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BINDING OF A NON-IONIC AZO DYE BY SODIUM SALT OF β -NAPHTHALENESULFONIC ACID-FORMALDEHYDE CONDENSATES. – EFFECT OF THE DEGREE OF THE CONDENSATION ON THE BINDING EQUILIBRIUM

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Abstract

The binding of a model azo disperse dye by β -naphthalenesulfonic acid and formaldehyde condensates (β NSF) in water was discussed. The binding constants, K , for the binding by β NSF with different degrees of condensation, $N = 2, 3, 4, 5, 7.2, 12$ and 40 were determined spectrophotometrically. The thermodynamic parameters, the enthalpy change, ΔH° and the entropy change, ΔS° calculated from the values of K in the temperature range $15-40^\circ\text{C}$ revealed following facts.

The value of K increases with N up to $N \approx 10$ and then level off gradually. This is ascribed to an increase in ΔS° with N ; the value is negative for β NSF with $N = 2, 3$ and 4 but it becomes positive for β NSF with $N = 12, 40$ under the low concentration of added salts. The value of ΔH° is negative irrespective of N but its absolute value decreases with the increase in N .

The increase in the concentration of added salts gives no appreciable change in the thermodynamic parameters for β NSF with $N = 3$ but for β NSF with $N = 12$ and 40 , the increase gives significant changes in the parameters; both values of ΔH° and ΔS° decrease significantly. These results may be explained in terms of the conformational change of polyelectrolytes. β NSF with $N = 12$ and 40 behave as a typical polyelectrolyte; their conformation varies from an expanded form to a compact one on addition of electrolytes. The extended conformation is favorable for the hydrophobic interaction between the linear dye and successive naphthalene nuclei of β NSF with a high degree of the condensation. The increase in the value of ΔS° with N may be explained in terms of the contribution of the hydrophobic bonding to the binding.

1. Introduction

The sodium salt of β -naphthalenesulfonic acid and formaldehyde condensates (abbreviated as β NSF) has been used as a dispersing agent in the production and use of disperse and vat dyes¹⁾. Hattori and co-workers have studied the structure and properties of β NSF in detail²⁻⁴⁾. They reported that 1) the most probable structure of β NSF is represented by [I]²⁾ and commercial products are a mixture of the condensates with $N = 2-9$ ^{3,5)}. 2) the dispersing power of β NSF for fine powders of zinc white and a vat dye increases with N up to $N = 9$ and 5 ⁴⁾ and 3) the condensates with $N > 5$ behave as a polyelectrolyte

in water⁴⁾. Valko pointed out that the polymeric structure is preferable as a dispersing agent⁶⁾.

We have already studied the interaction between β NSF ($N = 12$) and some disperse dyes in water through the measurements of the binding constants and discussed the binding equilibrium in terms of the thermodynamic parameters⁷⁾. In this paper, the effect of the degree of condensation of β NSF on the binding constant of a model azo disperse

dye will be discussed on the thermodynamic parameters of the binding.

2. Experimentals

2.1 Materials

The dye used (Dye 1) [II] was prepared by diazotizing aniline and coupling with *N,N*-Di(2-hydroxyethyl)toluidine, followed by purification by repeated recrystallizations from water; m.p. = 111–112°C, $pK_a = 3.53$ (25°C).

β NSF ($N=1$ –ca.12) was prepared by the reaction of one mole of β -naphthalenesulfonic acid (β NSA) and 0.8 mole of formaldehyde (FA) as reported by Hattori and Tanino³⁾. β NSF ($N=1$ –ca.40) was prepared similarly from equimolar amounts of β NSA and FA. By means of fractional precipitation*, the condensates were fractionated into five divisions, i.e., $N=1$ –3, $N=3$ –5, $N=6$ –8, $N=12$ ($N>9$) and $N=40$ ($N>9$). For the fractions with $N>9$, the average value of N was estimated from the viscometric measurements⁴⁾ and for the fractions with $N<9$, the values of N were determined from the TLC tests on micro crystalline cellulose powder (Tokyo Kasei Co.) by using a mixture of *n*-butanol, acetic acid and water (4:1:2 in volume) as solvent. Each spot on the plate was detected by spraying aqueous solution of C.I. Basic Red 13.

Monodisperse β NSF samples with $N=1$ –5 were isolated from the fraction including $N=1$, 2 and 3 and that including $N=3$, 4 and 5, by means of the column chromatography on cellulose powder; the eluent used were water saturated butanol for the former fraction, and a mixture of butanol, water and acetic acid (6:2:1 in volume) for the later. The effluent from the outlet of the column was passed in a flow cell in a photometer and the concentration of β NSF isolated in the effluent was detected by the UV absorption at 325 nm.

