INTERACTION OF HEMICYANINE DYES WITH THE MICELLES OF SODIUM DODECYLBENZENESULFONATE

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DECLARATION

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KASHIF NAEEM

DEDICATED TO

THE LAST PROPHET

MUHAMMAD (P.B.U.H)

THOSE WHO BELIEVED THAT HE IS THE LAST
MASSANGER OF ALLAH

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ABSTRACT

The critical micelle concentration (CMC) of sodium dodecylbenzenesulfonate (SDBS) in the presence of small amount of dialkylamino stilbazolium butyl sulfonate ($R = CH_3 - C_5H_{11}$) dyes was determined by conductivity method at 25 °C. The CMC of SDBS decrease linearly with an increase in the concentration of added dye within their low concentration regions. The rate of CMC decrease versus the concentration of each dye at limiting dilution, provide the slope -dCMC/dCa (= - k). Information concerning the solublization of dialkylamino stilbazolium butyl sulfonate dyes in an ionic surfactant (SDBS) was obtained from Hitachi Double-beam Model 220 UV-visible spectrophotometer at 25 °C. The partition coefficient K_x, of additives (dyes) between the bulk water phase and the micellar phase of SDBS was determined at 25 °C by differential spectroscopic method. The value of K_x are: for dye 1, 13424; for dye 2, 17713; for dye 3, 20039; for dye 4, 48729 and for dye 5, 671236. The standard free energy change of solublization, ΔG°_{p}, was also determined for above five dyes. The values of K_x and ΔG°_{p} for all dyes were again determined by an improved method which incorporate both conductance and differential spectroscopic data. The value of K_x with improved relationship are: for dye 1, 13426; for dye 2, 17872; for dye 3, 20402; for dye 4, 48319 and for dye 5, 669155. The free energy change per methylene group, i.e., ΔG° (CH_2) was also calculated which is -1.091 kJ/mol or - 0.261 kcal/mol in aqueous micellar solution of SDBS at 25 °C. The effect of micelle forming surfactant SDBS on the visible spectra of above dye was also reported. Incorporation of dye molecules in micelle shift the spectra towards higher wavlength and magnitude of the shift increase with increasing the hydrophobicity of dyes. The spectral shift of dyes also depends upon the nature of the surfactant head group, on this basis of inetraction of the five dyes with micelles of SDBS has also been discussed. The absorption spectra of all the dyes in aqueous solution was also studied. The maximum wavelength (λ_{max}) increase with increasing hydrophobicity of dye. The increase in λ_{max} is more prominent from dye 1 to dye 2 and this change is comparable as we go from dye 2 to dye 5. This is due the fact that there is removal of one

β-hydrogen with carbon atom from methyl group in dye 1, then their is simply extension of alkyl chain. The interaction coefficient (θ) between dye and surfactant (SDBS) was also evaluated and discussed.

1
INTRODUCTION

INTRODUCTION

Surfactant or surface active agent is a compound that affects the surface tension between two liquid phases. Generally, surfactants lower the surface tension. In a polar solvent and at a certain concentration (CMC, critical micelle cocentration), surfactant molecules associate to form micelles. The critical micelle concentration (CMC) is affected by the presence of organic additives in the solution at constant temperature. The CMC at which surfactant molecules aggregate to form micelle in the water is depressed in the presence of amphiphilic organic additives at low concentration, which strengthen hydrophobic bonding tendency in aqueous surfactant solution.[1-6] The non polar moieties of the surfactant molecules and those of the organic additives tend to be expelled from the bulk water and coaggregate together,[7] resulting in the partitioning of the organic additives between the micelle, and the surrounding aqueous solutions.

The application of surfactants in coating, oil recovery from mud, extraction of oil, ore extraction, cosmetics, food industries, automobiles, textile, phaemaceutical and agrochemical industry are to familiar.

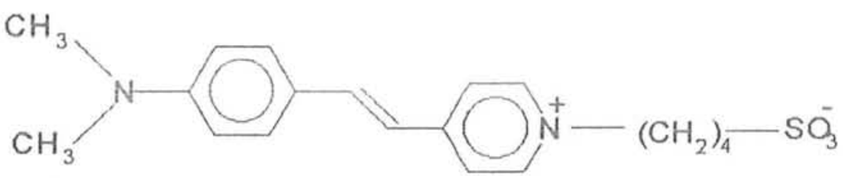
Surfactants contain molecules with different substituent groups of differing solubility characteristics. Most frequently, one group is polar and has strong attraction towards the solvent (lyophilic), while the other is non polar and having little attraction to the solvent (lyophobic). When water is used as solvent then these groups are called hydrophilic and hydrophobic respectively. Surfactants when dissolved in a solvent , distort the structure of the solvent and therefore increase the free energy of the solvent. They therefore concentrate at the surface where, by orienting so that thier lyophobic groups are directed away from the solvent , the free energy of the solution is minimized .

The distortion of the solvent structure can also be decreased (and the free energy of the solution reduced) by the aggregation of the surfactant molecules into clusters (micelles) with thier lyophobic groups directed towards the interior of the cluster and and thier lyophilic groups directed towards the solvent. Micellization is therefore a process alternative to adsorption at the interfaces for removing lyophobic groups from contact with the solvent, thereby reducing the free energy of the system. Whether micellization occurs in a particular case and, if so, at what concentration of monomeric surfactant, depends on the balance between the factors promoting and opposing the micellization .

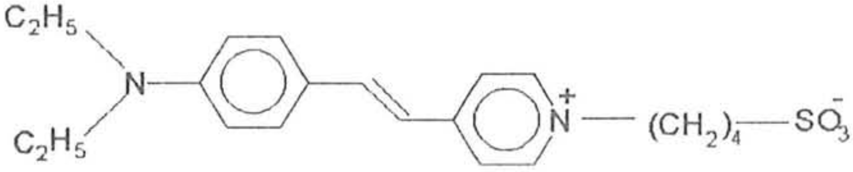
Amphiphilic organic additives with changing hydrophobicity have been used to determine the partition coefficients. It is known that the CMC lowering ability can be linked to the partition coefficient of the additive between the micelle and water.[8,9]

In the present work, amphiphilic hemicyanine dyes were used as organic additives in the solution of sodium dodecylbenzenesulfonate (SDBS). Amphiphilic hemicyanine dyes are basically amino stilbazolium dyes. These are zwitterionic dyes which are the derivatives of amino styryl pyridinium and its homologues with two and three conjugated double bonds.[10] The hemicyanine dyes are used most frequently as the fluorescence probes to follow the fast change of the electrical membrane potential during an action potential in neurons.[11] These dyes are also very effective voltage-sensitive probes in biomembranes and are popular fluorescence indicator of fast voltage transients in neurons in culture and in brain.[12] The probing of fast changes of the electrical potential in biological membranes is studied extensively in the light of the photophysical properties of the dyes. The dyes have characteristics spectra of absorption and from the spectra, the quantum yields, and the life times of fluorescence are calculated.

The physical behavior of the surfactant micelle can be viewed as the construction of the model membrane system to mimic a biological system like chloroplasts. This experimental model is useful for studying the interaction of biological surfaces with additive molecules. In the present work, five dyes are used in a series of dialkylamino stilbazolium butyl sulfonates as shown on next page.



