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Threading/dethreading processes in pseudorotaxanes. A thermodynamic and kinetic study

Margherita Venturi,*[a] Stephane Dumas,[a] Vincenzo Balzani,[a] Jianguo Cao[b] and J. Fraser Stoddart*[b]

[a] *Dipartimento di Chimica G. Ciamician, Università degli Studi di Bologna, via Selmi 2, 40126, Bologna, Italy. E-mail: margherita.venturi@unibo.it; Fax: +39 051 2099456; Tel: +39 051 2099543*

[b] *Department of Chemistry and Biochemistry, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, CA 90095, USA*

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Pseudorotaxanes are host–guest complexes made of a thread-like component penetrating a bead-like component. We have investigated, by a stopped-flow technique, the threading/dethreading kinetics of pseudorotaxanes formed between a tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene), and thread-like compounds consisting of a naphthalene ring system with appended –$(OCH_2CH_2)_n$OH groups (n from 0 to 3) on the 1 and 5 positions. The association and rate constants have been measured in MeCN (from 276 to 293 K) and H_2O (from 276 to 313 K). In MeCN solution, the association constant increases with increasing length of the appended chain (*e.g.*, $K_{ass} = 1.0 \times 10^3$ M^{-1} for $n = 0$ and $K_{ass} = 4.0 \times 10^4$ M^{-1} for $n = 3$, at 293 K); in H_2O, the association constants are larger than in MeCN, but almost independent of the chain length. Both the threading (k_t) and dethreading (k_d) rate constants are larger in MeCN than in H_2O and decrease with increasing chain length (*e.g.*, $k_t > 10^8$ and $k_t = 4 \times 10^6$ M^{-1} s^{-1} for $n = 0$ and $n = 3$, respectively, in H_2O at 276 K). Thermodynamic and kinetic parameters have been obtained and the role played by the length of the chains appended to the naphthalene ring system is discussed.

Introduction

In recent years much attention[1] has been focused on pseudorotaxanes,[2] which constitute a particular class of the larger family of host-guest complexes.[3] The interest in pseudorotaxanes is related to the fact that they are the supramolecular precursors of rotaxanes and catenanes, formed by post-assembly covalent modification during their template-directed synthesis,[4,5] and that they can be viewed as prototypes of simple molecular machines.[6,7] Although association constants have been measured for a variety of pseudorotaxanes,[8–11] and their chemically, photochemically, and electrochemically induced dethreading has been extensively investigated,[6,7] detailed studies on the kinetics of the threading and dethreading processes have seldom been reported.[11–13] Here, we describe (i) titration experiments used to obtain the association constants and (ii) investigations with a stopped-flow technique employed to measure the threading/dethreading rate constants of the pseudorotaxanes formed (Scheme 1) by the tetracationic cyclophane cyclobis(paraquat-*p*-phenylene), $\mathbf{5}^{4+}$, with the 1,5-dioxynaphthalene derivatives **1**–**4**, which consist of a naphthalene ring system with appended –$(OCH_2CH_2)_n$OH groups (n from 0 to 3) on its 1 and 5 positions. The experiments have been carried out in two solvents (MeCN and H_2O) and under different temperature and concentration conditions. The thermodynamic and kinetic parameters have been obtained and the spectroscopic behaviour examined.

Experimental

Absorption and emission spectra

The measurements were carried out in air-equilibrated H_2O (Milli-Q, 18.2 MΩ cm) or MeCN (Merck Uvasol®) solutions in the concentration range from 2.5×10^{-5} to 1.0×10^{-4} M. UV/Vis absorption spectra were recorded with a Perkin–Elmer λ16 spectrophotometer equipped with a thermostatted cell holder, and uncorrected luminescence spectra were obtained with a Perkin–Elmer LS-50 spectrofluorimeter mounting a Hamamatsu R928 phototube. The estimated experimental errors are 2 nm in relation to band maxima and ±5% on the molar absorption coefficients and fluorescence intensity.

