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Full Length Research Paper

Binding pattern of ferrocyphen upon interaction with cetyltrimethyl ammonium bromide in the presence of urea

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Cetyltrimethylammonium bromide (CTABr) have been titrated against Ferrocyphen (Dicyano-bis-(1, 10-phenanthroline) iron II complex) in aqueous solution as a function of urea concentration which gave a sigmoidal binding isotherm. A simple method was introduced for resolution and characterization of binding set on the basis of binding capacity concept to give hill coefficient > 1.0. Hill coefficient greater than one are the experimental hall mark of cooperativity in which initial binding events render subsequent binding events more favorable. The degree of cooperativity is sensitive to the concentration of urea. The results are interpreted in terms of dielectric constant and decrease in the hydrophobic interaction between the complex (ferrocyphen) and the surfactant monomers.

Key word: Binding isotherm, surfactant, cooperativity, hydrophobic ferrocyphen, binding capacity.

INTRODUCTION

Allosteric interaction between recognition sites is a ubiquitous regulatory mechanism in biological macro-molecules, including enzyme (Fersht, 1985), receptor (Falke and Koshland, 1987) and ribosome's (Nierhaus et al., 1988). Micelles are thought to mimic the active site in enzyme (Ige et al., 2007) and when the active and effect-tors site are equivalent, the allostery is termed coopera-tivity for which enzymes is the typical examples (Russell et al., 1990; Monod et al. 1963; Eigen and Nobel, 1967; Rebek, 1984). The ability of micelles to alter the physic-chemical properties of solutes has been extensively used in both equilibrium (Rudoif et al., 1987; Hinze, 1979) and kinetic determination and different separation techniques (Okada, 1997; Corstjens, 1995). Cooperative binding of amphiphilic substances such as surfactants and dyes to macromolecules is a very import ant phenomenon used to study colloidal properties and initial denaturation stage of the macromolecules (Kiyofumi, 2007). Urea is known to moderate the aggregation of surfactant monomer (Ana et al., 2005; Shashank et al., 2001). The neutral bulky fer-rocyphen with significant hydrophobic character and Cetyltrimethyl ammonium bromide (CTABr) were spe-cially selected for their overall varying hydrophobicity (Ige et al., 2007). For biological system where similar hydro-phobic interactions are known, the formation of an hydro-phobic core is the driving force for protein folding. It is possible by choice of the appropriate proteins to ensure only hydrophobic interaction (Chad and Marcey, 2004). This type of selectivity in hydrophobic binding has a more direct correlation to micelle -substrate binding system. It is therefore of interest to see how the moderation of protein folding via hydrophobic and hydrogen bond breaking by urea is mimic in a simple surfactant system. In the pre-sent study, the interaction of Ferrocyphen with Cetyltri-methylammonium bromide in the presence of urea has been studied using spectrophotometry techniques (Housaindokht, 2001) . Replotting of the binding isotherm gives Hill coefficient (greater than) > 1 which is the hallmark of cooperativity.

