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Full Length Research Paper

Binding data analysis for the interaction of ferrocyphen with sodium dodecylsulfate in the presence of sodium benzoate

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The binding of ferrocyphen [Fe($C_{12}H_8N_2$)$(CN)_2$] with sodium dodecylsulfate has been studied at various concentration of sodium dodecylsulfate as a function of aromatic counter ion (sodium benzoate) concentration. The unusual scatchard plot has been interpreted using binding capacity concept. The results represents two binding set for all the studied conditions. The value of Hill equation parameter have been estimated and used for calculation of intrinsic Gibbs free energy of binding.

Key words: Surfactant, ferrocyphen, ion- pair, counter ion, capacity concept.

INTRODUCTION

It is important to study the interaction of small ions and molecules, with macromolecules in order to understand the nature of transportation and distribution of these species in biological system because such interactions play a prominent role in transportation and distribution processes. In fact, most of biological functions have binding as a primary process. Binding of drugs, hormones, inhibitors etc. on to macromolecules has been widely studied (Karsten, 1997).

Ferrocyphen (dicyano-bis- 1, 10 -phenanthroline) iron II dihydrates with significant hydrophobic character and SDS were especially selected because for their hydrophobic nature (Ige et al., 2007). Ferrocyphen [Fe ($C_{12}H_8N_2$) $(CN)_2$] is neutral and significantly hydrophobic complex which might easily participate in co-micellization or strong solubilization by surfactant aggregate in suitable solvent (Oladega et al., 2007). In acidic medium ferrocyphen is known to be protonated via the equilibrium which is most likely to be found close to the miceller surface when interacting with SDS micelle.

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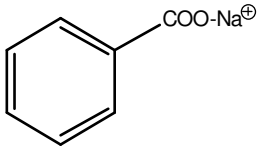
$$[Fe\,(C_{12}H_8N_2)\,(CN)_2] \xrightarrow{2H^+} [Fe\,(C_{12}H_8N_2)\,(CN)_2].2H^+ \quad (1)$$

The mechanism of interaction is due to the binding charged head groups of the surfactant to the site with opposite group of the protonated ferrocyphen, accompany with interaction of hydrophobic tail of the surfactant to hydrophobic portion of the ferrocyphen. Much of our chemical understanding on membrane structures has been obtained through the investigation of the model. Surfactant monolayer (Gaines, 1966; Goddard, 1975; Garshfeld, 1976) and bilayers (Tien, 1974) as well as phospholipids vesicles (Bangham, 1968; Tyrell et al., 1976; Quinn and Chapman, 1980) have been used most extensively as membrane models. It should however be realized that no model is perfect or is able to mimic faithfully all the aspects of complex membrane assemblies.

Hydrotropes are organic compound capable of increasing the solubility of organic and inorganic species in water or salt solutions (Umlong and Ismail, 2006). However, they are also use as solubilizing agents in drug formulations and in the formulations of surfactant systems for detergency (Balasubramanian and Friberg,

1993). They have been widely used in the formulation of surfactant systems for detergency. For example, report has shown on the increased antibacterial action of cresols in hydrotropic solution (Umlong and Ismail, 2006).



The solubilizing power of hydrotropes has also been employed in drug formulation and several other industrial applications (Balasubramanian Det al., 1989). Hydrotropes action or hydrotropy is considered to be similar to solubilization and sometimes it is also considered different from solubilization. Some of the examples of hydrotropes are sodium benzoate, sodium salicylate, sodium p-toluene sulfonate, resorcinol and pyrogallol (Balasubramanian et al., 1989; Roy and Moulik, 2003. Roy and Moulik, 2002).

Sodium benzoate belongs to the class of anionic hydrotropes and system containing cationic surfactant and this hydrotropes has been widely studies since its exhibit strong viscoelastic property (Umlong and Ismail, 2006). Benzoate ion has a strong effect on the miceller structure of anionic surfactants. In respect of cationic surfactants, benzoate ion is a counter ion and the opposite charges of the cationic surfactant and hydrotropes ion favors mixed micelle formation. Therefore, it is worth investigating the effect of hydrotropic property of sodium benzoate on the interactions of neutral hydrophobic ligand with anionic surfactant. The binding data for neutral ligands-surfactant interaction have been determined experimentally using spectrophotometric techniques (Olaseni et al., 2008).

