 \times 10^2$ L mol$^{-1}$ calculated from equation 7 without the $\left(\frac{M}{M_o}\right)^{1/2}$ term is in good agreement with the solid-liquid extraction value, indicating that the complexed durene essentially diffuses to the receiving hexane phase as a free durene

We also use equation 7 to calculate the $K_a$ values for the 1:1 cyclophane-aromatic hydrocarbon complexes from the transport rates reported by Diederich and Dick.[3] Again the calculated $K_a$ values are in good agreement with those obtained by the solid-liquid and liquid-liquid extraction methods[3] (Table 2). The complexed durene is again found to diffuse predominantly as a free durene, consistant with the fact that the condition of $[HG]_{H_2O} \gg [G]_{H_2O}$ is not fulfilled ($[G]_{H_2O} = [HG]_{H_2O}$ for $[\text{cyclophane}]_{H_2O} = 5 \times 10^{-4}$ M and $K_a = 2.0 \times 10^3$ L mol$^{-1}$).

Table 2. Association Constants of Cyclophane[a]-Aromatic Hydrocarbon (1:1) Complexes Calculated from Transport Rates

| Hydrocarbon | $r/r_o$[b] | $(M/M_o)^{1/2}$ | $K_a$, L mol$^{-1}$<br>Eq. 7 (This work) | <br>SL(LL)[c] |
|---|---|---|---|---|
| fluoranthene | 395 | 2.47 | $1.9 \times 10^6$ | $1.2 \times 10^6$ ($1.8 \times 10^6$) |
| pyrene | 430 | 2.46 | $2.1 \times 10^6$ | $1.1 \times 10^6$ ($1.8 \times 10^6$) |
| azulene | 3.6 | 2.88 | $1.5 \times 10^4$ | ($2.1 \times 10^4$) |
| naphthalene | 3.7 | 3.02 | $1.6 \times 10^4$ | $1.5 \times 10^4$ ($1.2 \times 10^4$) |
| durene | 1.8 | 2.96 | $4.7 \times 10^3$ ($1.6 \times 10^3$)[d] | $2.0 \times 10^3$ ($1.9 \times 10^3$) |

[a] Cyclophane is



[b] Through a $5 \times 10^{-4}$ M aqueous solution of the cyclophane at 20-22° and stirring rate of ~1250 rpm (ref. 3).

[c] SL = solid-liquid extraction; LL = liquid-liquid extraction (ref. 3).

[d] Assuming the complexed durene diffuses as a free durene, see text.

The rate of stirring affects the individual transport rate (a faster stirring rate results in a faster transport rate), but has no significant effect on the $K_a$ values (both the transport rates in the presence and in the absence of 1 measured under identical conditions). For examples, when the experiments were carried out without any stirring the $K_a$ value obtained for anthracene was $2.2 \times 10^4$ L mol$^{-1}$ ($2.7 \times 10^4$ L mol$^{-1}$ with stirring, Table 1), for naphthalene was $5.2 \times 10^2$ L mol$^{-1}$ ($4.7 \times 10^2$ L mol$^{-1}$ with stirring, Table 1) and for pyrene was $5.4 \times 10^4$ L mol$^{-1}$ ($5.4 \times 10^4$ L mol$^{-1}$ with stirring, Table 1).

The association constant $K_a$ is also not much affected by the concentration of the aromatic hydrocarbon in the source phase. For example, the $K_a$ values at $3 \times 10^{-2}$ M and $5 \times 10^{-3}$ M of pyrene in the source phase (transported through an aqueous solution of $5 \times 10^{-3}$ M of 1) were $4.8 \times 10^4$ and $5.4 \times 10^4$ L mol$^{-1}$ respectively.

However, $K_a$ is not entirely independent of the host concentration in the aqueous phase. For example, the $K_a$ values obtained at $5.0 \times 10^{-4}$ and $5.0 \times 10^{-3}$ M of 1 (pyrene concentration = $3.0 \times 10^{-3}$ M) were close to each other, $4.8 \times 10^4$ and $5.4 \times 10^4$ L mol$^{-1}$

respectively. But the $K_a$ value obtained at a higher concentration of 1, $5.0 \times 10^{-2}$ M, was significantly low ($1.9 \times 10^4$ L mol$^{-1}$). We attribute the low $K_a$ value at high host concentration to viscosity effect (a higher host concentration gives a more viscous aqueous phase and a smaller diffusion rate[7]). A similar observation was reported by Diederich and Dick.[3] From their transport rate data for pyrene, we obtained two close $K_a$ values of $2.1 \times 10^6$ (Table 2) and $2.3 \times 10^6$ L mol$^{-1}$ at host concentrations of $5 \times 10^{-4}$ and $5 \times 10^{-5}$ M respectively. But the $K_a$ value of $1.1 \times 10^6$ L mol$^{-1}$ at a higher host concentration of $5 \times 10^{-3}$ M was significantly low.

## Experimental Section

Materials. The aromatic hydrocarbons were purchased from Aldrich Chemical Company. 1 was prepared as described earlier.[4,5] A sample of 1 was converted to its acid form ($Na^+$ replaced by $H^+$) by passing an aqueous solution of it through a column of Dowex 50W-X8 hydrogen ion exchange resin and then evaporating the collected solution to dryness. A FAB mass spectrum of the acid form of 1 shows a peak at 1330 which is interpreted as the $[M + 2H]^+$ ion peak.

Ultraviolet spectra of the aromatic hydrocarbons were recorded using a Hitachi U-2000 spectrophotometer.

Transport experiments were carried out at room temperature (27-29°) using the U-tube described by Diederich and Dick.[3] A 15 mL aqueous solution of 1 ($5.0 \times 10^{-3}$ M) was placed at the bottom of the U-tube. Atop this aqueous phase in one arm of the tube was placed 8 mL of n-hexane containing the aromatic hydrocarbon ($3.0 \times 10^{-3}$ M) as the source phase. In the other arm 8 mL of *n*-hexane was placed atop the aqueous phase as the receiving phase. The aqueous phase was stirred with a magnetic stirring bar (10 mm long x 3 mm diameter) at a constant speed (medium speed used on a Gallenkamp magnetic stirrer). An identical experiment, but without 1, was used as the blank. Samples were taken from the receiving phase at regular intervals (~24 hours) for the determination of the amount of aromatic hydrocarbon transported, using electronic absorption spectroscopy. After each determination the sample was returned to the receiving arm.

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