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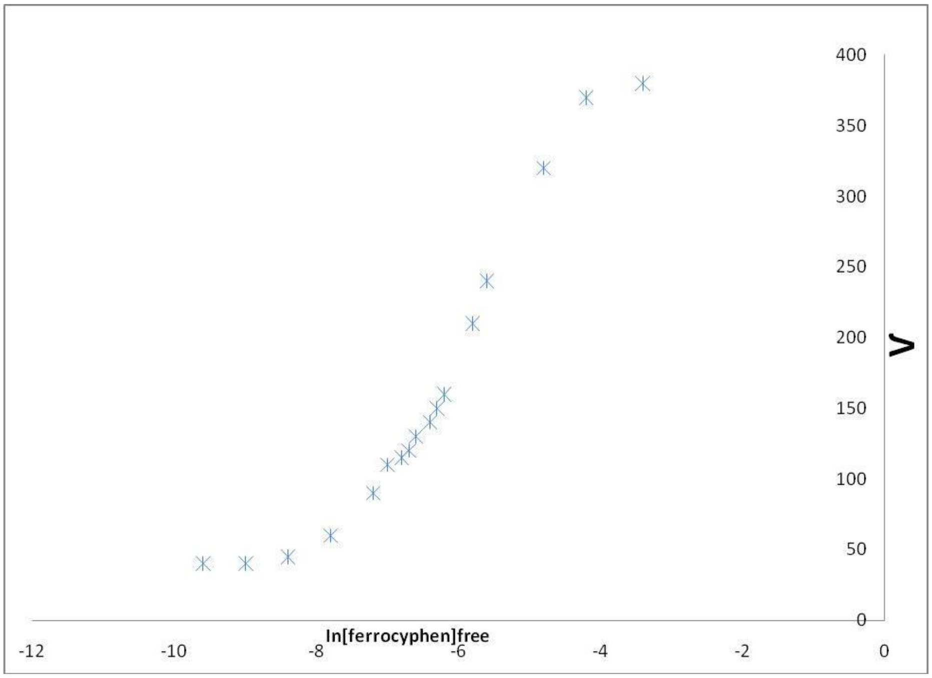

Figure 1. Binding isotherm of ferrocyphen interaction with CTABr in the presence of Urea at 25^{0} C.

EXPERIMENTAL

Materials

Cetyltrimethylammonium bromide (CTABr) was used as supplied without further purification. The degree of purity was ascertained by determining the critical micelle concentration (CMC) in aqueous medium at 25^{0}C. The value 9.1 x 10^{-4} moldm^{-3} was obtained which is in good agreement with the reported literature value (Peterson and Marzzacco, 2007).

1,10-phenanthroline, ferrous ammonium sulphate, urea and potassium cyanide were analytical grade (Sigma). Ferrocyphen was synthesized as reported in the literature (Alfred, 1960). The water used was glass distilled.

METHODS

The binding studies were carried out at a fixed temperature of 25.0 ± 0.1^{0}C. A wavelength scans of the complex in urea/ water/surfactant medium show no change in λ_{max} under the present experimental condition. Noticeable increase in absorbance was observed at fixed ferrocyphen and urea concentration with varying surfactant concentration. Fraction of the ferrocyphen bound was calculated from these changes in absorbance. All binding studies were carried out at surfactant concentration below the critical micelle concentration. The change in absorbance of the ferrocyphen was monitored using an - Heλios Pye-unicam double beam spectrophotometer fitted with a thermostable cell compartment. The absorbance was taken at 560 nm (the wavelength of maximum absorption) of Ferrocyphen in all the runs. The results were ana-lyzed using binding capacity concept.

Binding capacity is the homotropic second derivatives of the binding potential with respect to the chemical potential of the ligand (μ_s) and provides a measure of steepness of the binding isotherm Bordbar et al., 2004).

It represents the change in the number of moles of ligand per mole of macromolecule (ν) that accompanied a change in the chemical potential of that ligand.

RESULTS AND DISCUSSION

Figure 1 represent binding isotherm for a typical interact-tion of Ferrocyphen with Cetyltrimethyl ammonium bromide in the presence Urea and shows the variation of ν (average number of ferrocyphen bound to Cetyltrimethyl ammonium bromide molecule) versus In[ferrocyphen]$_{free}$ at specified experimental condition. The sigmoidal nature of this curve characterized cooperative binding (Cera et al., 1988).