(1) Dimethylamino stilbazolium butyl sulfonate



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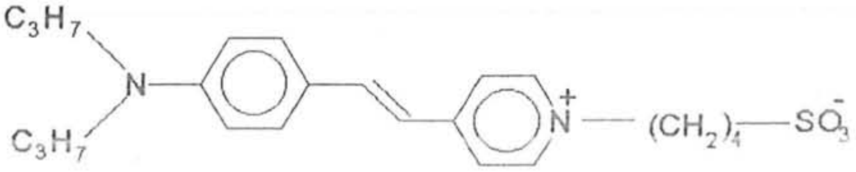
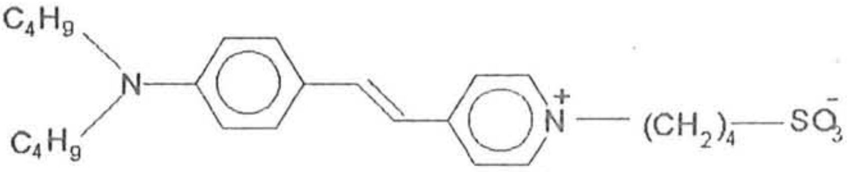
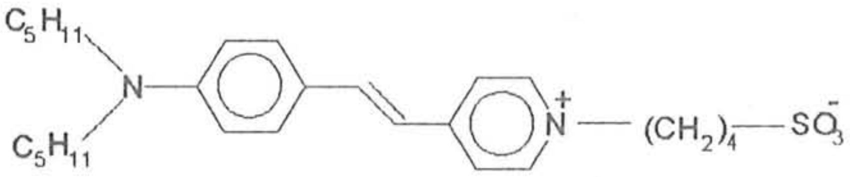


(3) Dipropylamino stilbazolium butyl sulfonate



(4) Dibutylamino stilbazolium butyl sulfonate



(5) Dipentylamino stilbazolium butyl sulfonate

The object of present work is to estimate the effect of these dyes and their hydrophobicity on the CMC of sodium dodecylbezenesulfonate (SDBS). It was done by using conductance measurements at 25 °C. The values of partition coefficient (K_x) and hence the standard the free energy change, ΔG°_p , of solubilization of these additives between the SDBS micelles and the surrounding aqueous solution was also calculated at 25 °C by a differential spectroscopic method.[13] ΔG°_p and $\Delta G^\circ(CH_2)$ for each dye was also calculated. The effect of sodium dodecylbezenesulfonate on the visible spectra of the hemicyanine dyes was also studied.

The absorption spectra of five hemicyanine dyes was measured as a function of anionic surfactant (SDBS) concentrations. The effect of aminostilbazolium butyl sulfonate group

$$[\ >N—C_6H_5—CH{=}CH—C_5H_4N^+—(CH_2)_4—SO_3^-\ ]$$

is assumed to be constant on solubilization of all the dyes in the micelles, and hence the role of dialkyl group present on all the dyes was made the basis of investigation. So $\Delta G^\circ(CH_2)$ for all the dyes was calculated based on this assumption. Where $\Delta G^\circ(CH_2)$ is the free energy of transfer per methylene group , from the bulk water to micelles.

The change in the λ_{max} of each dye caused by the micelle forming concentration of SDBS indicate the average incorporation site of dye in the micelle, which is inturn dependent on the dialkyl chain length of each dye.

Using the conductance and spectroscopic data, an interaction coefficient (θ) for the system was calculated following the linear relation used by Manabe for calculation of θ for 1-Alkanols.[13] θ may be looked upon as a measure of the penetrability of the micelles by the amphiphilic additives.

2

THEORETICAL

THEORETICAL

Part-I

2.1 SURFACTANT

Surfactant is a substance that, when present at low concentration is a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces or interfaces. In other words, surfactants are the organic compounds that have the property of reducing the surface tension of water and increase the wetting ability of surfactant solution.

Surfactants are used as antistatic agent in the manufactuere of plastic articles and as wetting agents in the formation of plastic coating. Surfactants solubilize flavor oils in beverages and improving the capicity of paper towel to absorb water. In the tanning of leather, they promote wetting and penetration. Surfactants have been proved extraordinary catalysts for organic reactions in the micellar media, increasing reaction rate to many fold. The applications of surfactans in pharmeceutical, cosmetic and pestisidal industries are all too familiar. The surfactants play an important role even in microelectronics and they are useful in fabricating a wide variety of components and materials ranging from ceramic substrates (to attach semiconductor chips) to magnetic storage media and printing inks.

Surfactant have a characteristics molecular structure consisting of a structural group that has very little attraction of the solvent, known as a lyophobic group, together with a group that has a strong attraction for the solvent called the lyophilic group. This is known as an amphipathic structure.[1] In an aqueous solution of a surfactant the lyophobic group is called the hydrophobic group of the surfactant and the lyophilic group is called the hydrophilic group of the surfactant. Depending on the chemical nature of these groups, surfactants are classified into four groups. The four classes of surfactants are anionic, cationic, zwitterionic and non-ionic surfactants.

1. **Anionic**:- The surface active portion of the molecule bears a negative charge.

e.g $RCOO^-Na^+$ (soap), $RC_6H_4SO_3^-Na^+$ (alkylbenzene sulfonate).

They are generally employed as detergent and builder. These are used as textile treating agent in preparation of raw material and for dyeing purposes etc.

2. **Cationic**:- The surface active portion bears a positve charge.

e.g $RNH_3^+Cl^-$ (salt of a long chain amine), $RN(CH_3)_3^+ Cl^-$ (quaternary ammonium chloride). They are excellent fungicide, germicide, softening and laveling agent. They are widely used in agrochemical and pharmaceuticals.

3. **Zwitterionic**:- The surface active portion have both positive and negative charges into the same molecule.

e.g $^+RNH_2CH_2COO^-$ (long chain aminoacid), $^+RN(CH_3)_2CH_2CH_2SO_3^-$ (sulfobetaine).

4. **Non-ionic**:- The surface active portion bears no apparent ionic charge.

e.g $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long chain fatty acid),

$RC_6H_4(OC_2H_4)_xOH$ (polyoxyethylenated alkyl phenol).

These are efficient in removing grease and oils from metal surfaces and fabrics. These are generally used in ore extraction, oil recovery and as degreasing agent.

2.1.1 SURFACTANT PROPERTIES

The molecules at the surface of the solvent (water) have higher potential energies than those present in the interior . This is because they interact more strongly with the molecule in the interior of the solvent than they do with the widely spaced gas molecule above it. Work is therefore, required to bring molecules from the interior to the surface.

When a surface active agent is dissolved in a solvent, the presence of the lyophobic group in the interior of the solvent causes a distortion of the solvent liquid structure, increasing the free energy of the system. It means that less work is needed to bring a surfactant molecule than a solvent (water) molecule to the surface. The surfactant, therefore, concentrates at the surface. On the other hand, the presence of lyophilic (hydrophilic) group prevents the surfactant from being expelled completely from the solvent of a separate phase.

The amphipathic structure of the surfactant therefore causes not only concentration of the surfactant at the surface and reduction of the surface tension of the solvent, but also the orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it.

2.1.2 MICELLIZATION

The most outstanding property of amphipathic ions characterize by a polar hydrophilic head and a non polar hydrocarbon tail, is their tendency to form large aggregates, the micelles, above a certain rather sharply defined concentration. So micelle is defined as "a colloidal particle together with its surrounding stabilizing layer".[14]

The surfactant molecules grouped together in a manner that their hydrophobic tails tend to coaggregate and their hydrophilic heads provide protection. The hundred or so molecule that accumulate together in this way constitute a micelle, as depicted in Figure A.

The ionic surfactants tend to be disrupted by the electrostatic repulsions between the head groups and normally limited between 10 and 100 molecules in a micelle. The interior of a micelle is like a droplet of oil, and the hydrocarbon chains are mobile, but slightly more restricted than in the bulk.[14]

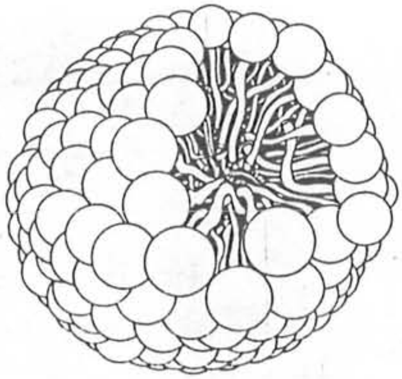


Figure A. A spherical micelle

A major source of stability of micelle is the existence of an electric charge on their surfaces. On account of this charge, ions of opposite charge tend to cluster nearby, and an ionic atmosphere is formed.