2.2 Measurements and Calculations

Absorption spectra were recorded on a Simadzu MPL-50L spectrophotometer equipped with a

thermostated housing; the temperature of the solution in the cell (path length = 1 cm) was controlled at 16.0, 20.0, 25.0, 30.0 and 35 $\pm$ 0.1°C.

Viscosities were measured by using two Ubbelohde type viscometers with flow times for water of 157 and 250 s, respectively; the temperature was controlled at 25 $\pm$ 0.02°C.

Calculations were made on an NEC PC-9801 VMO personal computer using relevant calculation programs.

3. Results and Discussion

Figs. 1 and 2 show the change in the absorption spectrum of Dye 1 in aqueous solution by the addition of β NSF with $N=2$ and 12, respectively. As seen in each figure, the absorption peak at 453 nm decreases and the absorption at about 550 nm increases as the concentration of β NSF is increased. Similar spectral changes were also observed for β NSF with different N . The absorption curves obtained for a series of measurements for the dye - β NSF systems passed through an isosbestic point as exemplified by the curves in Figs. 1 and 2; the point tends to shift to longer wavelength with N of β NSF. These findings

Fig. 1 Change in the absorption spectrum of Dye 1 as a function of the concentration of β NSF with $N=2$ at 20°C, pH=5.58 (0.02 mol/l acetate buffer).

Concentration of Dye 1: 4.00×10^{-5} mol/l
 Concentration of β NSF with $N=1$ (base mol/l)
 — : 0, — : 1.0×10^{-2} ,
 — : 2.0×10^{-2} , — : 3.0×10^{-2} ,
 and — : 4.0×10^{-2}

* The solubility of β NSF in water increases with the increase in N , whereas that in ethanol decreases with the increase in N .

Fig. 2 Change in the absorption spectrum of Dye 1 as a function of the concentration of β NSF with $N=12$ at 20°C , $\text{pH}=5.58$ (0.02 mol/l acetate buffer).

Concentration of Dye 1: 4.00×10^{-5} mol/l
 Concentration of β NSF with $N=12$ (base mol/l)
 —: 0, —: 4.0×10^{-5} ,
 —: 8.0×10^{-5} , —: 12.0×10^{-5} ,
 and —: 16.0×10^{-5}

indicate that the spectral changes shown in Figs. 1 and 2 are a result of the binding of Dye 1 by β NSF. Here we express the binding equilibrium by Eqs. 1 and 2.

$$K = \frac{x}{(a-x)(nP-x)} \quad (2)$$

where, K is the binding constant, n is the number of binding site in monomeric unit of β NSF (it was found that $n=1$ for Dye 1⁷⁾, P is the concentration of β NSF (monomeric unit basis), a is the initial concentration of dye and x is the concentration of bound dye.

By assigning ϵ_b , ϵ_f and ϵ_{app} as molar absorptivities of bound dye, free dye and apparent molar absorptivity of dye solution in the presence of β NSF at a wavelength of λ , where the value of ϵ_{app} is increased greatly by the binding. Eq. 2 is rewritten into Eq. 3 as,

$$\epsilon_{\text{app}} = - \frac{(\epsilon_{\text{app}} - \epsilon_f)(\epsilon_b - \epsilon_f)}{nP(\epsilon_b - \epsilon_f) - a(\epsilon_{\text{app}} - \epsilon_f)} \cdot \frac{1}{K} + \epsilon_b \quad (3)$$

Eq. 3 indicates that the plot of ϵ_{app} against $(\epsilon_{\text{app}} - \epsilon_f)(\epsilon_b - \epsilon_f) / \{nP(\epsilon_b - \epsilon_f) - a(\epsilon_{\text{app}} - \epsilon_f)\}$ gives a straight line with the slope, $-1/K$, and the intercept, ϵ_b . ϵ_b , ϵ_f and ϵ_{app} are determined experimentally. Starting with an approximate value of ϵ_b , close values of $-1/K$ and ϵ_b are determined by the iterative method.

Fig. 3 shows examples of the plots of Eq. 3 converged to the limiting values. Each plot falls on a straight line over the concentration ranges of β NSF used. The values of K were evaluated by means of the least square method. The binding constants for β NSF with various N at 15 – 40°C were determined from the similar plots.