The average number of ferrocyphen molecules bound to surfactant molecules has been calculated as,

$$\nu = \frac{[Ferrocyphen]_T - [ferrocyphen]_f}{[Surfactant]_T} \quad (1)$$

Where $[Surfactant]_T$ is the total concentration of surfactant. $[Ferrocyphen]_T$ and $[ferrocyphen]_f$ are the total and free concentration of ferrocyphen respectively. By considering the ideal behavior, binding capacity (θ) equal to

$$\theta = (\partial\nu/\partial\mu)_{T,P,\mu j\ l} = (\partial\nu/RT\partial In[L]_F)_{T,P,\mu j\ l} \quad (2)$$

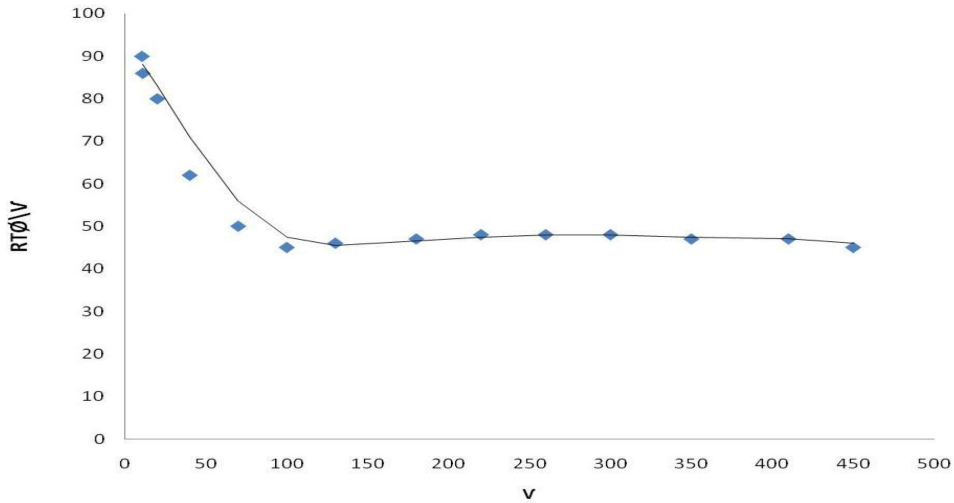

Figure 2. The plot of RTθ/ν versus ν for binding of ferrocyphen with CTABr in the presence of urea at 25^{0}c.

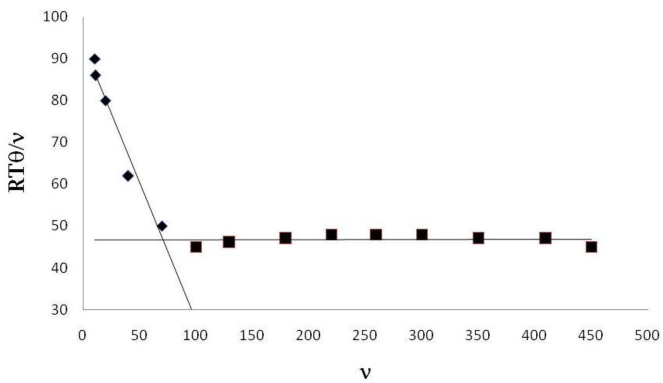

Figure 3. The plot of RTθ/ν versus ν for the interaction of ferrocyphen with CTABr at 25^{0}c in the presence of urea.

Where R, T and $[L]_F$ are gas constant, absolute temperature, and free concentration of Ferrocyphen[24]. However binding capacity can be estimated by calculating the steepness of the binding isotherm. This concept is directly related to the type and extent of cooperativity as expected by Hill coefficient, n_{HI} (Reza and Ramin, 2007). The value of θ at any ν can be determined by calculating the slope of the binding isotherm. The relationship between binding capacity θ, and Hill coefficient n_{Hi} can be obtain by assuming a particular definition for n_{Hi}.