Electrochemical measurements

Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) experiments were carried out in argon-purged MeCN (Romil Hi-Dry) solution at room temperature. The equipment and experimental procedures have been described previously.[14] The concentration of the compounds was 5×10^{-4} M; the experiments were carried out in the presence of tetraethylammonium hexafluorophosphate (0.05 M) as supporting electrolyte and ferrocene as an internal standard ($E_{1/2} = +0.395$ V *vs.* SCE).

Stopped-flow experiments

Stopped-flow experiments were performed in air-equilibrated H_2O (Milli-Q, 18.2 MΩ cm) or MeCN (Merck Uvasol®) solutions with an Applied Photophysics SX 18-MV equipment. The standard flow tube has an observation path length of 1 cm and the driving ram for the mixing system was operated at the recommended pressure of 8.5 bar. Under these conditions the dead-time was 1.35 ms, experimentally determined by using a test reaction.[15] For MeCN solutions a correction of the baseline was applied to minimise the dependence of the absorbance on the pressure. In all the experiments, solutions of the

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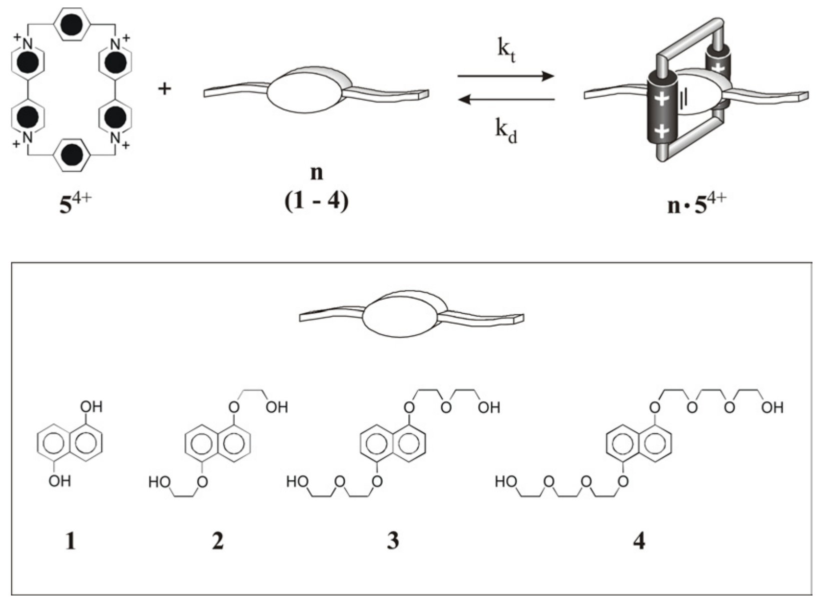

Scheme 1 Schematic representation of the threading/dethreading process involving the 1,5-dioxynaphthalene derivatives **1**–**4** and the cyclobis(paraquat-*p*-phenylene) cyclophane $\mathbf{5}^{4+}$. The structural formulas of the compounds are also shown.

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tetracationic cyclophane cyclobis(paraquat-*p*-phenylene), $\mathbf{5}^{4+}$ (as Cl^- and PF_6^- salt for H_2O and MeCN solutions, respectively), and the 1,5-dioxynaphthalene derivatives **1**–**4** were mixed in equimolar amounts to have, after mixing, a concentration range from 2.5×10^{-5} to 1.0×10^{-4} M. The reactions were monitored by the decrease of the fluorescence intensity above 305 nm (excitation at 295 nm), typical of threads **1**–**4**, and by the increase of the absorption in the 520–555 nm region, characteristic of reaction products. For the fluorescence measurements, a filter cutting off the emitted light below 305 nm was placed between the photomultiplier and the cell. In all the experiments the cell block and drive syringes were thermostatted by using a circulating constant temperature bath.