Table 1 shows the effect of the degree of condensation on the thermodynamic parameters of the binding; the enthalpy change, ΔH° , and the entropy change, ΔS° , were calculated using the standard thermodynamic relations. The numerical values given in Table 1 indicate that the binding occurs mainly by the contribution of the negative enthalpy term, but this contribution decreases with N . On the other hand, the entropy term gives negative contribution for the binding by β NSF with $N < 5$ but the value of ΔS° increases with N and becomes to give a positive contribution to the binding for β NSF with $N > 7$. Fig. 4 indi-

Fig. 3 Plots of Eq. 3 for the binding of Dye 1 by fractionated β NSF.

Degree of condensation of β NSF (N) and the wavelength used for the plots

—○—: $N=4$ ($\lambda=545 \text{ nm}$), —○—: $N=5$ ($\lambda=545 \text{ nm}$) and —●—: $N=12$ ($\lambda=550 \text{ nm}$)

Concentration of Dye 1: 4.0×10^{-5} mol/l

Temperature = 20.0°C , $\text{pH}=5.58$ (0.02 mol/l acetate buffer)

Table 1 Effect of the degree of condensation of β NSF (N) on the thermodynamics of the binding of Dye 1 by β NSF

<i>N</i>	pH (25 °C)	Temp. (°C)	$K \times 10^{-2} *$	ΔH° (kcal/mol)	ΔS° (e. u.)
2	5.58	15.0	2.64	-6.66	-12.0
		20.0	2.16		
		25.0	1.82		
		30.0	1.48		
3		15.0	25.3	-6.53	-7.10
		20.0	20.9		
		25.0	17.1		
		30.0	14.4		
4		15.0	123	-6.56	-4.02
		20.0	106		
		25.0	82.2		
		30.0	71.7		
5		15.0	277	-6.19	-1.23
		20.0	239		
		25.0	189		
		30.0	166		
7.2**		15.0	712	-5.73	2.28
		20.0	589		
		25.0	503		
		30.0	433		
12		15.0	1530	-4.36	8.62
		20.0	1340		
		25.0	1230		
		30.0	1060		
		35.0	929		
40	5.50	15.0	3190	-4.54	9.09
		20.0	2790		
		25.0	2400		
		30.0	2170		
		35.0	1970		

* The binding constants were determined in the presence of 0.02 mol/l acetate buffer and calculated on mole fraction basis.

** Consists of a large amount of β NSF with $N=7$ and small amounts of β NSF with $N=6$ and 8.

Fig. 4 Relation between the binding constant, K , and the degree of condensation of β NSF, N , for Dye 1 at 25°C, pH=5.58 (0.02 mol/l of acetate buffer).

ates that the value of K increases rapidly with N up to about $N=10$ and then approaches a levels off value gradually. A similar change in binding constant with N has been found for the binding of Congo Red (C. I. Direct Red 28) by amylose and amyloextrines⁸.

It has been reported that the dispersing power of β NSF increases with N up to $N=5-9$ ⁴. It is worthwhile to note here that both the dispersing power and the binding constant increase with N up to $N=ca.10$. As shown in Table 1, the later is attributed to increase in ΔS° .

Figs. 1 and 2 show that the appearance of a new absorption band at about 550 nm on the binding. This suggests the following binding mechanism⁷.

According to the scheme described above, a part of the fixed charges on β NSF are neutralized by the binding. The mechanism of the binding will be discussed in detail in a subsequent paper.

Fig. 5 shows the reduced viscosities of β NSF with $N=40$ dissolved in water, β NSF with $N=40$ behaves as a flexible chain polyions. In the absence of added salts, η_{sp}/C increases rapidly on dilution of the solution. A similar change in the viscosity was also observed for β NSF with $N=12$. These facts are explained as a result of the expansion of the polyion chains caused by the increase in the electrostatic repulsion between the fixed charges on the polyions due to the decrease in ionic strength of the solution on the dilution.

Fig. 5 Effect of electrolyte concentration on the reduced viscosity of β NSF with $N=40$ in water at 25°C .

Concentration of the added electrolytes

- : 0,
- : 0.005 mol/l acetate buffer (pH=5.50),
- : 0.02 mol/l acetate buffer (pH=5.50) and
- : 0.05 mol/l sodium chloride

C : concentration of β NSF (g/100ml water),

η_{sp}/C : reduced viscosity (ml/g)

The repulsive power is reduced by addition of electrolytes due to their shielding effect for the fixed charges; the conformation of the polyion varies from an expanded form to a compact one when the concentration of the added salt is increased. Therefore, the limiting value of η_{sp}/C decreases rapidly on addition of electrolytes.