The Hill coefficient is defined as the slope of Hill graph,

$$n_H = d\ln\left(\frac{y}{1-y}\right)/d\ln[l]_f = \frac{\left(\frac{1}{y(1-y)}\right)dy}{d\ln[l]_f} \quad (3)$$

Where y is the fractional saturation of the macromolecule by the ligand which is defined as follows.

$$y = \nu/g \quad (4)$$

From the definition of binding capacity, (i.e equation 1) the following equation can be written

$$n_H = RT\theta/gy(1-y) \quad (5)$$

$$\theta = n_H\nu(1-y)/RT \quad (6)$$

Equation (6) can be rearranged to the following form

$$RT\theta/\nu = n_H - n_H\nu/g \quad (7)$$

This equation suggests that the plot of $RT\theta/\nu_i$ versus ν_i for a system with g identical and independent sets, should be linear. The slope and the Y and X-Intercepts are equal to $-n_H/g$ n_H and g respectively. Where g_i and n_{Hi} are the number of binding sites and Hill coefficient for ith binding set respectively.

Figure 2 shows the variation of RTθ vs ν for binding of Ferrocyphen to Cethyltrimethyl ammonium bromide. For a system with relatively high difference in binding affinity of sets, every set behave independently, and so in which it can be assume ith the ith binding set has not been occupied until the full occupation of (i-1)th binding set has been occurred, for such system the curve of RTθ /ν vs ν can be divided into N-consecutive linear part, corresponding to N binding sets. For evaluation of this assumption, the typical plot of $RT\theta/\nu_i$ VS ν have been constructed for binding of Ferrocyphen to Cethyltrimethyl ammonium bromide at different experimental condition (Figure 3). Knowing n_{Hi} and g_i, the Hill plot were constructed for the estimation of Hill binding constant K_i by plotting $\ln(\nu_i/g-\nu_i)$ against In[Ferrocyphen] $_{free/moldm3}$.

Table 1. The collective values of Hill parameters for interaction of ferrocyphen with CTABr at 25^{0}C

[Urea]M	n_{H1}	g_1	$K_1(M^{-1})x10^4$	$\Delta G^1_{b,\nu}$ x 10^3	n_{H2}	g_2	$K_2(M^{-1})x10^4$	$\Delta G^2_{b,\nu}$ x10^3
0	16.73	181.07	11.50	-9.14	3.22	417.03	12.17	-18.12
4.0	41.31	203.11	10.17	-8.04	38.31	420.13	11.51	-22.14
5.0	51.02	213.01	9.88	-23.50	45.71	422.05	15.01	-35.40
6.0	20.78	114.16	27.88	-7.13	16.56	98.45	37.33	-10.23
8.0	13.01	93.67	34.98	-7.11	10.25	64.92	52.71	-6.01

Figure 3 shows the Hill plots for interaction of Ferrocyphen with Cethyltrimethyl ammonium bromide in the present of urea at 25^{o}C presence of urea. The intrinsic Gibbs free energy of binding per mole of ferrocyphen for ith binding set, $\Delta G^{(i)}_{b,\nu}$, can be calculated by the following equation (Bordbar et al., 1997)

$$\Delta G^{(i)}_{b,\nu} = -RTn_H \ln K_i + RT(1-n_{Hi})\ln[\text{Ferrocyphen}]_F \qquad (8)$$

Conclusion

There are at least two binding set in this system. The process shows positive cooperativity in both binding sets (n_{Hi}> 1) for all the studied condition (Table 1) . At low Urea concentration, local dielectric constant increases (Marilyn and Alfred, 1967).

It is suggested in the present work that this will necessary accompanied by enhancement of pre-micelle formations and a subsequent increase in n_{Hi} and g_i as well as decrease in binding constant. Above a critical concentration of 6.0 M of Urea, dielectric constant has no predominant effect (reduced). Increase in the concentration of urea clearly diminished the hydrophobic interaction between Ferrocyphen and the surfactant monomers by aggregating via hydrogen bonding to itself and water molecule creating cavities of various sizes where some Ferrocyphen molecule are trapped and increasing the solubility of monomers, therefore delaying the onset for pre-micelle formation leading to decrease in n_{Hi} and g_i value but increase in binding constant. Overall, the evidence presented supports the direct interaction mechanism of urea and further demonstrate how the properties of surfactant aggregate can be moderated with the use of an inert additive such as urea.

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