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Chiral recognition of 1,1′-binaphthyl-2,2′-diyl hydrogenphosphate using fluorescence anisotropy

Yafei Xu, Matthew E. McCarroll *

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, United States

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Abstract

The photophysical properties of 1,1′-binaphthyl-2,2′-diyl hydrogenphosphate (BNP) have been examined with particular emphasis to the effects of the chiral recognition of BNP by α-, β-, and γ-cyclodextrins (CDs). Fluorescence spectra and anisotropy values of the BNP enantiomers were measured in the presence and absence of the CDs under various conditions and the chiral recognition behavior are discussed based on the acquired fluorescence data. Small spectral shifts in the fluorescence emission allowed evaluation of the binding constant and enantioselectivity of the binding in β-, and γ-cyclodextrin, but significant shifts were not observed in the case of α-cyclodextrin. Fluorescence anisotropy proved to be an effective technique to study the enantioselective interactions, even in the case of α-cyclodextrin where a smaller binding constant and enantiodiscrimination were confirmed. The differential thermodynamics of binding were examined by fluorescence anisotropy and are discussed with reference to the general structural characteristic of the cyclodextrins examined. Interestingly, BNP was found to exhibit opposite thermodynamic trends for β-cyclodextrin at low (1 mM) and high (11 mM) cyclodextrin concentrations, indicating the possibility of complex of even different modes of enantiodiscrimination in this system.

Keywords: Fluorescence; Polarization; Anisotropy; Cyclodextrin; BNP; Binaphthyl phosphate; Thermodynamics; Chiral recognition; Chirality; Chiral selectivity; Molecular recognition

1. Introduction

Chiral recognition and separation play important roles in pharmaceutical and biotechnology fields [1,2]. Various techniques have been utilized in the studies of chiral recognition with a wide variety of molecules including microcalorimetry, UV–vis absorption spectrometry, NMR, mass spectrometry, thermal analysis and various chromatographic methods [3,4,5–18]. Fluorescence spectroscopy is a useful tool for the study of molecular recognition and chiral discrimination. It can provide useful information about host–guest interactions with a high sensitivity. Various approaches using fluorescence spectroscopy have been used for the study of chiral recognition [19–30]. Most of them, however, involve the measurements of fluorescence emission intensities, spectral shifts and quenching effects. Recently, we have explored the use of fluorescence polarization (anisotropy) in the study of chiral recognition [30–35]. A strong correlation between chiral selectivity and anisotropy ratio was observed for different chiral compounds with various selectors. Unlike intensity measurements, fluorescence anisotropy is based primarily on the measurement of molecular rotation mobility, rather than changes in emission spectra. Thus, it eliminates the requirement of enantioselective spectral perturbations and is more broadly applicable. Briefly, the binding of a chiral fluorophore to a selector, such as cyclodextrin, results in a slower rotational rate and an increased anisotropy value [36]. Often the two enantiomers of a chiral compound will interact with differing stabilities (i.e. chiral recognition). In this scenario the enantiomer that binds more strongly will have a larger binding constant and will exhibit larger fluorescence anisotropy values. The magnitude of this difference has been shown to correlate well with the selectivity expressed in the system [32,33,35] and can be used to evaluate enantioselective interactions. In this work, steady state fluorescence spectroscopy was used to study the complexation, chiral recognition and the enantioselective thermodynamics of 1,1-binaphthyl-2,2′-diyl hydrogenphosphate (BNP) with α-, β- and γ-cyclodextrins (CDs). Fluorescence spectra and anisotropy values of the BNP enantiomers were measured in the presence

* Corresponding author. Tel.: +1 618 453 6475; fax: +1 618 453 6408.
E-mail address: mmccarroll@chem.siu.edu (M.E. McCarroll).

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and absence of the CDs under various conditions and the chiral recognition behavior are discussed based on the acquired fluorescence data.

2. Experimental

2.1. Fluorescence anisotropy measurements

A modular spectrofluorometer (Photon technology International Inc., London, Ontario, Canada) equipped with double monochromators and a photon counting PMT detector was used for all fluorescence anisotropy measurements. A Xe lamp was used as an excitation source. Measurement temperature was controlled and adjusted using a NESLAB thermocirculator (NESLAB Instruments, Inc., Newington, NH). Quartz cuvettes were used for all fluorescence measurements.

2.2. Sample preparation

Solutions used in this experiment were prepared with phosphate buffer (50 mM, pH 6.9) and the concentration of BNP ranged from 10 to 50 μM The α-, β- and γ-CD solutions were prepared by dissolving solid CD in phosphate buffer (50 mM, pH 6.9). All solutions were mixed by sonication for ~20 min and allowed to equilibrate for at least 30 min. β-Cyclodextrin was a gift from Cerestar USA, Inc. (Hammond, IN). The α- and γ-cyclodextrin, as well as the pure enantiomers of BNP, were purchased from Aldrich (Milwaukee, WI) and were used as received. The enantiomeric purity of the BNP was stated as ≥98% for the *R*-enantiomer and ≥97% for the *S*-enantiomer. Water used in all experiments was purified by a Milli-Q system (Millipore Inc. Milford, MA) to a resistivity of at least 18 MΩ cm^{-1}. All other chemicals were used as received.