EXPERIMENTAL

Materials

Sodium benzoate (Fluka > 99.5%) was used without further purification. Sodium dodecylsulfate (SDS) was purchased from Sigma chemical company. The degree of purity was ascertained by determining the critical micelle concentration (CMC) in aqueous medium at 25.0 ± ℃ using a conductivity method. The value 8.2 x 10^{-3} moldm^{-3} was obtained in perfect agreement with the literature value (Ige et al., 2007). Ferrous ammonium sulphate hexahydrate, potassium cyanide were analytical grade purchased from British Drug House chemical. Ferrocyphen was synthesized as reported in the literature (Ige et al., 2007) and the purity was ascertained by taken the visible spectrum in water-ethanol medium. Observed wavelength of maximum absorbance λ_{max} value 560nm is in excellent agreement with the literature value (Ige et al., 2007). All solutions were prepared with double distilled water.

Methods

These binding studies were carried out at a fixed temperature of 25℃ using a thermostarted double beam spectrophotometer (UV-3100 Shimadzu model, Japan). A wavelength scans of the complex in sodium benzoate/ water - surfactant medium show no change in λ_{max} under this experimental condition. All binding studies were carried out at surfactant concentration below the CMC because at SDS concentrations below the critical micelle concentration (CMC), SDS dissociated completely. The absorbance was taken at 560 nm (the wavelength of maximum absorption) of ferrocyphen in all the runs while the unusual scatchard plot was analyzed using binding capacity concept.

RESULT AND DISCUSSION

Figure 1 is the binding isotherm (the average number of ferrocyphen ion bound per molecule of SDS ($\bar{\nu}$) as a function of logarithm of the free ferrocyphen concentration [ferrocyphen]$_f$ at specified condition) of ferrocyphen-SDS interaction.

The scatchard plots are shown in Figure 2. Scatchard in his original paper pointed out that the curvature may indicate different intrinsic constant of deviation from independent probability (Garshfeld, 1976).

For system with one set of binding sites positive and negative cooperatives, this curve should be downward and upward respectively. These cases have not been observed in the interaction of ferrocyphen - SDS in the presence and absence of aromatic counter ion (sodium benzoate), however, they are upward and concave characteristic of cooperative binding. These unusual cases is due to the nature of interaction between ferrocyphen - SDS in the presence of aromatic counter ion which has a hydrophobic character.

Thus this system has two sets of binding site, involving an electrostatic and hydrophobic interaction. For analyzing the binding data, the concept of Wyman binding potential, Π (P, T, μ_1 μ_2…) which is pressure P and temperature T relates to chemical potential, μi as;

$$vi = \frac{\partial \Pi}{\partial \mu i} \qquad T,P, \mu_j \neq i \qquad (2)$$

The homotropic second derivative of the binding potential with respect to chemical potential of ligand for ideal solution is as follows;

$$\theta = \partial \nu_i / \partial \mu_i = \partial \upsilon_i / RT \partial \ln[ferrocyphen]_f = \partial^2 \pi / \partial \mu_i^2 . \qquad (3)$$

It provides measure of the steepness of binding curve and was designed as the binding capacity. It depicts the change in the number of mole of ligands per mole of macromolecule that accompanies a change in the chemical potential of that ligand and thus, from slightly different point of view is a measure of macromolecular capacity for grabbing ligand at any specified binding state, so it can be a measure of cooperativity as expected by the Hill coefficient, n_H, to binding capacity in order to extract a relationship between them. n_H is defined as the slope of