Results and discussion

Spectroscopic and electrochemical properties

The absorption spectrum ($\lambda_{max} = 260$ nm, $\varepsilon_{max} = 40\,000$ M^{-1} cm^{-1}) and the electron-acceptor properties ($E_{1/2} = -0.29$ and -0.71 V *vs.* SCE for the first and second reduction, respectively, in MeCN solution) of cyclobis(paraquat-*p*-phenylene) ($\mathbf{5}^{4+}$) are well-known.[9a,b,16] The 1,5-dioxynaphthalene derivatives **1**–**4** exhibit weak absorption bands below 330 nm and a strong and structured fluorescence band with maximum at 350 nm (see, *e.g.*, Fig. 1, inset). On mixing solutions of $\mathbf{5}^{4+}$ with each of the compounds **1**–**4**, the naphthalene-based fluorescence of the threads is quenched and a weak and broad absorption band appears in the visible region (see, *e.g.*, Fig. 1), which is assigned to the charge-transfer (CT) interactions between the electron-donating 1,5-dioxynaphthalene ring system of the threads and the electron-accepting bipyridinium units of the cyclobis(paraquat-*p*-phenylene) cyclophane.[17] The wavelengths of the maxima and the molar absorption coefficients of the CT bands are similar (Table 1) but not identical for the four pseudorotaxanes. The maximum of the band moves to the red with increasing the electron-donor power of the thread, as measured from the oxidation potentials (Table 1). The reason why the value of the molar absorption coefficient is larger for the shorter thread will be discussed below. It is also interesting to note that, for the four investigated pseudorotaxanes, the maxima and the molar absorption coefficients of the CT bands are identical in the two examined solvents (H_2O and MeCN), and do not change upon varying temperature in the 276–313 K range. Both the increase in absorbance of the CT band and the quenching of the fluorescence band of the free thread can be used for titration experiments aimed at measuring the association constants.

Intercomponent interactions

Pseudorotaxane superstructures composed of the cyclobis(paraquat-*p*-phenylene) cyclophane and thread-like compounds consisting of a dioxyarene moiety with appended ethylenoxy chains are known[8,9a,18] to be stabilised by a variety of interactions. An obvious one is the CT interaction between the electron-donating dioxyarene moiety of the thread and the electron-accepting bipyridinium units of the cyclobis(paraquat-*p*-phenylene) cyclophane. It has been shown,[8a] however, that, although the presence of an aromatic core is necessary for the guest to reside in the cavity of the host, a very important contribution to complexation comes from C–H···O

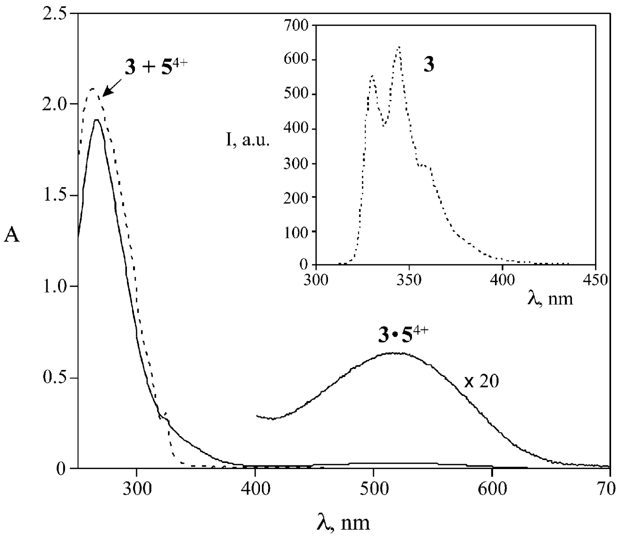

Fig. 1 Absorption spectrum (solid line) of the pseudorotaxane $\mathbf{3}\cdot\mathbf{5}^{4+}$ (4.1×10^{-5} M) compared with the sum of the absorption spectra (dashed line) of the separated components (MeCN solution, 293 K). Inset shows the fluorescence spectrum of the thread-like component **3** ($\lambda_{exc} = 295$ nm); $\mathbf{3}\cdot\mathbf{5}^{4+}$ does not display any emission.