2.3. Theory

A theoretical treatment detailing the relationship between the measured steady-state fluorescence anisotropy and association constants has been previously introduced [32]. Because fluorescence anisotropies are additive, the measured anisotropy of a fluorophore interacting with a selector is a weighted average based on the fractional distribution between the rapidly rotating free species and the more slowly rotating bound species. Assuming a 1:1 association stoichiometry the fractional distribution can be represented in terms of the binding constant, K, the concentration of free selector, S, and the anisotropy of the free and bound species, r_f and r_b, respectively (Eq. (1)).

$$r_{avg} = r_b \frac{K[S]}{K[S]+1} + r_f \left[1 - \frac{K[S]}{K[S]+1}\right] \quad (1)$$

Many factors can affect the average anisotropy value in a given system and can lead to artifacts. Non-enantioselective factors, however, affect both enantiomers equally and do not lead directly to a difference in anisotropy values between two enantiomers. Thus, the enantioselectivity can be specifically examined by the ratio of anisotropy values, as is shown in Eq. (2),

$$\frac{r_{avg,R}}{r_{avg,S}} = \frac{r_{b,R}}{r_{b,S}} \frac{K_R}{K_S} \frac{K_S[S]+1}{K_R[S]+1} \quad (2)$$

which effectively demonstrates the ratio of anisotropy values is a function of the differences in anisotropy values of the two diastereomers ($r_{b,R}$ and $r_{b,R}$), the binding constants, K, and the concentration of free selector, S. We have recently shown [32] that the natural logarithm of Eq. (2) can be related to the differential thermodynamics of enantioselective binding (Eq. (3)).

$$\ln\left(\frac{r_{avg,R}}{r_{avg,S}}\right) = \frac{-\Delta\Delta H^\circ}{RT} + \frac{\Delta\Delta S^\circ}{R} + \ln\left(\frac{r_{b,R}}{r_{b,S}}\right) + \ln\left(\frac{K_S[S]+1}{K_R[S]+1}\right) \quad (3)$$

Hence, the fluorescence anisotropy can be used as a sensitive measure of the chiral selectivity [33] and to investigate the thermodynamic parameters of enantioselective interactions [32].

3. Results and discussion

3.1. Fluorescence emission spectra of BNP

In aqueous solution (phosphate buffer 50 mM, pH 6.9), BNP emits a single broad fluorescence emission band between 350 and 400 nm with a maximum of 378 nm that shifts to shorter wavelengths in less polar solvents (Fig. 1). The observed shift can be attributed to the decreased polarity of the BNP environment with the addition of the organic solvents, which increases the energy difference between ground and excited states of BNP [37].

Fig. 2 shows the fluorescence emission spectra of BNP in the presence of α- and β-CD. A blue-shift in maximum emission was observed for β-CD complexes whereas no emission shift is shown for α-CD complexes. The γ-CD complex shows a shift similar to that of β-CD, albeit at a slightly lower intensity (data is not shown). The observed spectral shifts can be attributed to the formation of inclusion complexes of BNP with β- and

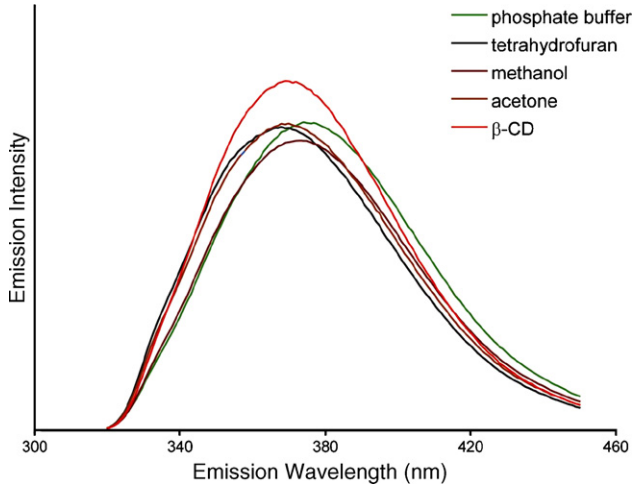

Fig. 1. Fluorescence emission spectra of BNP in various solvent systems.