At any interface there is always an unequal distribution of elctrical charges between the two phases. So both sides of the interface acquire a net charge of particular sign, giving rise to a potential across the interface and the so called electirical double layer. Helmholtz, Gauy-Chapman and Stern tried to explain the exact distribution of the neutralizing charges (counter ion or gegen ion).[1] The critical micelle concentration in aqueous solution reflects the degree of binding of the counter ion to the micelle. Increased binding of the counter ion, in aqueous systems, causes a decrease in CMC of the surfactant. The extent of binding of the counter ion increases with increase in its polarizability and valence, and decreases with increase in its hydrated radius. Thus in aqueous medium, for the anionic lauryl sulphates, the CMC decrease is in the order[1]

$$Li^+ > Na^+ > K^+ > Cs^+ > N(CH_3)_4^+ > N(C_2H_5)_4^+ > Ca^{+2}, Mg^{+2}$$

There is fairly immobile layer of ions that stick tightly to the surface of the micelle, and which may include water molecules (if that is support medium). The radius of the unit from the center of the micelle upto the sphere that captures this rigid layer is called the radius of shear, and it is a major factor in determining the mobility of the particle (micelle).

The charged central unit attracts an oppositely charged ionic atmosphere, and so there is also a diffused cloud of opposite charge. The inner shell of charged end the outer atmosphere is referred to as the electric double layer. The structure of atmosphere can be described in the same way as in the Debye Huckel model of ionic solutions.[14]

Micelle form only above a certain concentration of a surfactant, which is typical of the system, this lower limit is called the critical micelle concentration (CMC). Physical properties in an aqueous solution of surfactant show abrupt change in a certain narrow concentration range and micelle formation occurs at this concentration. Conversely, these sudden change in physiochemical properties have been used to determine the CMC. Change in some physical properties in CMC region[15] are shown in Figure B.

Phillips[16] had used the definition that CMC is the concentration at which the properties of the surfactant solution change in the most abrupt manner, i.e.,

$$\left(\frac{d^3\phi}{dTc^3}\right)_{T_C = CMC} = 0$$

Where (ϕ) is any additive property which varies linearly with the concentration of micellized end of unassociated surfactant.

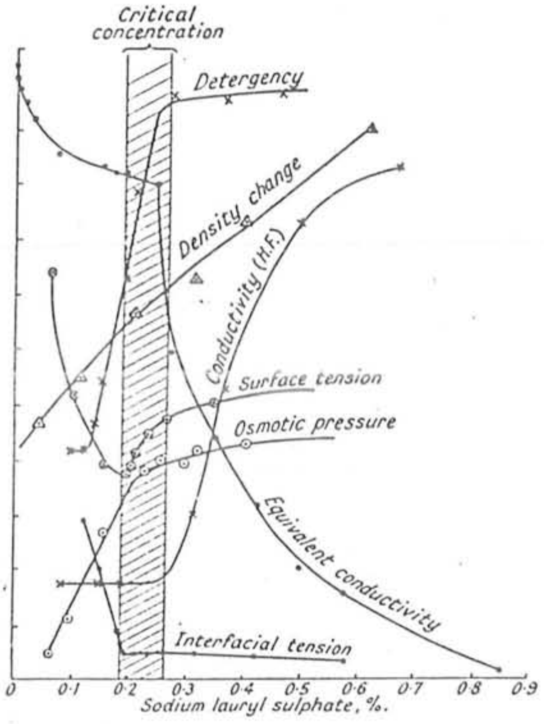


Figure B. Physical property curves for aqueous sodium dodecyl sulfate

2.1.3 ROLE OF SURFACTANTS IN SOLUBILIZATION

One of the most important properties of aqueous micellar solutions that is directly related to micelle formation is solubilization. Solubilization may be defined as the spontaneous dissolving of a substance by the reversible interaction with the micelle of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solulbilized material. Solvent-insoluble materials may be dissolved by the solubilizaion mechanism, the importance of the phenomenon from the practical point of view is that it makes possible the dissolving of substances in solvents ion which they are normally insoluble. In solubilization, the solubilized material is in the same phase as the solubilizing solution, and the system is consequently thermodynamically stable.

If the solubility of a normally solvent-insoluble materials is plotted against the concentration of the surfactant solution that is solubilizing it, we find that the solubility is very slight at concentrations below the CMC of the surfactant but rises abruptly once the CMC has been reached as shon in Figure C. This indicates that solubilization is a micellar phenomenon, since it occurs only to a negligible extent at the concentration where micelles, if they exist at all, are found in insignificant numbers.

Solubilization within surfactants is probably the most important mechanism for the removal of small amounts of oily soil from substrates. Oily soil removal from both hard and textile surfaces becomes significant only above the CMC for non-ionic and even for the anionic surfactants having low CMC, and reaches its maximum only at several times that concentration. Since the adsorption of surfactants at interfaces involves the monomeric, rather than the micellar form of the surfactant, whereas solubilization involves only the micellar form, this appears to indicate that in these cases solubilization is a more important factor in the cleaning process than mechanisms dependent on adsorption (e.g wetting , soil rollback).

The extent of solubilization of the oily soil depends on the chemical structure of the surfactant, its concentration in the bath, and the temperature. At low bath concentrations , solubilization is more or less spherical-shaped micelles and only a relatively small amount oily soil can be solubilized. Where as at high surfactant concentrations (10-100 times the CMC), solubilization is more similar to microemulsion formation, and the high surfactant concentration can accomodate a much larger amount of oily matter.[1]

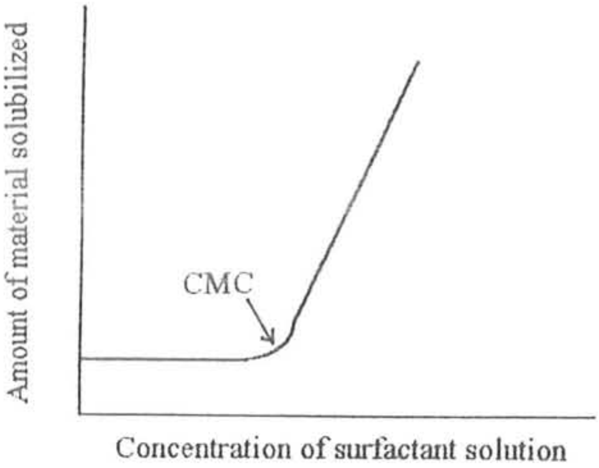


Figure C. Plot of amount of material solubilizedas a function of surfactant concentration

2.1.4 EFFECT OF ORGANIC ADDITIVES ON CMC

Small amounts of organic materials may produce marked changes in the CMC in the aqueous media. There are two classes of organic materials that markedly effect the CMC of aqueous solution of surfactants.

Class I materials effect the CMC by being incorporated into the micelles, and Class II materials that change the CMC by modifying solvent-micelles or solvent-surfactant interactions. Materials in the first class are generally polar organic compounds, such as alcohols and amides. They effect the CMC at much lower liquid phase concentration than those in the second class.

Members of Class I reduced the CMC and members of Class II change the CMC, but the bulk phase concentration usually are considerably higher than those at which Class I members are effective. The members of this Class II change the CMC by modifying the interaction of water with the surfactant molecule or with the molecule, doing this by modifying the structure of water, its dielecteric constant or its solubility parameter. Members of this class include urea, formamide, short chain alcohols, dioxane and other polyhydric alcohols such as fructose and xylose.

Part-II

2.2 CONDUCTIVITY

The conductance G (Siemens or mho) of a conductor is the inverse of resistance (ohm). It is the resistance between the two electrode immersed in the solution under investigation. If the electrode posses an effective cross-sectional area A (m) and are a distance one meter apart then

$$R = \frac{\rho 1}{A}$$

where ρ (ohm.m) is the specific resistivity and K_s ($ohm^{-1}\ m^{-1}$) the specific or electrolytic conductivity. K_s and ρ are the intrinsic properties of the solution at a given temperature and pressure while G and R also depend on the dimensions of the measuring systems. In practice 1/A, called the cell constant (m^{-1}) is determined by measuring the resistance, when the cell is filled with the solution of known specific conductivity.