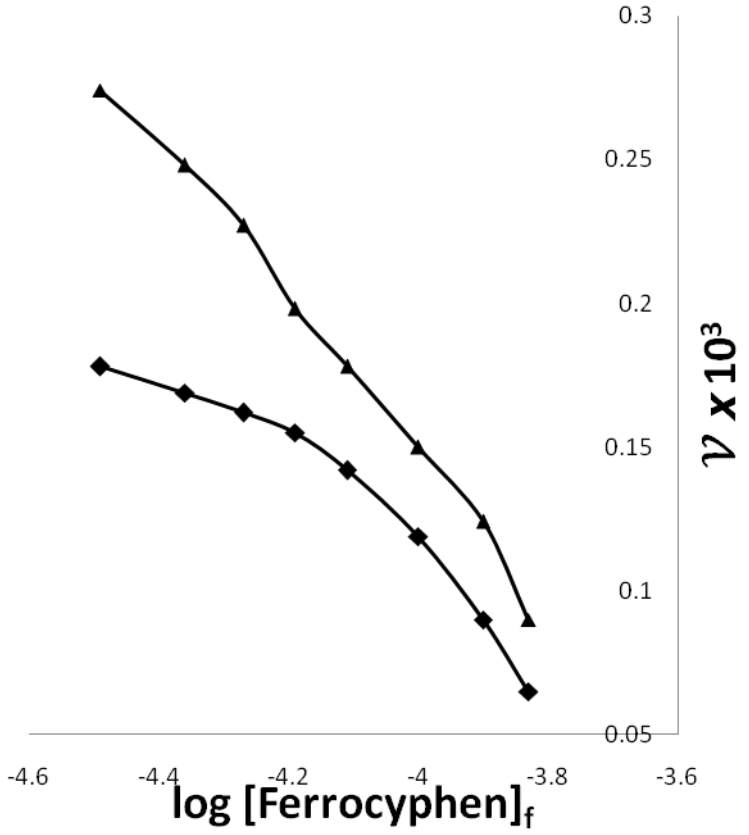


Figure 1. Binding isotherms for binding ferrocyphen with SDS in the presence [■] and absence [♦].

the Hill plot;

$$n_H = \frac{dln(y/(1-y))}{dln[ferrocyphen]f} = \frac{1}{y(1-y)} \frac{dy}{dln[ferrocyphen]f} \quad (4)$$

Where; y is the fractional saturation of surfactant by ligand which is defined as follows;

$$y = \frac{\nu}{g} \quad (5)$$

Where; g is the number of binding sites.

From the definition of binding capacity (2), the following equation can also be written;

$$n_H = \frac{1}{gy(1-y)} RT\theta \quad (6)$$

$$\theta = n_H \nu (1 - y) / RT \quad (7)$$

Equation (7) is rearranged to the following form.

$$RT\theta/\nu = n_H - n_H (\nu/g). \quad (8)$$

For a system with one set of binding sites and identical n_H, it can be suggested that the plot ($RT\theta/\nu$) versus ν should be linear, where the slope, y and x-intercepts are $-n_H/g$, n_H and g, respectively.

Using the Hill equation for one set of binding sites, the binding data of this system can be analysed using equation (9) as following;

$$\nu = \frac{g(K[ferrocyphen]_f)^{n_H}}{1+(K[ferrocyphen]_f)^{n_H}} \quad (9)$$

Figure 3 shows the variation of ($RT\theta/\nu$) versus ν for interaction of ferrocyphen -SDS in the presence of sodium benzoate for one hypothetical system with different cooperativity.

These plots are not linear representing more than one set of binding sites for interaction of ferrocyphen - SDS in the presence of sodium benzoate. The initial and final

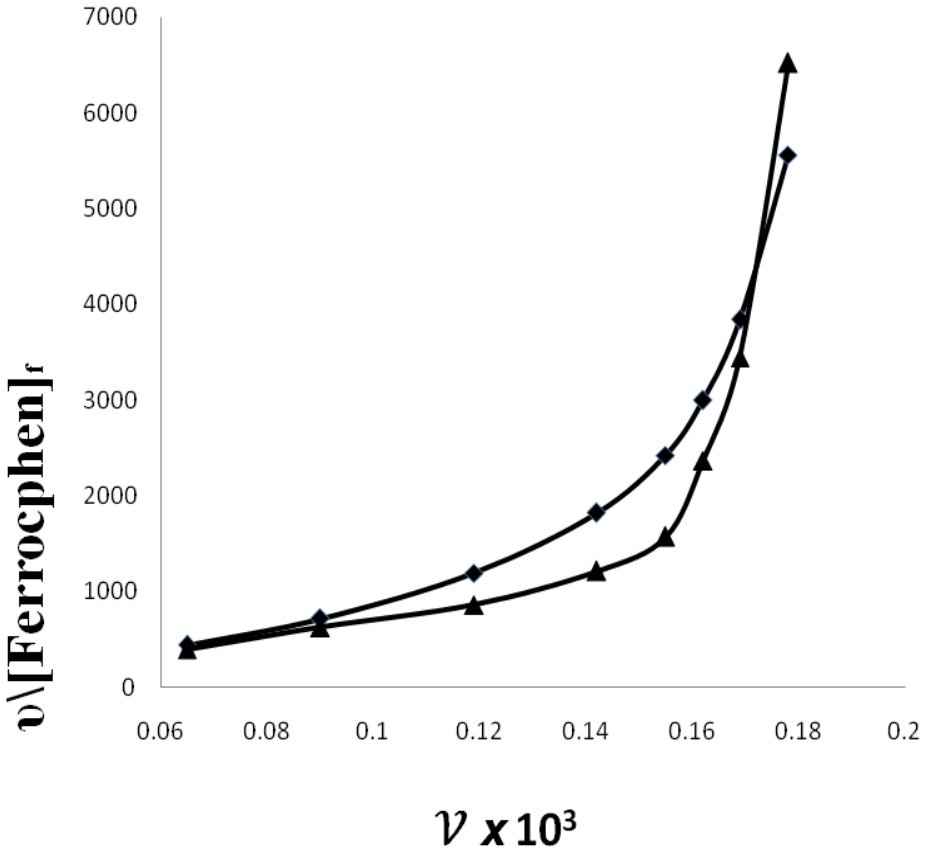


Figure 2. The scatchard plots for binding ferrocyphen with SDS in the presence [■] and absence [♦] of sodium