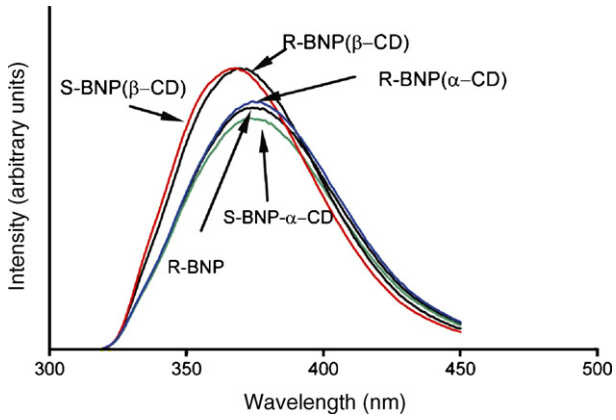

Fig. 2. Fluorescence emission spectra of the enantiomers of BNP in the presence of α- and β-CD.

γ-CDs and the resulting hydrophobic microenvironment. This interpretation is supported by the fact that the fluorescence shifts are very similar to those observed in organic solvents (Fig. 1). Also, *S*-BNP exhibited a greater spectral shift than did *R*-BNP, suggesting that *S*-BNP forms more stable complex with β- and γ-CD than does the *R*-enantiomer, as confirmed by elution order in CE and by fluorescence anisotropy measurements. By contrast, α-CD complexes do not show any apparent spectral shifts and intensity enhancement, which can be ascribed to its smaller size of CD cavity that is not large enough to include the bulky naphthalene ring of BNP in a stable inclusion complex.

Fig. 3 shows the comparison of the measured anisotropy for *R*- and *S*-BNP with α-, β- and γ-cyclodextrin. Significant differences in anisotropy are observed in each case, with β- and γ-CD complexes displaying a much higher anisotropy than α-CD, which can be explained by a larger fraction of bound species as a result of a better size match between the analyte and the cavity of β- and γ-CD. By contrast, the α-CD complex shows the lowest anisotropy value (∼0.002), which is consistent with the size exclusion of BNP by the smaller cavity of α-CD. This result is in agreement with that of the spectral study discussed in previous section.

Fig. 4 shows the anisotropy ratios of BNP enantiomers with α-, β- and γ-CDs. The concentrations of β- and γ-CD were 11 mM. A higher concentration of α-CD (42 mM) was used in the case of α-CD to increase the number of bound species. Various degrees of chiral recognition were observed for all three CDs. The complexes of β-CD exhibited the largest anisotropy ratio while α-CD displayed smaller values. Based on size considerations, BNP can form a stable complex with β-CD by insertion of one of the naphthalene rings into the cavity of β-CD. A high level of chiral recognition is achieved due to the precise conformational complementarity and restricted movement of BNP. In comparison with β-CD, γ-CD has a larger cavity. Thus, it can be expected that the BNP enantiomers would have increased motional freedom, reducing the observed chiral discrimination, as is evidenced by the relatively small differential anisotropy observed, especially in comparison with the β-CD system.

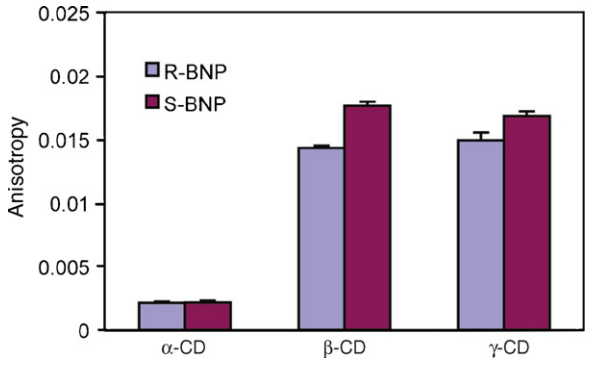

Fig. 3. Anisotropy of BNP with α-, β- and γ-CDs.

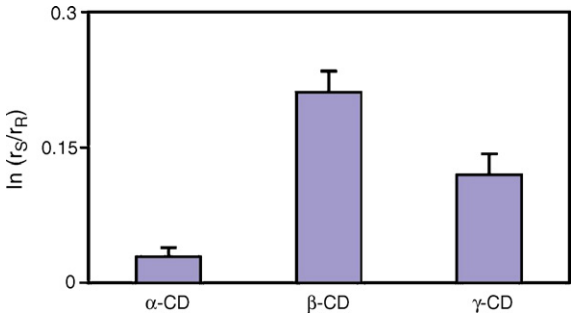

Fig. 4. Anisotropy ratio of BNP with α-, β- and γ-CD.

The α-CD system does not form a stable inclusion complex with BNP due to the small cavity size. The observed small difference in anisotropy of *R*- and *S*-BNP complexes can be primarily attributed to hydrophilic interactions, such as hydrogen bonding. BNP may form a head-to-head complex with α-CD via hydrophilic interactions of the phosphate moiety. A similar situation has been reported for complexes formed between BNP and linear oligosaccharides, in which BNP was reported to form a non-inclusion complex via hydrogen bond interactions [38]. The magnitude of the chiral selectivity of BNP with α-CD measured by CE in our laboratory (data not shown) is very close to that of BNP-oligosaccharides complexes reported in literature [38].