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Table 1 Wavelength maxima and molar absorption coefficients of the charge-transfer bands of the pseudorotaxanes formed by cyclophane $\mathbf{5}^{4+}$ with compounds **1**–**4** (MeCN and aqueous solution). Potential values of the irreversible oxidation process involving the free compounds **1**–**4** (MeCN solution, 293 K).

Compound	λ/nm	ε/M^{-1} cm^{-1}	Compound	E^a/V
$\mathbf{1}\cdot\mathbf{5}^{4+}$	555	1150	**1**	+0.9
$\mathbf{2}\cdot\mathbf{5}^{4+}$	538	1100	**2**	+1.0
$\mathbf{3}\cdot\mathbf{5}^{4+}$	520	780	**3**	+1.2
$\mathbf{4}\cdot\mathbf{5}^{4+}$	520	780	**4**	+1.2

[a] Potential value estimated from the DPV peak and is reported in V *vs.* SCE.

interactions involving the oxygen atoms of the ethylenoxy chains and the α and/or β protons of the bipyridinium units of the tetracationic cyclophane. An investigation of a series of *p*-polyphenylene guests, symmetrically substituted with ethylenoxy side arms of various length and functionality, has suggested[8a] that the binding in MeCN solution is substantially influenced by a chelate effect involving the oxygen atoms of the thread. Theoretical studies have indeed demonstrated that C–H···O interactions play the most important role in controlling the formation of supramolecular species based on bipyridinium and dioxyarene components,[18] as well as in similar systems.[19,20]

It should also be noted that, in compounds of the type examined in this research, CT interactions give a relatively small contribution to complex formation; nevertheless, they are responsible for the changes in the light absorption and emission signals that enable the measurements of the association constants and threading/dethreading rate constants

Thermodynamic parameters

Fig. 2 shows the increase in absorbance at 538 and 520 nm upon titration of **2** and **3**, respectively, with $\mathbf{5}^{4+}$ in MeCN solution at 293 K. The association constants, obtained by curve fitting of a single titration experiment, are recorded in Tables 2 and 3. The equation employed for the fitting can be easily derived from the equilibrium constant expression of the considered reaction (Scheme 1); for more details see ref. 21. From the corresponding van't Hoff plots, the thermodynamic parameters have been obtained. As expected for exothermic processes, the association constants decrease with increasing temperature.

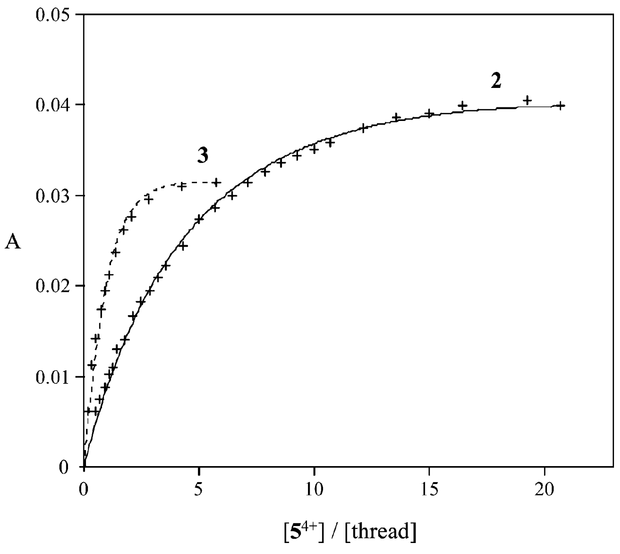

Fig. 2 Increase in absorbance at 538 and 520 nm upon titration of **2** (4.7×10^{-5} M) and **3** (5.0×10^{-5} M), respectively, with $\mathbf{5}^{4+}$ in MeCN solution at 293 K.

Table 2 Association constants (M^{-1})^a and thermodynamic parameters (kcal mol^{-1})^b in aqueous solution.