It is obvious that K_s will depend on the characteristics and the concentration C ($mol.m^3$) of the electrolyte present in the solution, and therefore, the molar conductance Λ_m ($m^2.S.mol^{-1}$) is defined by $\Lambda_m = K_s / C$, for a single electrolyte $C_{\nu+}A_{\nu-}$ which is present to the extent of C ($mol.\ m^{-3}$), and if it dissociates according to

$$C_{\nu+}A_{\nu-} \quad ===== \quad \nu{+}C^{Z+} \; + \; \nu{-}\ A^{Z-}$$

then its equivalent concentration is given by

$$C_{eq} \;=\; \nu + Z + C \;=\; \nu \ - |Z -|$$

The Zi symbol represents the algebric charge number of the subscripted species i , while |Zi| is its arithmetic charge number. Thus the equivalent conductance Λ_{eq} ($m^2\ ohm^{-1}$ $equivalent^{-1}$) is defined by

$$\Lambda_{eq} = \frac{K_S}{C_{eq}} = \frac{m}{\nu + Z+} = \frac{m}{\nu - |Z -|}$$

If an electric field X (V/m) is applied between the electrode in a uniform solution, any ion 'i' moves in the direction of the fields with a steady state velocity Vi (m/s), i.e., proportional to the potential gradient i.e., Vi = UiX. Where Ui is the mobility of the ions ($m^2.sec^{-1}.V^{-1}$).

Consider and imaginary reference plan of area A in the solution and perpendicular to the applied field. In time t seconds all the ions of the type i, contained in the volume Vit (m)xA(m^2) or Vi t Aci mole of i pass across the plane. These carry an electric charge of |Zi| F vi ACi coulomb(C), where F is the Faraday constant for singly charged ions. The total flux of charge is coulomb transferred across the reference in both directions by all the anions and cations is therefore $\Sigma i \ | Zi | Fvi \ t \ Aci$. The current I (ampere) is obtained on dividing by t . Now according to Ohm's law IR = X.1. Then specific conductivity K_s is given by

$$K_s = \frac{1}{AX} = \Sigma i \ | Zi | FUiCi$$

The molar conductance of i, λ_i ($m^2.ohm^{-1}.mol^{-1}$) which is directly [proportional to the mobility Ui will be $\lambda_i = | Zi | Fui = | Zi | \ \lambda_{ieq}$, Where λ_{ieq} is the equivalent ionic conductance ($m^2.ohm^{-1}.equivqlent^{-1}$). Combining this equation with equation $C_{ieq} = | Zi | Ci$ then the specific conductivity will be $K_s = \Sigma i \ \lambda_i \ Ci = \Sigma i \ \lambda_{ieq} \ C_{ieq}$. If only one electrolyte is present in the solution and this specific conductance will be represented as $K_s = \Lambda_m C = \Sigma i \ \lambda_i \ Ci = \lambda_{+\nu}C + \lambda_{-\nu -}.C$

The equation $\Lambda_m = K_s / C$ is defined as the molar conductance of the electrolyte. For uni-univalent electrolyte which dissociate completely $\Lambda_m = {}_{v+}\lambda_{+} + {}_{v-}\lambda_{-}$,where λ_{+} and λ_{-} are the respective conductance of cation and anion.

In case of binary symmetrical electrolyte which is incompletely dissociated is solution, a degree of dissociation α is defined as $C_{+} = C_{-} = \alpha C$

$$\Lambda_m = \frac{K}{C} = \Sigma i \, \lambda_i \, (Ci / C) = \alpha (\lambda_{+} + \lambda_{-})$$

2.3 DEBYE-HUCKEL MODEL

For the interpretation of experimental conductance data many equations based on different models have been proposed . The basic model of all conductance equation is the same as proposed by Debye and Huckel.[17] In this model ions in solution are supposed to be rigid sphere with charges on their centers immersed in a continuum having the properties of the macroscopic fluid with dielectric constant and viscosity with charges on their centers immersed in a continuum having the properties of the macroscopic fluid with dielectric constant and viscosity. Onsager[18] derived the following expression propose by Kohlrasch to represent the molar conductance of a symmetrical electrolytic solution.

$$\Lambda_m = \Lambda_o - S / C^{1/2} \qquad (1)$$

where Λ_m is the molar conductance of an electrolytic solution of concentration C ($mol.dm^{-3}$) and Λ_o is the limiting molar conductance of an electrolyte in a very dilute solution, i.e., $C \cong 0$. The coefficient S is theoretical limiting slope and is given by

$$S = \alpha \Lambda_m + B \qquad (2)$$

where $\alpha = (Ze^2) K / 3 \ [2 + (2)^{1/2}] DK_B \ T C^{1/2}$

and $B = Z^2 e \ F K / 3\pi \, n \, C^{1/2}$

where F is Faraday constant

and

$$K = \left(\frac{8\pi e^{2} N\mu}{1000\ D\ K_B\ T} \right)^{1/2}$$

where K is the reciprocal of the ionic atmosphere, μ is the ionic strength as $\mu = \Sigma\ C_i\ Z_i$, N is the Avogadro's number, e is the charge on electrons , C_i the concentration of ions, K_B the Boltzmann constant and D is the dielectric constant of the solvent or the medium.

Pitts[19] and Fuoss-Onsager[20] improved the Debye-Huckel equation (2) by introducing a parameter "a" the closest distance at which ions may approach in the solutions in order to take into consideration of short range interactions. The Fuoss-Onsager equation was further modified by Fouss and Hsia,[21] recalculating equation was further modified to relaxation field which were neglected in previous derivations. Hence, the equation takes a general form

$$\Lambda_m = \Lambda_o - \frac{\alpha\ \Lambda_o\ C^{1/2}}{[[1+K_a]\ [1+K_a / (2)^{1/2}]]} - \frac{B\ C^{1/2}}{1+K} + G(K_a) \qquad (3)$$

where $G(K_a)$ in the general is a complicated function of the variable K_a. By further mathematical treatment equation (3) takes the form.

$$\Lambda_m = \Lambda_o - SC^{1/2} + EC\ \ln C + J_1 C - J_2\ C^{3/2} \qquad (4)$$

Equation (4)is commonly employed to simplify the analysis of experimental conductance data. From the various schools of conductance theories,[22,23] E is defined as

$$E = E_1\ \Lambda_o - 2\ E_2 \qquad (5)$$

where $E_1 = (\ K_a\ b\ )^2 / 24\ C$

and

$$E_2 = - \frac{K_a\ b\ B}{16\ C^{1/2}}$$

and $b = Ze^2/DK_B$, the presence of E has been introduced for the representation of interionic short range forces. For various theoretical treatments different expression for J_1 and J_2 are functions of E_1 and E_2, and depend on the solvent properties as well as on the interionic distance, are fully discussed.[20-22] This equation is commonly utilized for univalent symmetrical electrolytes.

2.4 THE PARTITION COEFFICIENTS

It is well known that, in a surfactant micellar system, an organic additive is partitioned between surfactant micelle and bulk water phase, obeying the partition law. The value of CMC decreases linearly with an increase in the concentration of additive (C_a), within their low concentration regions. Therefore, we get a straight line through the plot of CMC Vs C_a. A limiting slope ($-\Delta CMC/\Delta C_a$) is calculated from this line at $C_a = 0$.

A relation between the limiting slope at the zero concentration of an additive, and the partition coefficient K of the additive between the aqueous phase and micellar phase was proposed by Shirahama and Kashiwabara[6] (in present notations) as ,

$$-\Delta \ln CMC / \Delta C_a = \text{constant}.\ K$$

$$\ln(-\Delta \ln CMC / \Delta C_a) = \ln K + \text{constant} \qquad (6)$$

Manabe and Koda,[24] proposed certain factors which replaced the constant of above equation, and it is expressed as

$$\ln(-\Delta \ln CMC / \Delta C_a) = \ln CMC_o + \ln \theta + \ln K$$

or

$$K = \frac{(-\Delta CMC / \Delta C_a)}{\theta \, . \, CMC_o} \qquad (7)$$

Another expression $K_x = K n_w$, n_w is the number of moles of water (55.5) per dm^3, is obtained. CMC_o is the critical micelle concentration of a surfactant without additive at 25 °C. θ is a constant, this parameter represents the interaction of the surfactant with the additives.

2.4.1 STANDARD FREE ENERGY CHANGE OF TRANSFER (ΔG°_{p})

The standard free energy change of transfer of the organic additive from water to micelle, ΔG°_{p} is given by the relationship

$$\Delta G^{\circ}_{p} = - R T \ln K_x \qquad (8)$$

where K_x is the partition coefficient, R is the gas constant and T is the absolute temperature.