3.2. *Effects of CD concentration on chiral recognition*

For a given host–guest system, the measured anisotropy is dependent on the association constants, the fluorescence anisotropy of the bound fluorophore and the concentration of host (chiral selector). For a given analyte-selector solution, association constants and the anisotropy values of the bound species should be constant at a given temperature and the measured anisotropy is a function of selector concentration. In general, the measured (average) anisotropy increases with increasing selector concentration due to an increase in fraction of bound fluorophore. Fig. 5 shows the variation of the measured anisotropy of BNP as a function of concentration for β- and γ-CD. As is expected, the average anisotropy increases with increasing CD concentrations in the both cases. The anisotropy initially increased quickly and gradually approached a constant value. In the range of CD concentrations evaluated, *S*-BNP displayed a higher anisotropy value than did *R*-BNP for the both CDs. However, the anisotropy of *R*- and *S*-enantiomers changes dif-

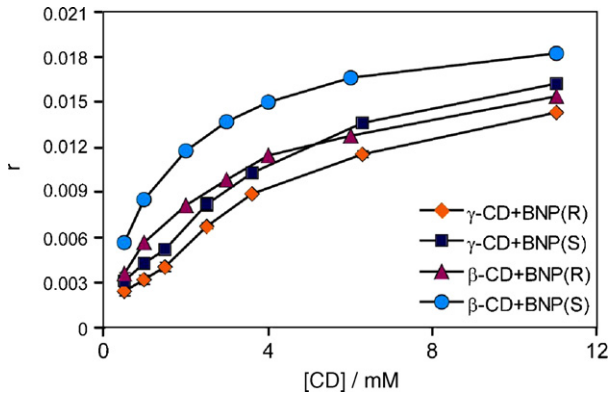

Fig. 5. Fluorescence anisotropy as a function of CD concentration for the enantiomers of BNP with β- and γ-CD.

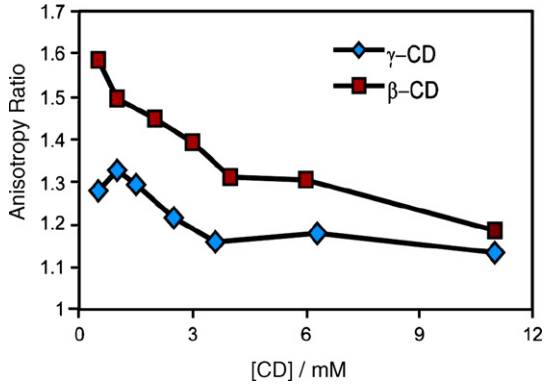

Fig. 6. Plots of *r*/*r* vs. [CD] for BNP with β- and γ-CD.

ferently as a function of CD concentration, resulting in a varying anisotropy ratio. Fig. 6 shows the anisotropy ratio of BNP complexes as a function of CD concentration with β- and γ-CDs. The measured anisotropy ratio shows a maximum value at a low CD concentration (between 1 and 2 mM). Thus, a high level of chiral recognition could be achieved at much lower concentrations of CDs, an interesting result in light of the fact that selectivity is typically not dependent on the selector concentration.

To further investigate the effect of CD concentration on the anisotropy ratios of BNP–β-CD complexes, the change in the emission spectra was measured with varying β-CD concentration (Fig. 7). The intensity enhancement and blue-shifts in

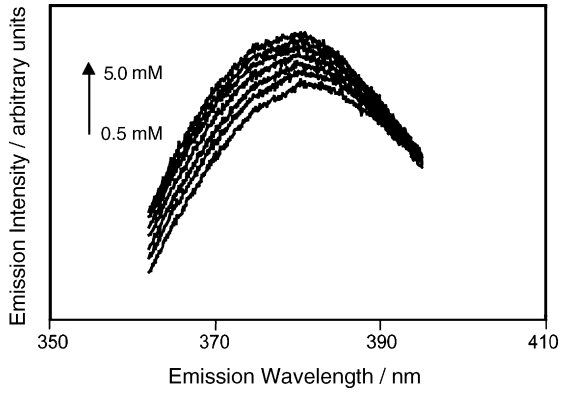

Fig. 7. Variation of fluorescence emission of *R*-BNP with concentration of β-cyclodextrin.

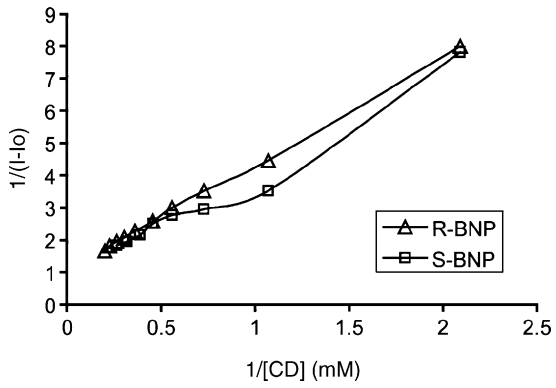

Fig. 8. Double reciprocal plots for *R*- and *S*-BNP with β-CD.

fluorescence emission are observed with increasing CD concentration. Fig. 8 shows the double reciprocal plots of ΔI versus [β-CD] for *R*- and *S*-BNP complexes.