If a part of the fixed charges on β NSF is neutralized on the binding and lose their charge as expressed by Eq. 5, the polyion chain conformation becomes more random. This may contribute to increase in ΔS° of the system, particularly for β NSF with large N such as $N=12$ or 40.

At the moment, three possible reasons may be cited for the increase in ΔS° on the dye binding with N ;

i) release of the electrostricted water molecules in the vicinity of the charged group, ii) an increase in the randomness of the polyion chain conformation and iii) hydrophobic bonding, the release of water molecules from their ordered structure in the vicinity of hydrophobic parts of the dye and β NSF.

The reason i) may be unable to explain the increase in ΔS° with N since it seems to be independent of N .

If a part of the fixed charge on β NSF is neutralized on the binding, the conformation of β NSF varies from an expanded form to a more compact one. This results in the decrease in η_{sp}/C of the β NSF in water; the viscosity of β NSF with $N=40$ dissolved in aqueous solution of Dye 1 should be lower than that in water. However, no appreciable differences between the viscosities of β NSF with $N=40$ dissolved in water and that in the dye solutions were observed at 25.0°C ; the concentration of Dye 1 was 1.00×10^{-4} mol/l (in the absence of electrolytes) and 4.00×10^{-5} mol/l (in the presence of 0.005 and 0.02 mol/l of acetate buffer, pH=5.50), respectively. The binding constants given in Table 1 were determined using $a=4.00 \times 10^{-4}$ mol/l and $P=4-20 \times 10^{-4}$ base mol/l in the presence of acetate buffer (pH=5.50). Under this conditions, the number of bound dye per monomeric unit of β NSF with $N=40$ is calculated to be 0.12–0.08 at 25°C . However, in the presence of acetate buffer, which is required for the reproducible measurement of the binding constant, the conformation of β NSF with $N=40$ is already in a fairly compact form as shown in Fig. 5. Consequently, it seems that the further increase in the flexibility of the polyion chain on the binding is small.

Under the conditions of the viscosity measurements, the number of bound dye per monomeric unit of β NSF with $N=40$ is estimated to be only 0.017 at the most, e.g. at $C=0.05\text{g}/100\text{ ml}$ (2.064×10^{-3} base mol/l) with $K=3930\text{ l/mol}^{**}$. Consequently, it seems that the reason ii) gives a small contribution to the increase in ΔS° with N shown in Table 1.

As is well known, Congo Red is a typical planar and linear dye. The binding constant of Congo Red with amylose and amyloextrins increases with their chain length⁸⁾ in spite of their helical structure in water⁹⁾. Giles has pointed out that the affinity of planar azo dyes and leuco vat dyes to regenerated cellulose increase linearly with log (molecular conjugated chain length of dyes)¹⁰⁾.

Dye 1 molecule is linear and the two benzen

** The value determined in the presence of 0.02 mol/l acetate buffer of pH=5.50.

rings are coplanar, so that the contribution of hydrophobic interaction between Dye 1 and β NSF to the binding will become greater when a number of naphthalene nuclei of β NSF lie successively linear as shown in Fig. 6. It seems that the main

reason for the increase in ΔS° with N is attributable to reason iii); the increase in ΔS° with N may be explained in terms of hydrophobic bonding.

Table 2 shows the effect of added salts on the thermodynamic parameters of the dye binding by

Table 2 Effect of electrolytes on the thermodynamics of the binding of Dye 1 by β NSF

<i>N</i>	Concentration of Electrolyte	pH (25°C)	Temp. (°C)	$K \times 10^{-3} *$	ΔH° (kcal/mol)	ΔS° (e. u.)
3	0.02 mol/l acetate buffer	5.58	15.0	2.53	-6.53	-7.10
			20.0	2.09		
			25.0	1.71		
			30.0	1.44		
	0.1 mol/l acetate buffer	5.52	16.9	3.23	-6.79	-7.35
			20.0	2.83		
			25.0	2.35		
			30.0	1.96		
12	0.01 mol/l acetate buffer	5.59	15.0	172	-3.39	12.22
			20.0	160		
			25.0	144		
			30.0	135		
			35.0	115		
	0.02 mol/l acetate buffer	5.58	15.0	153	-4.36	8.62
			20.0	134		
			25.0	123		
			30.0	106		
			35.0	92.9		
	0.05 mol/l acetate buffer	5.56	15.0	167	-6.11	2.67
			20.0	131		
			25.0	121		
			30.0	95.3		
	0.1 mol/l acetate buffer	5.52	16.0	227	-9.68	-9.02
			20.0	167		
			25.0	140		
			30.0	98.8		
			35.0	97.2		
40	0.005 mol/l acetate buffer	5.50	20.0	249	-4.37	9.79
			25.0	218		
			30.0	193		
			35.0	172		
			40.0	153		
	0.005 mol/l acetate buffer + 0.01 N NaCl		16.0	263	-5.52	5.72
			20.0	227		
			25.0	201		
			30.0	171		
			35.0	144		
	0.005 mol/l acetate buffer + 0.02 N NaCl		16.0	264	-6.01	4.01
			20.0	233		
			25.0	186		
			30.0	162		
			35.0	140		
	0.005 mol/l acetate buffer + 0.04 N NaCl		16.0	312	-10.5	-11.2
			20.0	240		
			25.0	175		
			30.0	135		