Compound	T/K	$K_{ass} \times 10^{-5}$ ($\Delta G°$)	$\Delta H°$	$T\Delta S°$
$\mathbf{1}\cdot\mathbf{5}^{4+}$	276	17		
	283	13		
	293	9.0 (−8.0)	−5.7	+2.3
	303	7.8		
	313	4.6		
$\mathbf{2}\cdot\mathbf{5}^{4+}$	276	9.9		
	283	7.5		
	293	6.2 (−7.8)	−5.0	+2.8
	303	3.9		
	313	3.2		
$\mathbf{3}\cdot\mathbf{5}^{4+}$	276	37		
	283	24		
	293	14 (−8.2)	−10.5	−2.3
	303	7.2		
	313	3.8		
$\mathbf{4}\cdot\mathbf{5}^{4+}$	276	17		
	283	11		
	293	6.1 (−7.8)	−9.4	−1.7
	303	3.4		
	313	2.3		

[a] $K_{ass} = [\mathbf{n}\cdot\mathbf{5}^{4+}]_{eq}/[\mathbf{n}]_{eq} \times [\mathbf{5}^{4+}]_{eq}$, using $[\mathbf{n}]_{eq} = [\mathbf{n}]^{\circ} - [\mathbf{n}\cdot\mathbf{5}^{4+}]_{eq}$ and $[\mathbf{5}^{4+}]_{eq} = [\mathbf{5}^{4+}]^{\circ} - [\mathbf{n}\cdot\mathbf{5}^{4+}]_{eq}$; values obtained from a single titration experiment; the standard deviation of the experimental data fitting indicates that the K_{ass} values are affected by an error <10%. [b] The experimental data fitting according to the van't Hoff equation indicates that the enthalpy and entropy values are affected by errors of <10% and <15%, respectively.

In H_2O, there is no definite trend (Table 2) in the K_{ass} values on changing the length of the chain appended to the 1,5-dioxynaphthalene ring system of the thread. The $\Delta S°$ values (positive for **1** and **2**, negative for **3** and **4**) reveal, however, that the chain length does play a role and that the similar $\Delta G°$ values are, in fact, the result of compensation by different factors. Assuming that the effect on the solvent stability is approximately the same in the four systems, the values of the association constants can be related to an interplay of CT and C–H···O interactions between the host and guests. For compounds **1** and **2**, which exhibit no or a limited capacity to form hydrogen bonds with the tetracationic cyclophane $\mathbf{5}^{4+}$, the

Table 3 Association constants (M^{-1})^a and thermodynamic parameters (kcal mol^{-1})^b in MeCN solution.

Compound	T/K	$K_{ass} \times 10^{-5}$ ($\Delta G°$)	$\Delta H°$	$T\Delta S°$
$\mathbf{1}\cdot\mathbf{5}^{4+}$	293	0.1 (−4.0)		
$\mathbf{2}\cdot\mathbf{5}^{4+}$	293	0.4 (−4.8)		
$\mathbf{3}\cdot\mathbf{5}^{4+}$	276	21		
	283	11		
	293	5.7 (−6.4)	−12.2	−5.9
$\mathbf{4}\cdot\mathbf{5}^{4+}$	276	20		
	283	9.9		
	293	4.0 (−6.2)	−15.2	−9.0

[a] $K_{ass} = [\mathbf{n}\cdot\mathbf{5}^{4+}]_{eq}/[\mathbf{n}]_{eq} \times [\mathbf{5}^{4+}]_{eq}$, using $[\mathbf{n}]_{eq} = [\mathbf{n}]^{\circ} - [\mathbf{n}\cdot\mathbf{5}^{4+}]_{eq}$ and $[\mathbf{5}^{4+}]_{eq} = [\mathbf{5}^{4+}]^{\circ} - [\mathbf{n}\cdot\mathbf{5}^{4+}]_{eq}$; values obtained from a single titration experiment; the standard deviation of the experimental data fitting indicates that the K_{ass} values are affected by an error <10%. [b] The experimental data fitting according to the van't Hoff equation indicates that the enthalpy and entropy values are affected by errors of <8% and <10%, respectively.