Interestingly, a non-linear relationship between [β-CD] and ΔI is observed for *S*-BNP omplexes while an linear relationship is observed for *R*-BNP. It seems that *S*-BNP exhibits different behavior with varying CD concentrations. The reciprocal plots of [β-CD] versus ΔI for *S*-BNP is curved downward in a range of low CD concentration (<3 mM) while it shows linear behavior at high concentrations (>5 mM), possibly indicating that the complexation of *S*-BNP with β-CD is governed by different mechanisms at high and low CD concentrations. For example, a 1:1 stochiometry is indicated at a range of higher CD concentration (>5 mM) by the linear relationship that is observed. A more complicated mechanism may be involved at lower CD concentrations. Evaluations assuming both the first order and second order complex formation show a non-linear relationship for *S*-BNP–β-CD, which rules out the possibility of the formation of purely 1:1 or 1:2 complexes between β-CD and *S*-BNP. The downward curvature may indicate the formation of more 2:1 complexes between them, i.e. at a low CD concentration; two BNP molecules may complex with one β-CD to form 2:1 complexes. This is agreement with the results of anisotropy measurement discussed earlier in this section which showed a much higher anisotropy ratio at a low CD concentration.

Fig. 9 shows the double reciprocal plot for BNP enantiomers at high CD concentrations (>6 mM), from which the

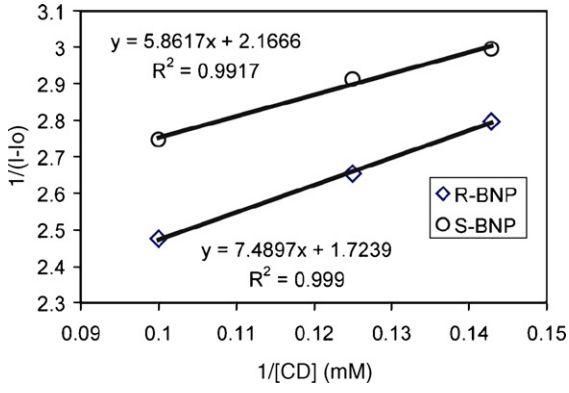

Fig. 9. Double reciprocal plot for BNP enantiomers at high CD concentrations.

Table 1
Thermodynamic and anisotropy data for BNP with CDs

Selector	[CD] (mM)	$\Delta\Delta H$	$\Delta\Delta S$	$\Delta\Delta G$	r_S/r_R
α-CD	42	−2.06 ± 0.24	−6.62 ± 0.8	−0.09 ± 0.34	1.029 ± 0.011
β-CD	1	−2.87 ± 0.18	−5.92 ± 0.62	−1.11 ± 0.26	1.560 ± 0.073
β-CD	11	0.79 ± 0.05	4.38 ± 0.13	−0.52 ± 0.08	1.240 ± 0.030
γ-CD	11	3.27 ± 0.18	11.96 ± 0.59	−0.29 ± 0.25	1.127 ± 0.025

corresponding association constants, K_R and K_S are determined ($K_R = 230.2\ M^{-1}$ and $K_S = 369.6\ M^{-1}$). The *S*-enantiomer exhibited a larger association constant, indicating preferential inclusion of *S*-BNP by β-CD. These results are consistent with the anisotropy measurements showing a larger anisotropy value for the *S*-BNP complex.

3.3. Temperature dependence of anisotropy and anisotropy ratio

From a fundamental perspective, both the anisotropy and anisotropy ratio are temperature dependent. The stability of an inclusion complex generally decreases with increasing temperature, but ultimately depends on the thermodynamics of the systems. Thus, the anisotropy typically decreases with increasing temperature due to an increase in the fraction of rapidly rotating free species, which is in addition to the increased rotational rate due to temperature dependent Brownian rotation. With regard to chiral recognition processes, the anisotropy ratio of the enantiomers may increase or decrease with increasing temperature, depending on the characteristics of the temperature dependence of the individual complexation processes involved.