points of these plots are fitted as linear equations with high correlation coefficient. Each linear line can be correlated to one set of binding sites. With respect to the slope and intercept of these lines the value of n_H and g for each set, have been estimated. The Hill equation for two set of binding sites is as following (Sabury et al., 1996).

$$\nu = \frac{g_1(K[ferrocyphen]_f)^{n_{H_1}}}{1+(K[ferrocyphen]_f)^{n_{H_1}}} + \frac{g_2(K[ferrocyphen]_f)^{n_{H_2}}}{1+(K[ferrocyphen]_f)^{n_{H_2}}}. \quad (10)$$

Where; g_1, k_1 and n_H are the number of binding sites, binding constant and Hill coefficient for the first binding set, respectively and g_2, k_2, and n_{H2} are the corresponding parameter for the second binding set. The estimated binding parameters of Hill equation are listed in Table 1.

The intrinsic Gibbs free energy of binding per mole of surfactant for the first and the second binding set can be obtained by the following equation (10).

$$\Delta G^{(1)}_{,b,\nu} = -RTn_{H_1} \ln k_1 + RT(1-n_{H_1}) \ln[ferrocyphen]_j \quad (11)$$

$$\Delta G^{(2)}_{,b,\nu} = -RTn_{H_2} \ln k_2 + RT(1-n_{H_2}) \ln[ferrocyphen]_f \quad (12)$$

From Table 1, n_H>1 indicating positive cooperativity. It can be seen that binding strength at second binding set has been decrease by increasing benzoate concentration while value for the first set remain constant (Table 1). Electrostatic and hydrophobic interactions are the driven force in the first set while only hydrophobic interaction predominates in the second set. In the absence of benzoate ion, the reverse is the case that is, first set of interaction is hydrophobic and the second set is the electrostatic and hydrophobic interaction [Ige et al., 2007]. Once benzoate is added, mixed micelle is formed because there is decrease in the CMC of the resulting solution of ferrocyphen,sodium benzoate and SDS mixture. The two site of benzoate ion binding site are (1) location between the surfactant head group and (2) exterior surface of micelle. Such a two site binding give rise to intercalated and surface-bound benzoate ion. But this ion will not choose the site between the head group due to electrostatic repulsion, but will choose the second site around the exterior surface of SDS micelle that is, between the stern layer and the shear surface leading to ion -pair formation with the sodium counter-ion present in