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major driving force for association probably arises from CT interactions, which are expected to be slightly stronger (Table 1) in the case of the better electron donor **1**. On passing from compounds **1** and **2** to threads **3** and **4**, the C–H···O interactions become more important, whereas the CT interactions decrease because **3** and **4** are poorer electron donors (Table 1). The thermodynamic data (Table 2) show that a further increase of the chain length from $n = 2$ to $n = 3$ has a minor effect.

In MeCN solution the association constants (Table 3) are much lower than in H_2O, a result that can be accounted for considering the hydrophobic character of the threads, particularly the shorter ones. The association constants increase with increasing chain length from **1** to **3** (*i.e.*, n from 0 to 2), just as in the case of the analogous threads with a p-phenylene core.[8a] Since the donor power of the thread component decreases on going from **1** to **3** (Table 1), this result shows indeed that an important contribution to the stability of the pseudorotaxane comes from C–H···O interactions involving the oxygen atoms of the ethylenoxy chains. Again, no further increase is observed on going from **3** to **4**, showing that the stronger C–H···O interactions involve the second and third oxygen atoms of the ethylenoxy chains. The slightly different π–π stacking arrangements in the various pseudorotaxanes can account for the above-mentioned differences in the values of the molar absorption coefficients of the CT band (Table 1).

It should also be noted that the $\Delta S°$ values for **3** and **4** are very negative in both the examined solvents (Tables 2 and 3).

Kinetic parameters

The kinetics of the threading process were studied by stopped-flow experiments in MeCN and H_2O by monitoring changes in the intensity of the CT absorption band and of the fluorescence band of the thread on mixing equimolar amounts of the two components. In the case of each system, experiments were performed as a function of temperature and for each temperature three different concentrations were investigated. Fig. 3 shows the traces obtained on mixing **3** and $\mathbf{5}^{4+}$ with a concentration, after mixing, of 2.5×10^{-5} M in aqueous solution at 293 K. Qualitatively similar results were obtained in each experiment performed with **3** and **4**. However, no spectral change was observed in the experiments performed with **1** and **2** in either MeCN or H_2O, even when the smallest concentration anticipated to give a detectable signal and the lowest temperature were used. This finding means that, for **1** and **2**, an equilibrium is reached within the dead-time of the equipment used, that is the threading process is too fast to be measured with our equipment ($k_t > 10^8$ M^{-1} s^{-1}).

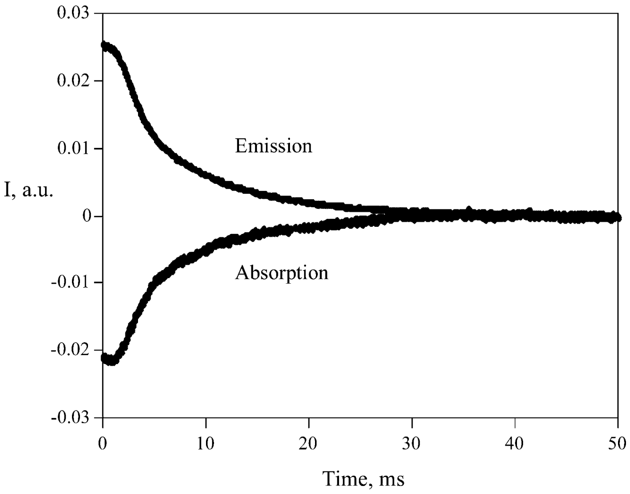

Fig. 3 Stopped-flow traces for the change in absorption ($\lambda = 520$ nm) and emission intensity ($\lambda > 305$ nm) on mixing equimolar amounts (after mixing, 2.5×10^{-5} M) of **3** and $\mathbf{5}^{4+}$ in aqueous solution at 293 K.