Fig. 10A–C shows the anisotropy of the enantiomers of BNP with α-, β- and γ-CDs as a function of the reciprocal tem-

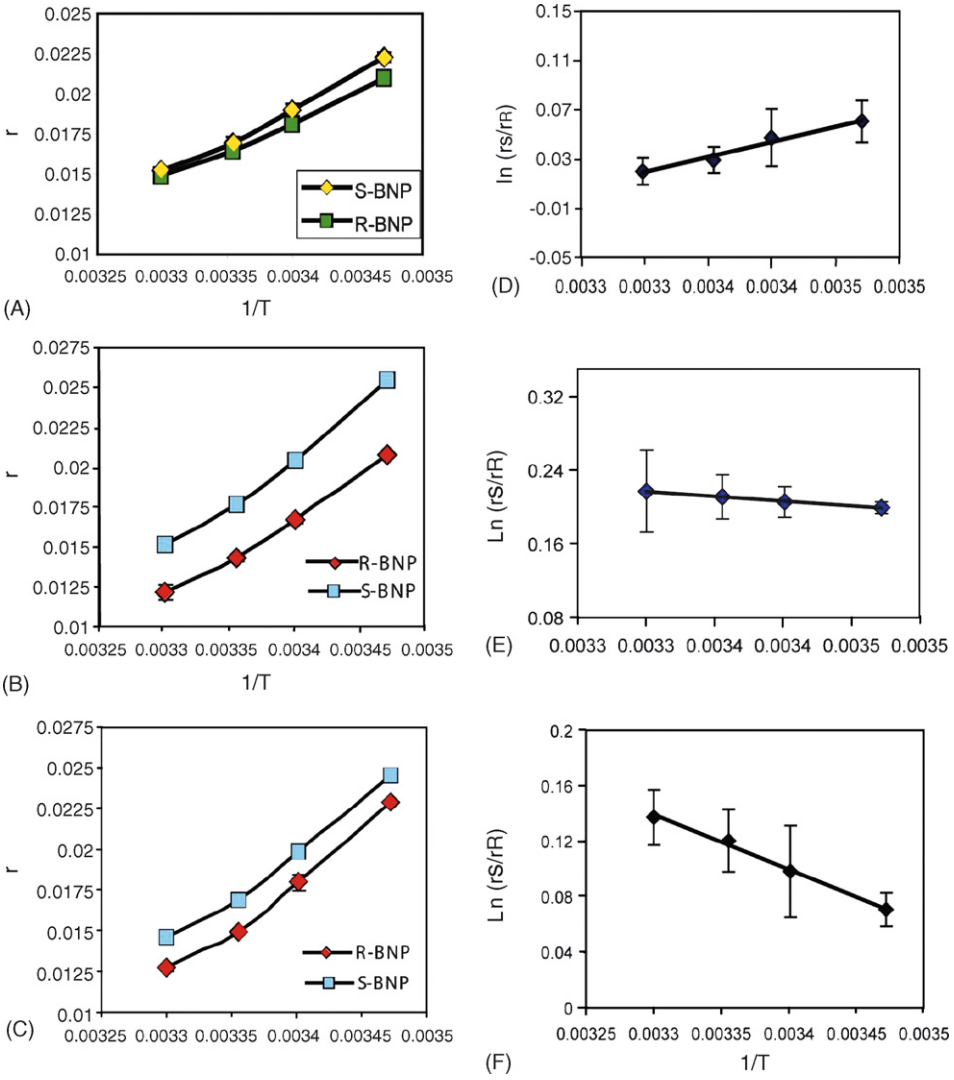

Fig. 10. Anisotropy (A–C) and anisotropy ratio (D–F) of the enantiomers of BNP with α-, β-, and γ-CD.

perature. The measured anisotropy decreases with increasing temperature for all three CDs, though the slopes and intercepts vary for the different CDs. Fig. 10D–F shows the natural logarithm of the anisotropy ratio for the data shown in A–C. For the BNP–β-CD and BNP–γ-CD systems the anisotropy ratio increases with increasing temperature, whereas it decreases with increasing temperature for α-CD complexes. Thus, a high degree of chiral recognition can be achieved at a higher temperature for β and γ-CD, while better enantiodiscrimination occurs at a lower temperature for α-CD.

As discussed in Section 2.3 and demonstrated previously [32], the temperature dependence of the anisotropy ratio can be used to evaluate the thermodynamics of the chiral recognition processes. The corresponding thermodynamic properties, $\Delta\Delta H_{R,S}$ and $\Delta\Delta S_{R,S}$, can be estimated from the slopes and intercepts of the temperature-dependent plots. Table 1 shows the anisotropy and thermodynamic parameters determined from the resulting plots for different CD complexes. The differential free energy changes, $\Delta\Delta G_{R,S}$, were calculated from the estimated $\Delta\Delta H_{R,S}$ and $\Delta\Delta S_{R,S}$. A negative slope and a positive intercept are observed in the cases of β- and γ-CD complexes, whereas a positive slope and a negative intercept are obtained for α-CD complexes. These results indicate a less favored (positive) enthalpy change and more favored (more positive) entropy changes with β- and γ-CD while more favored (more negative) enthalpy change and less favored entropy change for α-CD complexes. These indicate an enthalpically dominant process for chiral recognition by α-CD but an entropical-driven process by β- and γ-CDs. This result is agreement with the thermodynamic parameters reported by Kano et al. [38] that detailed a positive differential enthalpy change and positive differential entropy change for the formation of the β-CD–BNP complex. Hence, the chiral recognition process becomes more entropically dominant for the BNP–CD system in the order of α-, β- and γ-CDs. A possible explanation is an increase in the motional freedom of the analyte in the cavities of CDs. However, the extent of chiral recognition depends on differential free energy change that is a sum of contributions of differential enthalpy and entropy changes involved. Inspection of Table 1 shows the largest differential free energy change (absolute value) increases in an order of α-, γ- and β-CDs, which is in agreement with the anisotropy data. Although the γ-CD complex shows a larger enthalpy and entropy changes than that of β-CD, the differential free energy change is comparatively small due to the enthalpy and entropy compensation. The BNP–α-CD complex shows a small free energy change, which likely results from the much weaker host–guest interactions of this system.