Part-III

2.5 ULTRAVIOLET VISIBLE SPECTROSCOPY

When an electromagnetic radiation is passed through a material and the absorption of energy over a range of frequencies is measured, the relation ship between energy and frequency is given by,

$$\Delta E = h\nu$$

where ΔE is the difference in the energy between the ground state and the excited state of the molecule.When UV light is passed through a liquid sample the rotational motion of molecule is more or less ceased and molecule vibrates only and gives electronic transition with UV light.

Electronic transitions involve the promotion of σ , π or n.(non bonding or lone pair) electrons from their ground states to higher energy states. These processes require radiation in the relatively higher energy ultraviolet and visible portions of the spectrum.[25] UV light disturbs only the electronic energy states, i.e., the molecule is excited from ground electronic state to some higher electronic state, vibrational levels remain unaffected by these transitions.The regions of the electronic spectrum and the type of transition which occurs in each is shown in Figure D.

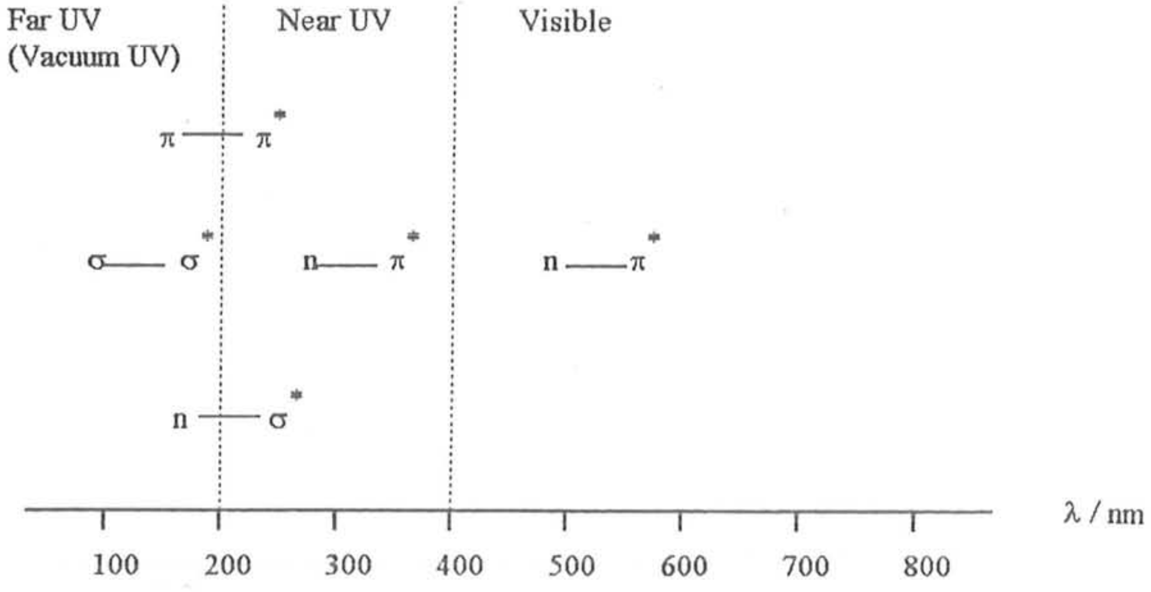


Figure D. Different transition in UV-visible region

The wavelength at which absorption occurs depends upon how firmly the electrons are bound in the molecule. The electron in a single covalent bond are tightly bound, and radiation of high energy, or short wave length is required for their exitation. For example, alkanes which contain C—H and C—C bonds , show no absorption over 160 nm. This is $\sigma-\sigma^*$ transition. Electrons in a double or triple bond are rather easily exited to higher pi orbitals. A transition is designated $\pi-\pi^*$ when a pi- electron is raised from a pi- bonding orbital to a pi-antibonding orbital. In conjugated molecules (i.e., those containg a series of alternating double bonds) the absorption is shifted to longer wave lengths (red shift). Most application of UV and visible spectroscopy to organic compounds are based on $n-\pi^*$ and $\pi-\pi^*$ transitions and hence require the presence of chromophoric groups in the molecule. These transition occur in the region of the spectrum (about 200-700 nm) which is convenient to use experimentally. As the dyes used in present work contain conjugated double bonds, so it is possible to measure their absorption spectra using UV-visible spectrophotometer.

The intensity of an electronic absorption is given by simple equation

$$A = \log \frac{I_0}{I_t} = \varepsilon b c$$

where A is the absorbance by the sample, c is the concentration of sample (mol per dm^3), b is the path length of the sample (cm), I_o is the intensity of light falling on the sample, and I_t is the intensity transmitted by the sample. ε is the molar extinction coefficient (cm^{-1} mol^{-1} dm^3). The simple relation we obtain is

$$A = \varepsilon b c$$

It is obvious that absorbance A, is directly proportional to the concentration C, of the sample in the solution.

2.6 DIFFERENTIAL SPECTROSCOPIC METHOD

The differential absorption spectroscopic method[13] has been used previously to determine the partition coefficients of homologous ω-phenyl alkanols in micellar solution of sodium dodecyl sulphate. The differential absorbance, ΔA, depends on surfactant concentration C_s , at a given concentration of organic additive C_a This can be explained in a way that for the organic additive in water, Lambert-Beer's law holds an experimentally confirmed

$$A_w = \varepsilon^f C_a \qquad (9)$$

where A_w and ε^f represent the absorbance and the molar absorptivity, respectively, at a given wavelength. As $\Delta A \rightarrow 0$ below CMC, it is supposed that equation (9) also holds in nonmicellar surfactant solution.

On the other hand, in the micellar region a portion of the organic additive (C_a^m) is considered to be solubilized in micelles and the other (C_a^f) still remains monomerically in the bulk water region, the total concentration, C_a is related as

$$C_a = C_a^f + C_a^m \qquad (10)$$

Assuming that the Lambert-Beer's law also holds for the solubilized organic additives as well as the monomer species,the absorbance A_s of a micellar solution can be expressed as

$$A_s = \varepsilon^f C_a^f + \varepsilon^m C_a^m \qquad (11)$$

where ε^m is the molar absorptivity for the solubilized organic species. The differential absorbance, ΔA, corresponding to the experimentally determined quantity is represented from equation (9-11).

$$\Delta A = A_s - A_w = \Delta\varepsilon \, C_a^m \qquad (12)$$

where $\Delta\varepsilon$ denotes $\varepsilon^m - \varepsilon^f$

A quantity, j is defined as

$$j = C_a^m / C_a \qquad (13)$$

The physical meaning of j is the fraction of the amount of solubilized organic additive in that of added organic additive. It is expressed that, at a certain concentration C_a , j is equal to zero in the non micellar region upto the CMC and increases with increasing C_s

above the CMC. As C_s increases upto infinity, j approaches unity , since almost all added organic additive should be solubilized in the micelles : $C_a^{\,m} \cong C_a$. Thus equation (13) can be re-written through equation (12) as

$$j = \Delta A / \Delta A_\infty \tag{14}$$

where ΔA_∞ represents ΔA at infinity of C_s.