* Calculated on mole fraction basis.

Fig. 6 An assumed conformation of β NSF with higher degree of condensation in an extended form.

The figure was drawn using the bond lengths C-C and C-H in naphthalene, 1.40 and 1.08 Å, and C-S and S-O in sulfonic acid, 1.78⁽¹¹⁾ and 1.45 Å⁽¹¹⁾, respectively.

β NSF with $N=3, 12$ and 40 , respectively. As described before, β NSF with $N=12$ and 40 behave as polyelectrolyte as shown in Fig. 5 but β NSF with $N=3$ does not so. For β NSF with $N=3$, the thermodynamic parameters of the dye binding were only slightly changed on increasing of the concentration of the added salts (acetate buffer). On the other hand, for β NSF with $N=12$ and 40 , the contribution of ΔH° to the binding increased but that of ΔS° decreased as the concentration of the added salt was increased. In the presence of the highest concentration of the added salt, the value of ΔS° became negative as in the case of the binding by β NSF with $N=2$ or 3 . This means

that when β NSF with higher N , $N=12-40$, is in a very compact conformation, the contribution of the hydrophobic bonding to the binding becomes very small as in the binding by β NSF with $N=2$ or 3 . The expanded conformation, where the successive naphthalene nuclei of β NSF with large N will lie as linear as possible, is favorable to the hydrophobic bonding.

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β ナフタレンスルホン酸ホルマリン縮合物ナトリウム塩に対する 非イオンアゾ色素の結合 — 結合平衡に対する縮合度の影響

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水に溶解したモデルアゾ分散染料 (Dye 1) と β -ナフタレンスルホン酸ホルマリン縮合物ナトリウム塩 (β NSF) との相互作用を高分子電解質に対する色素の結合平衡として取り扱い、結合平衡に対する β NSF の縮合度 (N) の影響を結合平衡の熱力学関数値から検討した。結合定数 (K) は $15-40^\circ\text{C}$ で分光法で測定した。 β NSF は合成品から $N=2, 3, 4, 5, 7.2, 12$ ($N>9$), 40 ($N>9$) の成分を分離して用いた。

K の値は $N\approx 10$ 迄は N の増加と共に急激に増加し、その後次第に頭打ちとなった。これは ΔS° の寄与による。 ΔS° の値は N と共に増加し、 $N=2, 3, 4$ では負であるが、

$N=12, 40$ では正となった。 ΔH° は $N=2-40$ まですべて負であったがその絶対値は N と共に減少した。これより、結合反応に対する Dye 1 と β NSF の疎水部分との間の相互作用の寄与が N の増加と共に増加して ΔS° が増加すると推論された。

$N=3, 12, 40$ の成分に対して結合反応に対する電解質添加の影響を調べた。 $N=3$ の成分では添加電解質濃度が増加しても結合反応の熱力学関数値は殆ど変化しないが $N=12, 40$ では、電解質濃度が増加すると ΔH° , ΔS° 共に減少する。特に ΔS° は正から負に変化する。これは $N=12, 40$ の成分が水中で高分子電解質として挙動する

特性から説明された。

電解質濃度の低いところでは β NSF ($N=12, 40$)の分子鎖は伸長したコンホメーションをとり、 β NSFのナフタレン核はなるべく直線状に並ぼうとするので細長い形をした Dye 1 と β NSF との間の疎水結合の形成には好都合となる。添加塩の濃度が高まると分子鎖はコンパク

トなコンホメーションとなり、疎水結合の形成には不利となるので ΔS° は減少する。 N の大きな β NSF ではナフタレン核がなるべく直線状に並ぶコンホメーションをとるとき結合反応に対する疎水結合の寄与が大きいと推論された。