Fig. 11 shows the plots of the natural logarithm of the anisotropy ratio of BNP in the presence of β-CD and as a function of reciprocal temperature at two different CD concentrations (1 and 11 mM). Very interestingly, opposite trends were observed at the two CD concentrations. The plot obtained at a low CD concentration displays a positive slope and negative intercept while it shows a negative slope and positive intercept at a high CD concentration. The thermodynamic parameters estimated from the resulting plots (Table 1) suggest an enthalpically dominant process at a low CD concentration but an entropically dominant process at a high CD concentration. This is consistent with the results obtained from the studies of fluorescence emission spectra and the anisotropy measurements discussed before, which revealed distinct behaviors of BNP–β-CD complexes at different CD concentrations. This result is also in agreement with results obtained in capillary electrophoresis studies (data not shown).

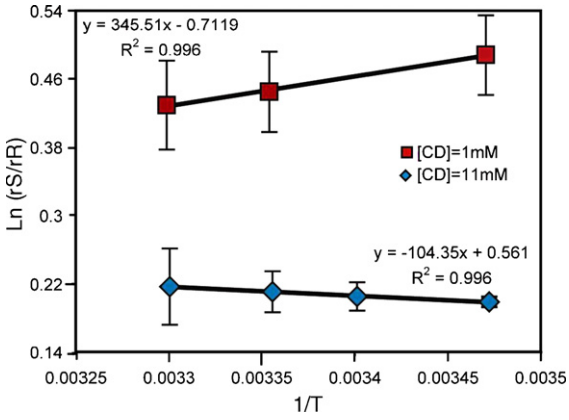

Fig. 11. Temperature dependence of BNP and β-CD at CD concentrations of 1 and 11 mM.

4. Summary

A comparative study of the complexation and chiral recognition behavior toward BNP was conducted by combination of fluorescence anisotropy and fluorescence spectral measurements using native α-, β- and γ-CDs as chiral selectors. The blue-shifts and intensity enhancement in fluorescence emission that were observed in the cases of β- and γ-CD can be attributed to the formation of inclusion complexes. The observed spectral shifts differ for *R*- and *S*-enantiomers, allowing spectral investigation of enantiodiscrimination between *R*- and *S*-BNP. However, spectral shifts were not detected for the α-CD system. Using the technique of fluorescence anisotropy, however, all three CD systems could be examined and were found to exhibit differential anisotropy values. Of three systems examined, β-CD showed the largest chiral recognition to BNP while α-CD exhibited the smallest. In the cases of β- and γ-CD, both the anisotropy ratio and the fluorescence spectral shifts were found to be significantly dependent on CD concentrations. Specifically, the double reciprocal plots showed differing trends at different CD concentrations. Anisotropy ratio was also found to vary significantly with CD concentration. The highest anisotropy ratio is found at a lower CD concentration for β- and γ-CD, indicating that the chiral recognition of BNP with β-CD is governed by different mechanisms at varying CD concentrations. The thermodynamic parameters estimated from anisotropy data suggested that chiral recognition of BNP with β-CD is enthalpically dominant at a low CD concentration while it is an entropically dominant process at a high CD concentration. In the case of α-CD, the chiral discrimination appears to be driven by enthalpic considerations at all concentrations.