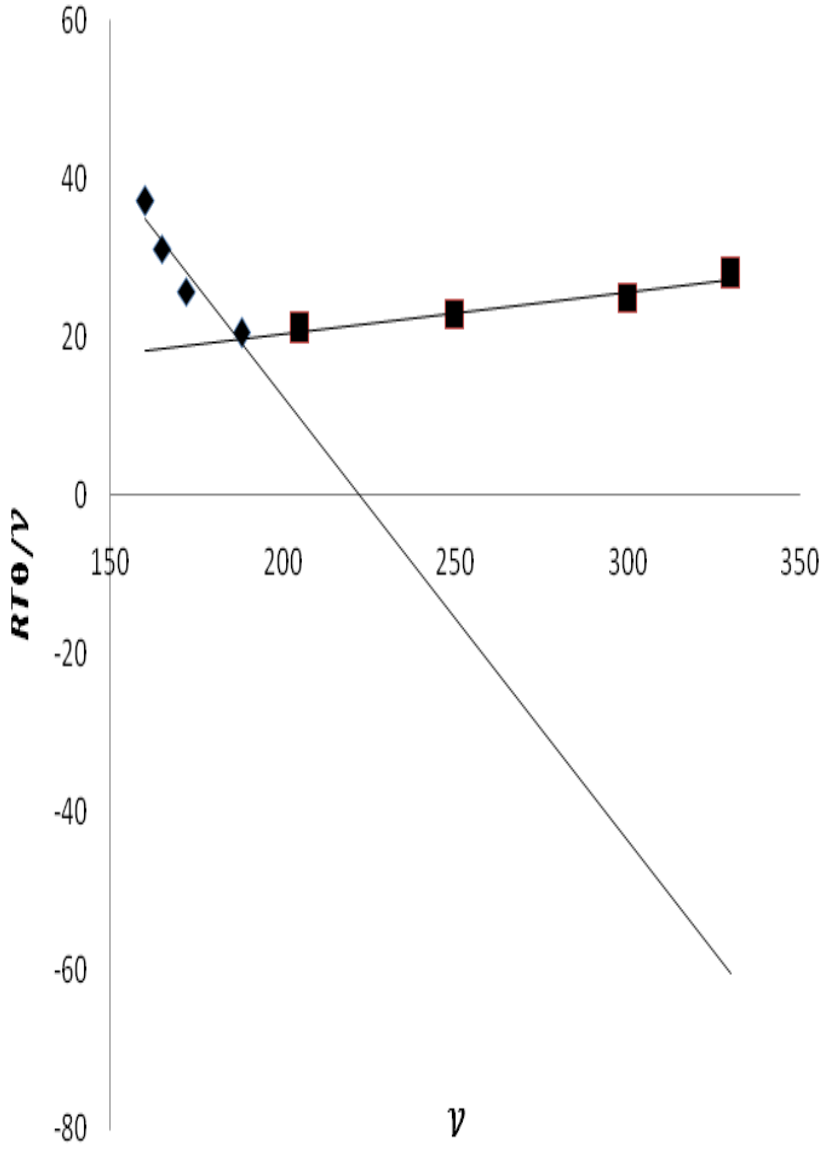


Figure 3. The plot of $^{RT\theta}/_{\nu}$ versus ν for the interaction of ferrocyphen with SDS in the presence of sodium benzoate at 25°C.

Table 1. The values of binding parameter for interaction of ferrocyphen SDS in the presence of Sodium Benzoate (NaB) at 25°C and at fixed concentration of ferrocyphen.

[NaB]mol.kg-^{1}	n_{H1}	g_1	$(K_1\backslash M)10^3$	$\Delta G^1_{b,v}x10^3$	n_{H2}	g_2	$(K_2/M)10^3$	$\Delta G^2_{b,v}x10^3$
0.000	18.2	114.22	43.11	- 22.18	9.22	360.33	44.14	8.07
0.200	22.0	120.14	37.06	- 16.14	14.21	321.16	39.37	- 13.44
0.250	34.1	220.66	36.77	- 13.22	26.29	364.11	28.22	- 10.37
0.300	16.3	216.31	38.17	- 33.36	32.18	398.21	24.06	- 21.34
0.350	10.1	180.38	37.11	- 41.28	8.13	116.32	22.71	- 34.77
0.400	6.2	98.47	38.23	- 58.27	4.24	100.05	20.26	- 42.93
0.450	2.5	60.24	37.16	- 65.14	1.55	94.26	19.43	- 58.01

the stern layer.

Conclusıon

Unusual scatchard plots for this system were observed. The existence of two sets of binding sites in these systems has been shown by involving application of the binding capacity concept. It is the homotropic second derivative of the binding potential with respect to the chemical potential of the ligand and provides a measure for the steepness of the binding isotherm (Saboury, 2002). The result provides evidence for the existence of two sets of binding's sites concerning the interaction between ferrocyphen and sodium dodecylsulfate as an anionic surfactant in the presence of sodium benzoate.

Positive cooperativity were recorded in both binding set ($n_{Hi} > 1$) for all of the studied condition. The positive cooperativity in first binding set without benzoate ion represent electrostatic interaction due to fact that the protonated ferrocyphen will be found close to miceller surface while the positive cooperativity in the second binding set refers to essentially hydrophobic nature of interaction in this set. The positive cooperativity in the first binding set in the presence of benzoate ion represent hydrophobic interaction because benzoate ion is consider to form mixed micelle with SDS by going to the surface of the SDS micelle and then forming ion-pair with the bound counter-ion. This will definitely promote hydrophobic interaction.

The positive cooperativity recorded in the second binding set, is due to electrostatic interaction accompany by hydrophobic interaction because the mixed micelle spontaneously break at random along its length and a reverse reaction occur in which one micelle combine with another.

Overall, the effect of sodium benzoate in this binding studies, is attributed to mixed micelle formation with SDS. It is considered that the benzoate ion reside outside the layer of the SDS and form ion-pair with the sodium ions bound to the micelle.

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