The partition coefficient K_x is in fact the ratio of mole fractions between the bulk and micellar phase, and is defined as

$$K_x = \frac{X_a^{\,m}}{X_a^{\,f}} \tag{15}$$

where $X_a^{\,f}$ and $X_a^{\,m}$ are the mole fractions of organic additive in the respective phases and are related with concentrations of species in the solubilization system.

$$X_a^{\,m} = \frac{C_a^{\,m}}{(C_a^{\,m} + C_s^{\,m})} \;;\quad X_a^{\,f} = \frac{C_a^{\,f}}{(C_a^{\,f} + C_s^{\,f} + n_w)} - \frac{C_a^{\,f}}{n_w} \tag{16}$$

where $C_s^{\,f}$ and $C_s^{\,m}$ represent concentration of surfactant in monomeric and miceller states, respectively. Under the present experimental condition , both $C_a^{\,f}$ and $C_s^{\,f}$ in the denominator of $X_a^{\,f}$ are negligible relative to n_w , the number of moles of water per liter. For convenience, another partition coefficient K_c , expressed in molar concentration units is defined as

$$K_c = \frac{C_a^{\,m} / (C_a^{\,m} + C_s^{\,m})}{C_a^{\,f}} \tag{17}$$

where K_c is related with K_x as $K_c = K_x / n_w$, using equations (13) and (14) , equation (17) is rewritten as a linear form :

$$\frac{1}{\Delta A} = \frac{1}{K_c \, \Delta A_\infty \, (C_a^{\,m} + C_s^{\,m})} + \frac{1}{\Delta A_\infty} \tag{18}$$

Based on the present model of solubilizatuion system it is expected that , as C_s approaches infinity , C_a^m approaches C_a and C_s^m to C_s^{mo} respectively, where C_s^{mo} represents $C_s - CMC_o$ (CMC_o is the CMC of surfactant in water). Then, at infinite C_s equation (!8) is simplified as

$$\frac{1}{\Delta A} = \frac{1}{K_c \Delta A_\infty (C_a + C_s^{mo})} + \frac{1}{\Delta A_\infty} \tag{19}$$

Equation (19) shows that K_c is obtained from the plot of $1/\Delta A$ against $1/(C_a + C_s^{mo})$. The intercept provides the value of ΔA_∞, the slope of the linear relation provides the value of partition coefficient K_c.

Now assuming the linear relation

$$C_s^f = C_s^{fo} + \frac{d\, C_s^f}{d\, C_a^f} \,.\, C_a^f \tag{20}$$

It is based on the relation

$$CMC = CMC_o + \frac{d\, CMC}{d\, C_a} \cdot C_a \tag{21}$$

At the CMC it follows

$$\begin{aligned} C_s^m &= C_s - C_s^f \\ C_s^m &= C_s - (C_s^{fo} - k\, C_a^f) \end{aligned} \tag{22}$$

where $k = d\, C_s^f / d\, C_a^f$ and C_s^f (C_s^f on the absence of additive) is taken to be CMC_o. On the other hand , C_a^m in equation (18) is written from the definition of j as

$$C_a^m = j\, C_a \tag{23}$$

Since $C_a^f = (1-j)\, C_a$, we obtain

$$C_a^m + C_s^m = j\, C_a + C_s^{mo} - k\, C_a (1-j) \tag{24}$$

where $C_s^{mo} = C_s - C_s^{fo} = C_s - CMC_o$, same as in equation (19). Substituting equation (24) in equation (18), the resultant equation is

$$\frac{1}{\Delta A} = \frac{1}{K_c \Delta A_\infty [C_s^{mo} - k C_a + (1 + k) C_a /]} + \frac{1}{\Delta A_\infty} \qquad (25)$$

The plot of $1/\Delta A$ against $1/[C_s^{mo} - kC_a + (1+k) C_a /]$ gives another way to calculate partition coefficient K_c. Intercept gives ΔA_∞ and the slope gives the value of partition coefficient K_c.

2.7 APPROXIMATE NUMBER OF ADDITIVE MOLECULES PER MICELLE

Approximate number of additive molecules incorporated in a single micelle can be calculated by using the following equations[1,28,29]

$$n = \frac{C_m}{M} \qquad \text{and} \qquad M = \frac{C_s - CMC}{N}$$

where C_m is the concentration of the additive solubilized in the micelle, M is the micelle concentration, C_s is the total surfactant concentration, and N is the mean aggregation number of surfactant. The concentration of the solubilized additive, C_m can be determined by employing the following relation[30]

$$C_m = \frac{A_o - A}{\varepsilon_o - \varepsilon_m}$$

where A_o is the absorbance of additive solution in the absence of surfactant, A is the absorbance at the same wave length in the presence of surfactant, ε_o is calculated from A_o, and ε_m is determined at higher surfactant concentration above CMC where the absorbance of the additive–surfactant solution becomes almost constant.

3

LITERATURE REVIEW

LITERATURE REVIEW

Much more work, which is related with anionic surfactants have been reported by several researchers.[24,32,33] The effect of additives on the critical micelle concentration (CMC) of SDS has been investigated by Shirahama and Kashiwabara.[6] Hayase and Hayana[9] explained the effect of alcohols on the CMC depression in aqueous SDS solution. Shah, Awan and co-workers[38] investigated the solubilization of phenol and benzyl alcohol by cationic and anionic surfactants micelles.

Abu-Hamdiyyah and Kumari[34] evaluated the distribution coefficeient of amphiphilic additives between water and CTAB miclles using CMC data. They explained the solubilization tendency and hydrophobic interaction of 1-alkanols in water, heavy water and urea solution.[35] Abu-Hamdiyyah also related the distribution coefficient with the ability of additive to strengthen the hydrophobic bonding and its ability to increase the effective micellar degree of ionization.[36] Manabe and Koda[37] investigated the effect of 1-alkanols on ionization of SDS micelles and study also include a new approach to calculate the interaction coefficient.

Davidson and Jencks[39] studied the effect of concentrated salts solutions on merocyanine dye. Colichman[40] has investigated the spectral study of long chain quaternary ammonium salts in bromophenol blue solutions. Minch and Shah[41] reported the spectroscopic studies of hydrophobic association of merocyanine dyes in cationic and anionic surfactnats micelles.

Now work has been done on sodium dodecylbenzenesulfonate (SDBS) micelles. In this work, solubilization of amphiphilic hemicyanine dyes by an anionic surfactant (SDBS) micelles has been studied by differential spectroscopic method.[13] The standard free energy change of transfer of dye from water to micelles, ΔG^{o}_{p} and standard free energy change per methylene group, ΔG^{o}_{p} (CH_2) have also been calculated.

The spectroscopic investigation of the solubilization of different dyes by surfactants micelles were done by several authors.[28, 41--51] A vast literature,[11, 52--58, 61--63] on solubilization and amphiphilic hemicyanine dyes in the field of chemistry and biology is available and has been utilized for this study.

4
EXPERIMENTAL

EXPERIMENTAL

4.1 MATERIALS

Sodium dodecylbezenesulfonate (SDBS), was obtained from Fluka and was used without further purification. The five amphiphilic hemicyanine dyes, i.e., (Dimethylamino) stilbazolium butyl sulfonate – (Dipentylamino) stilbazolium butyl sulfonate were provide from Prof. Fromherz's Lab in Ulm, Germany. KCl and methanol (A.R Grade) was the product of E-Merck and were used as received. The water used was distelled twice.

4.2 CONDUCTANCE MEASUREMENT

4.2.1 CONDUCTIVITY METER

The conductance measurements were made on Microprocessor Conductivity Meter (WTW), LF 2000/C model of Wissenchaftlinch Technische Werkstatten (Germany).It can detect the conductance of very dilute solutions as 1 ppm accurately. It has digital range from 10^{-3} μ S cm^{-1} to S cm^{-1}. It displays specific conductance. Cell constant was selected according to the experimental conditions (0.1 cm^{-1}), and reference temperature was selected at 25 °C.

Electrode used in this work had cell constant 0.11cm^{-1}, which was coated with platinum black in order to avoid the polarization effect. There was a temperature detector immersed in the analyzing solution. Thermostat made by Japan Coda Company, was used to control the temperature with ± 0.01°C.

4.2.2 CALIBRATION OF THE ELECTRODE

The electrode was calibrated to avoid the polarization effect. This can be confirmed by evaluating the cell constant of the known concentration. The aqueous solution of KCl (0.0118 mol/dm^3) were prepared and their conductances were measured at 25 °C, the cell constants were calculated from the relationship

$$K = \frac{\Lambda_m C}{G^0} \times 1000 \qquad (26)$$

where Λ_m = molar conductance of KCl solution of concentration C (mol/dm^3). G^o is the conductance of respective solution. The molar conductances used in expression (26) were calculated from the equation.

$$\Lambda_m = 149.93 - 94.65\, C^{1/2} + 58.74\, C \ln C + 198.4\, C^{3/2} \qquad (27)$$

The coefficient in this equation were taken from reference.[31] The equation (27) is applicable upto 0.012 mol/dm^3 concentration of aqueous KCl solutions at 25 ^{0}C, and with the accuracy of ± 0.013 %. The conductance data for the cell constant is given in Table 8. The average value of cell constant obtained from equations (26) and (27) was 0.1306 cm^{-1}.