References

[1] N.M. Maier, P. Franco, W. Lindner, J. Chromatogr. A 906 (2001) 3–33.
[2] S.C. Stinson, Chiral chemistry, Chem. Eng. News 79 (2001) 45–56.
[3] Y. Liu, Y. Zhang, S. Sun, Y. Li, C. R, J. Chem. Soc., Perkin Trans. 2 (1997) 1275–1278.
[4] M. Rekharsky, Y.J. Inoue, Am. Chem. Soc. 122 (2000) 4418–4435.
[5] T. Kurtan, N. Nesnas, F.E. Koehn, Y.Q. Li, K. Nakanishi, N. Berova, J. Am. Chem. Soc. 123 (2001) 5974–5982.
[6] J.L. Clark, J.J. Stezowski, J. Am. Chem. Soc. 123 (2001) 9880–9888.
[7] J. Horsky, J.J. Pitha, J. Inclusion Phenom. Mol. Recognit. Chem. 18 (1994) 291–300.
[8] K.B. Lipkowitz, S. Raghothama, J. Yang, J. Am. Chem. Soc. 114 (1992) 1554–1562.
[9] M. Maletic, H. Wennemers, D.Q. McDonald, R. Breslow, W.C. Still, Angew. Chem. Int. Ed. 35 (1996) 1490–1492 (in English).
[10] J.Z. Zhang, Acc. Chem. Res. 30 (1997) 424.
[11] D.W. Armstrong, T.J. Ward, R.D. Armstrong, T.E. Beesley, Science 232 (1986) 1132–1135.
[12] W.H. Pirkle, P.G. Murray, J. Org. Chem. 61 (1996) 4769–4774.
[13] T. Fornstedt, G. Gotmar, M. Anderson, G. Guiochen, J. Am. Chem. Soc. 121 (1999) 1164–1674.
[14] E. Yashima, C. Yamamoto, Y. Okamoto, J. Am. Chem. Soc. 118 (1996) 4036–4048.
[15] K. Kano, J. Phys. Org. Chem. 10 (1997) 286–291.
[16] M. Lammerhofer, E.C. Peters, C. Yu, F. Svec, J.M.J. Frechet, W. Lindner, Anal. Chem. 72 (2000) 4614–4622.
[17] H.H. Yarabe, S. Shamsi, I.M. Warner, Anal. Chem. 71 (1999) 3992–3999.
[18] B. Chankveltadze, Capillary Electrophoresis in Chiral Analysis, John Wiley & Sons, West Sussex, U.K., 1997, pp. 141–222.
[19] T.D. James, K. S, S. Shinkai, Nature 374 (1995) 345–347.
[20] R. Corradini, G. Sartor, A.R. Marchelli, A. Spisni, J. Chem. Soc., Perkin Trans. 2 (1992) 1979–1983.
[21] A.R. Al Rabaa, F. Tfibel, F. Merola, P. Pernot, M. Fontaine-Aupart, J. Chem. Soc., Perkin Trans. 2 (1999) 341–352.
[22] J. Lin, Q.-S. Hu, M.-H. Xu, L. Pu, J. Am. Chem. Soc. 124 (2002) 2088–2089.
[23] U. Pischel, S. Abad, M. Miranda, Chem. Commun. 9 (2003) 1088–1089.
[24] M.-H. Xu, J. Lin, Q.-S. Hu, L. Pu, J. Am. Chem. Soc. 124 (2002) 14239–14246.
[25] T.J. Liu, Y.J. Chen, K.S. Zhang, D. Wang, D.W. Guo, X.Z. Yang, Chirality 13 (2001) 595–600.
[26] G. Beer, J. Daub, K. Rurack, Chem. Commun. (Cambridge, United Kingdom) (2001) 1138–1139.
[27] Y. Abe, T. Shoji, M. Matsubara, M. Yoshida, S. Sugata, K. Iwata, H. Suzuki, Chirality 12 (2000) 565–567.
[28] S. Pagliari, R. Corradini, G. Galaverna, S. Sforza, A. Dossena, R. Marchelli, Tetrahedron Lett. 41 (2000) 3691–3695.
[29] E. Alvarez-Parrilla, P. Ramos Cabrer, L. de la Rosa, W. Al-Soufi, F. Meijide, V. Tato, J. Supramol. Chem. 15 (2003) 207–211.
[30] M.E. McCarroll, F. Haddadian, I.M. Warner, J. Am. Chem. Soc. 123 (2001) 3173–3174.
[31] Y. Xu, M.E. McCarroll, J. Phys. Chem. A 108 (2004) 6929–6932.
[32] Y. Xu, M.E. McCarroll, J. Phys. Chem. B 109 (2005) 8144–8152.
[33] I.W. Kimaru, Y. Xu, M.E. McCarroll, Anal. Chem. 78 (2006) 8485–8490.
[34] Y. Xu, M.E. McCarroll, J. Photochem. Photobiol. A: Chem. 178 (2006) 50–56.
[35] M.E. McCarroll, I.W. Kimaru, Y. Xu, Evaluation of chiral recognition in cyclodextrins using fluorescence anisotropy, in: A. Douhal (Ed.), Cyclodextrin Materials Photochemistry, Photophysics and Photobiology, Elsevier, Oxford, 2006.
[36] J.R. Lakowicz, Principles of Fluorescence Spectroscopy, second ed., Kluwer, 1999.
[37] E. von Lippert, Electrochemistry 61 (1957) 962–975.
[38] K. Kano, Y. Kato, M. Kodera, J. Chem. Soc., Perkin Trans. 2 (1996) 1211–1217.