The stopped-flow traces obtained for **3** and **4** under the various experimental conditions, coupled with the independently measured association constants (Tables 2 and 3), were treated to afford the k_t and k_d values by using the relaxation method[22] and a conventional kinetic analysis applied to opposing second- and first-order reactions[23] (Scheme 1). As far as the latter method is concerned, the experimental traces were analyzed by using the SPECFIT[24] computer fitting programme. In each case the fitting was performed for $t \geq 2$ ms and covered more than 70% of the reaction. The two employed methods gave k_t and k_d values in very close agreement; their values are reported in Table 4.

The rate constants for the threading process are of the order of 10^7 M^{-1} s^{-1}. They are quite comparable for **3** and **4** and slightly larger in MeCN than in H_2O. We should also recall that the threading process is too fast ($k_t > 10^8$ M^{-1} s^{-1}) to be measured for the shorter threads **1** and **2**. The dethreading rate constants for **3** and **4** are in the range 10^0–10^3 s^{-1}; again, they are quite comparable for **3** and **4**, and larger (about 50 times) in MeCN compared with H_2O. Judging from the values of the association constants and the lower limit for the threading rate constant, the dethreading rate constants for **1** and **2** have to be at least one order of magnitude larger than those obtained for **3** and **4**. Clearly, the effect of increasing chain length is important, but the difference in the rate constants is quite small on passing from $n = 2$ to $n = 3$, particularly for the dethreading process. For comparison purposes, we note that the threading and dethreading rate constants for a recently studied[11] calixarene-based pseudorotaxane in CH_2Cl_2 are several orders of magnitude smaller than those found for the present systems.

Fig. 4 shows an example of kinetic traces obtained at different temperatures. From the increase of the values of the rate constants on increasing temperature (Eyring plots, see, *e.g.*, Fig. 4 inset), the activation parameters have been obtained (Table 5). The following points should be noted. (i) The activation barrier for dethreading is, as expected, larger than that for the threading process and both barriers are, as expected, much smaller than those observed for slipping/deslipping processes in some related rotaxanes.[12a–c] (ii) The values of the activation parameters are practically the same for **3** and **4**. (iii) The activation barriers are slightly larger for aqueous solutions,

Table 4 Rate constants for the threading (k_t, M^{-1} s^{-1}) and dethreading (k_d, s^{-1}) processes.[a]

		H_2O solution[b]		MeCN solution[b]	
Compound	T/K	$k_t \times 10^{-7}$	k_d	$k_t \times 10^{-7}$	k_d
$\mathbf{3}\cdot\mathbf{5}^{4+}$	276	0.8	1.9	2.2	110
	283	1.1	4.4	2.5	230
	293	1.8	13.2	3.0	530
	303	2.3	32.5		
	313	3.3	88.0		
$\mathbf{4}\cdot\mathbf{5}^{4+}$	276	0.4	2.1	2.0	110
	283	0.6	5.0	2.2	220
	293	0.9	15.0	2.8	700
	303	1.3	36.4		
	313	2.2	93.8		

[a] The threading processes involving compounds **1** and **2** are too fast to be monitored by using the stopped-flow technique. [b] Average of the data obtained for three different concentrations by following the appearance of the charge-transfer absorption band and the quenching of the thread luminescence, and by treating the stopped-flow traces with the relaxation method and a conventional kinetic analysis (see text); estimated error <10%.