4.2. 3 THE PROCEDURE FOR CONDUCTANCE MEASUREMENTS

Critical micelle concentration (CMC) of the surfactant (SDBS) was determined from the plot of specific conductivity versus concentration of the SDBS. Measurements of the conductivity were carried out in a water thermostat controlled within ± 0.01°C at 25 °C for SDBS. Solution was prepared by weight in the following way. An aqueous solution with a given concentration of an additive was prepared, and a portion of it was used for the preparation of SDBS solution with its concentration 10^{-3} mol/dm^3. Some amounts of the SDBS solution was successively added into a conductivity cell in which a certain amount of the aqueous additive solution had been previously added . Therefore, the concentration of the additive was kept constant in an experimental run.

4.3. ULTRAVIOLET VISIBLE SPECTROSCOPY

4.3.1 DOUBLE-BEAM SPECTROPHOTOMETER

All the absorptions by the sample in the visible range were measured on a Hitachi Double-beam Model 220 UV-visible spectrophotometer at 25 °C. The instrument has two light paths, one for the sample and other for the blank or reference. The detector alternately sees the reference and the sample beam and the out put of the detector is proportional to the ratio of the intensities of the two beams I_t/I_o. The cells used for the visible spectrophotometry were square cuvettes 1 cm thick (internal distance between parallel walls). The temperature was maintained at 25 °C for a solution by using Japan Coda company thermostat.

4.3.2 THE PROCEDURE FOR DIFFERENTIAL ABSORPTION SPECTRA MEASUREMENT

An additive solution (amphiphilic hemicyanine dyes) with a given concentration was prepared by volume. Then a portion of a solution was used as the solvent of SDBS solutions. The differential absorption spectra was measured by setting the cuvette filled with additive solution in the reference side and that of the SDBS solution at the same additive concentration in the sample side of the spectrophotometer. These measurements were made at 25 °C by using the thermostat.

4.3.3 THE PROCEDURE FOR VISIBLE ABSORPTION SPECTRA MEASUREMENT

The visible absorption spectra of five amphiphilic hemicyanine dyes each of concentration 10^{-5} mol/dm^3 solution were measured at 25 °C. Then the visible absorption spectra of 10^{-5} mol/dm^3 dye solutions containing SDBS in the concentration range 10^{-4}

upto10^{-3} mol/dm^3 were taken on the spectrophotometer. The concentration of each dye was kept constant during the study. All the spectra of one dye were taken as close together in time as possible using the same stock solutions. The reproducibility of duplicate λ_{max} determination was ±1 nm.

5

RESULTS & DISCUSSION

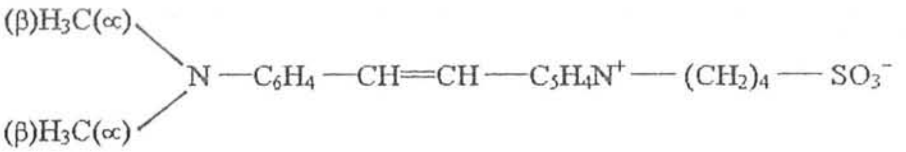
DISCUSSION

Part-I

5.1 HYDROPHOBIC INTERACTION OF HEMICYANINE DYES IN SODIUM DODECYLBENZENESULFONATE (SDBS)

5.1.1 WAVELENGTH SHIFTS

Table 1 displays the wavelength λ_{max} and maximum absorbance of all the dyes in aqueous solution. The λ_{max} against number of carbon atoms (m_p) in dialkyl chain of all the hemicyanine dyes (Dyes 1- 5) without surfactant is shown in Figure 1. Figure 1 shows that there is a significant change in the λ_{max} going from dye 1 to dye 2. But in the case of dye 3, dye 4 and dye 5, this shift becomes some what constant.



$$((\beta)H_3C(\propto))_2N-C_6H_4-CH{=}CH-C_5H_4N^+-(CH_2)_4-SO_3^-$$

It is evident from the structure of the dye that there are 3 β-hydrogens attached to ∝-carbon in both the methyl groups in case of dye 1. Now for dye 2, 1 β-hydrogen is replaced by another carbon atom, which give rise to dominant λ_{max} shift. But in the case of dye 3, dye 4 and dye 5, no more β-hydrogens are replaced by carbon atoms and the alkyl chain extends normally which results in small change in the λ_{max} value while going from dye 2 to dye 5. In case of dyes having high hydrophobicity, there is slight change in the λ_{max} values which can be considered due to steric factor.

Figure 2 shows the effect of surfactant concentration (C_s) on the λ_{max}. Tables 2-6 displays the effect of various concentration of SDBS on the values of maximum absorbance A, wavelength at maximum absorbance λ_{max} and the electronic transition energy ΔE_T (Joules) of the solutions of all the dyes respectively at 25 °C.

It is evident from the data given in Tables 2-6, that with the increase of surfactant concentration (C_s), the visible spectra of the dyes shift to a higher wavelength indicating more number of dye molecules are incorporated into the micelles, therefore, the surfactant concentrations cause a red shift in the spectra of dyes. It is due to the formation of 1:1 complex between the dye and the surfactant, as observed between alkyl salts and merrocyanine dyes by Davidson and Jencks,[39] i.e.,

Compound	Salt concentration (mol/dm^3)	λ_{max} nm
Pure dye	0	443
$(CH_3)_4N^+Br^-$	1.2	448
$(CH_3)_4N^+Cl^-$	1.2	447

There is a clear red shift from 443 nm to 448 nm and 447 nm for both salts respectively. In this case, the complex formed by the salts resembles to the complex formed between dye and CTAB which results in the red shift.[39]

In present work, when the dye hydrophobicity is low (dye 1 to dye 3), the hydrophobic part of the dye molecule is still directed towards the aqueous region (in pre-micellar region), and butyl sulfonate group towards anionic head of the surfactant which causes the repulsive interactions between the dye and surfactant. These interactions may let the pyridinium moiety of the dye molecule to interact strongly with the surfactant head group, so the red shift is observed. On the other hand, when the dye hydrophobicity is high(dye 4 and dye 5), the dialkyl chain of the dye interacts with the alkyl chain of surfactant. The dye orients itself parallel to the surfactant molelcule with positively charged pyridinium nitrogen and negatively charged head of surfactant lying side by side interacting strongly. While the butyl sulfonate group remains directed towards the aqueous region and thus causing almost negligible repulsion with the anion head of the surfactant. These strong interactions result in the shift of the spectra towards smaller wavelength called blue shift.[59,60] In the case of, dye 4 and dye 5, an unexpected blue shift is observed in the pre-micellar region of surfactant. This phenomenon can be explained by considering the interactions present between the negatively charged head of anionic surfactant SDBS and positively charged pyridinium moiety of the dye.[59,60]

When the concentrations of the surfactant are well above the CMC, the values of λ_{max} becomes almost uniform and do not change much with the increasing surfactant concentration. It is so because a large number of dye molecule are incorporated into the micelles. The absorbance, A increase more intensively with the increase of surfactant concentration (C_s) and finally becomes almost constant. This increase in absorbance is regarded to be caused by the penetration of dye molecules into the micelles. Red shift in the micellar phase is due the fact that the micellar phase is less polar than the aqueous phase. This phenomenon is called solvochromatism. It is the phenomenon in which the absorption spectra of dye shifts to higher wavelengths due to decreasing solvent polarities. In water D1-ASP (Amino styryl pyridinium) system $\lambda_{max} = 448.8$ nm and in DMSO, $\lambda_{max} = 470$ nm.[59,60]

The value of red shift is greater for the dye having high hydrophobicity. The red shift also depends on the nature of the charge (positive or negative) present on the surfactant head group. The red shift values for the same amphiphilic hemicyanine dyes in aqueous micellized anionic and cationic surfactants was also observed by Awan and Shah.[68] They observed in the case of LDS (anionic surfactant), the red shift is more for dye 1, i.e., $\Delta\lambda_{max} = 26.0$ nm, while for CTAB (cationic surfactant) the value is less, i.e., $\Delta\lambda_{max} = 8.8$ nm. Hence we conclude that the peak or red shift for dye 1 is more prominent in anionic surfactant solution than in cationic surfactant solution. The head group of LDS contains negative charge group (SO_4^-), this negative charge is neutralized to some extent by the positive charge present on the dye molecule. Due to this positive charge, the dye molecule is attracted by the negative head group of LDS and in turn, dye molecules are penetrated more deeply into anionic micelles. In addition, the more hydrophobic dyes are more solubilized then less hydrophobic dyes. The reason for less red shift in case of cationic micelles is that the positive head group of surfactant interact with the benzene ring present in the dye,[64] and consequently a dye molecule does not penetrate very deeply into the CTAB micelles, unless the dye hydophobicity is higher enough to overcome the interactions with head group of CTAB. Bunton and Sepulveda,[65] while investigating the hydrophobic and coloumbic interactions in the micellar binding of phenols suggested that the effect of the negative charge present on the solubilizate is not particularly large.