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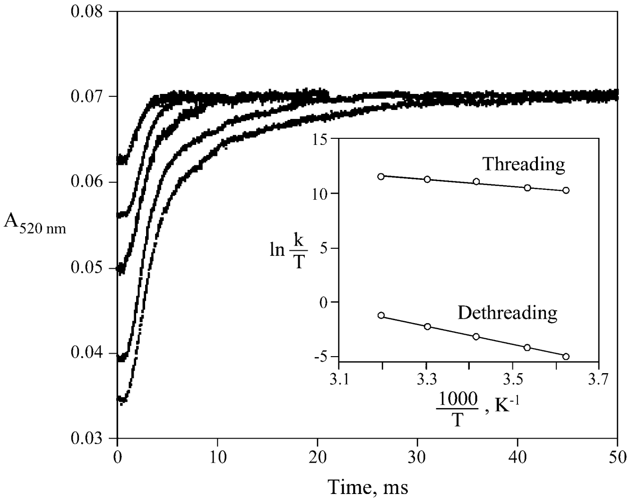

Fig. 4 Stopped-flow traces for the change in absorption at 520 nm on mixing equimolar amounts (after mixing, 1.0×10^{-4} M) of **3** and $\mathbf{5}^{4+}$ in aqueous solution at different temperatures. The inset shows the Eyring plots for the threading and dethreading processes.

particularly in the case of the dethreading processes. (iv) In H_2O, the most important contribution to the barriers of both the threading and dethreading processes is enthalpic in nature. (v) In MeCN, the activation energy for the threading process is mainly determined by an entropic factor, while for dethreading, a small increase in entropy lowers the high enthalpic barrier. The results obtained show that an increase in chain length from $n = 2$ to $n = 3$ does not cause substantial differences in the rates of the threading and dethreading processes and that the barrier has a different nature in the two solvents.

Conclusions

We have investigated the stability and, by a stopped-flow technique, the threading/dethreading kinetics of the pseudorotaxanes formed by 1,5-dioxynaphthalene derivatives bearing ethylenoxy chains of different lengths with the tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene). The experiments with $\mathbf{5}^{4+}$ have been carried out in H_2O and MeCN solutions. The results obtained show that (i) the association constants are larger in H_2O, whereas both the threading (k_t) and dethreading (k_d) rate constants are larger in MeCN, (ii) the association constants are almost independent of the chain length in H_2O, whereas in MeCN they increase with increasing length of the polyether chain, (iii) the threading and dethreading processes are too fast to be measured using the stopped-flow technique for threads **1** and **2**, while their rates are not substantially different in the case of threads **3** and **4**, (iv) the activation barriers are slightly larger for aqueous solutions, particularly in the case of the dethreading processes, and (v) although the activation barriers are comparable in the two solvents, the enthalpic and entropic contributions are different. The results obtained show that both the thermodynamic and kinetic parameters are governed by contrasting factors related to charge-transfer and C–H···O interactions, which, in turn, are determined by the nature of the solvent and the length of the ethylenoxy chains.

Table 5 Activation parameters (in kcal mol^{-1}) at 293 K for the threading ($\Delta H_t^{\neq}$, $T\Delta S_t^{\neq}$, and $\Delta G_t^{\neq}$) of ***n*** into $\mathbf{5}^{4+}$, and dethreading ($\Delta H_d^{\neq}$, $T\Delta S_d^{\neq}$, and $\Delta G_d^{\neq}$) of $\boldsymbol{n}\cdot\mathbf{5}^{4+}$ processes, where **n = 3** and **4**.

	H_2O solution		MeCN solution	
Activation parameters^a	**n** = **3**	**n** = **4**	**n** = **3**	**n** = **4**
$\Delta H_t^{\neq b}$	+6.1	+7.4	+2.4	+2.7
$T\Delta S_t^{\neq b}$	−1.4	−0.4	−4.7	−4.5
$\Delta G_t^{\neq c}$	+7.5	+7.8	+7.1	+7.2
$\Delta H_d^{\neq d}$	+17.0	+16.9	+14.2	+17.0
$T\Delta S_d^{\neq d}$	+1.4	+1.3	+0.8	+3.7
$\Delta G_d^{\neq c}$	+15.6	+15.6	+13.4	+13.3

^{a} The errors have been derived from the experimental data fitting according to the Eyring equation. ^{b} Estimated error <7%. ^{c} Estimated error <10%. ^{d} Estimated error <6%.

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