5.1.2 CHANGE IN ABSORBANCE VALUES

There is a continuum of environment from the hydrated micelle surface to a non-polar core. The solubilizate may be adsorbed on the surface oriented near the surface (short penetration), or burried deeply (deep penetration), or it may be trapped in the hydrocarbon core. Moreover, the solubilization is a dynamic equilibrium process and the solubilizate may spend different residence times at different levels between the core and the surface of micelle. In case of dye 1 and dye 2 (Tables 2,3), the absorbance values show same trend due to the reason that dye 1 and dye 2 orient near the surface with negligible Van der waal interactions with the hydrocarbon core of the micelles. While in the other case of dye 4 and dye 5 (Tables 5,6), the dialkyl chain of the dyes strongly interact with the non-polar hydrocarbon core of the micelles and keeps the molecule rigid (deep penetration). In the case of dye 3 (Table 4), the random absorption values show that there is imbalance of hydrophilic and hydrophobic forces, which keeps the dye some what dynamic into the micelle.[57]

5.1.3 APPROXIMATE NUMBER OF DYE MOLECULES INCORPORATED PER MICELL

Approximate number of dye molecules incorporated per micelle (n) have been calculated using a relationship.[1,28,29]

$$n = \frac{C_m}{M} \quad \text{and} \quad M = \frac{C_s - CMC_O}{N}$$

Where C_m is the concentration of the dye solubilized in the micelle, M is the micelle concentration, C_s is the total surfactant concentration, CMC_O is the CMC of surfactant in water at 25 °C and N is the mean aggregation number of surfactant, available in literature.[66] Concentration of the solubilized dye C_m can be determined by employing the following relationship[30]

$$C_m = \frac{A_o - A}{\varepsilon_o - \varepsilon_m}$$

where A_o is the absorbance of dye solution in the absence of surfactant, A is the absorbance at the same wavelength in the presence of surfactant, ε_o is calculated from A_o, and ε_m is determined at higher surfactant concentration above CMC where the absorbance of the dye-surfactant solution becomes almost constant.

Table 7 shows the approximate number of dye molecules incorporated per micelle of SDBS for all the dyes. At a particular concentration of surfactant C_s, n increases with the increase of hydrophobicity of the dyes. However, the approximate number of dye molecules incorporated per micelle of SDBS are less as compared to other anionic and cationic surfactants systems.[67,68] This less number of dye molecules incorporated in single micelle of SDBS is due to the fact that the aggregation number of SDBS is just 24, whereas aggregation numbers of other surfactants, e.g., LDS, SDS, CTAB are 63, 71 and 80 respectively.[69,70] So SDBS micelle allows only limited number of dye molecules to incorporate into single micelle. Otherwise, incorporation of large number of dye molecules may disturb the micelle structure.

Part-II

5.2 SPECIFIC CONDUCTANCE AND DEPRESSION IN CMC

Almost from the very beginning of the study of the properties of surfactants solutions (actually, soap solutions), it was recognized that their bulk properties were unusual and indicated the presence of colloidal particles in the solutions. When the surfactant concentration of an anionic surfactant of the type Na^+R^- in water is plotted against any physical property, e.g., specific conductance, surface tension, osmotic pressure, or density change etc., the curve is obtained, instead of being the smoothly decreasing curve characteristic of ionic electrlytes of this type has a sharp break in it, at low concentrations. This break in the curve, is interpreted as evidence of the formation at that point of micelles from the unassociated molecules of surfactant with part of the charge of the micelle neutralized by associated counterions. The concentration at which this phenomenon occurs is called the *Critical Micelle Concentration* (CMC). The structure of the micelle in aqueous medium, at concentrations not too far from the CMC and in the absence of the additives that are solubilized by the micelles, can be considered to be roughly spherical with an interior region containing the hydrophobic groups of the surfactant molecules, of the radius approximately equal to the length of a fully extended hydrophobic group, surrounded by an outer region containing the hydrated hydrophilic groups and bound water.[1]

5.2.1 CMC OF SDBS SOLUTION

Critical micelle concentration of SDBS was verified by conductance method. Gershman[71] determined the CMC of SDBS at 60 °C which is 1.2×10^{-3} mol/dm^3. The cell constant for conductivity meter for the calibration purpose was calculated using KCl solution and shown in Table 8. The value of average cell constant find out to be 0.1306 cm^{-1}. The specific conductance data for SDBS without dyes solutions at various surfactant concentration is given in Table 9. The specific conductance data is plotted against the square root of respective concentration values in Figure 3. The critical micelle concentration (CMC) is evaluated by drawing two tangents joining the initial and end points, respectively. The verified CMC of SDBS is 6.3×10^{-4} M at 25 °C.

5.2.2 DEPRESSION IN CMC BY THE ADDITION OF DYES

Depression in CMC depends on the balance between the hydrophobic and hydrophilic forces. For shorter chain additives, the hydrophilic group has more chance of hydrogen bonding with water, so that the orientation of surfactant molecule is near the interface. For longer chain additives, the possibility of penetrating into the hydrophobic core is more. Additive molecules infact increase the hydrophobic or hydrophilic capability of a molecule, so that affecting the hydrphobic and hydrophilic force balance.

Small amounts of organic additive may produce marked change the CMC in aqueous media. Shorter chain additives are most probably adsorbed mainly in the outer portion of the micelle close to the water-micelle interface. The longer chain additives are probably adsorbed mainly in the core of micelle. Adsorption of the additives in these fashions decreases the work required for micellization, in the case of anionic surfactants probably by decreasing the mutual repulsion of the ionic heads in the micelle. Depression of the CMC appears to be greater for the straight chain compounds than for branched chain compounds and increases with chain length to a maximum when the length of the hydrophobic group of the additive approximates that of the surfactant.[1,72]

Specific conductance data SDBS in presence of small amounts of dyes are given in Tables 10-14 and the respective CMC plots are given in Figures 4-23. The depression in the CMC values of the surfactant SDBS was observed for all hemicyanine dyes, i.e., from dye1 to dye 5, at various dye concentrations. The values of depression in CMC for all dyes are given in Table 15, and respective plots in Figure24.

It has been observed that the depression in CMC is to lesser extent with dye 1 as compared to more hydrophobic dyes, e.g., dye 5. The change in CMC for alcohols and alkanols has been observed for various surfactants by a number of workers,[13,32,38] showing the same trend. Two main factors have been considered for CMC lowering[6,37]: an increase in entropy of mixing of surfactant with the solubilized dye in micelles, and the decrease in the electrical work of micellization of the surfactant-ion due due to decrease of the surfactant charge density caused by the solubilized dye.

The trend of depression in CMC (Figure 24) is more evident for more hydrophobic dyes, because as the hydrophobicity of dye molecule increases, the chance for it to penetrate into the micelle increases causing a more stable system. As the hydrophobic part of surfactant molecule is oriented inside the micelle, the hydrophobic part of dye is incorporated more inside the micelle then to the stern layer. For dye 2 and dye 3 moderate change in CMC is observed but the trend of depression in CMC is common in all the dyes.

5.2.3 RATE OF CMC DEPRESSION

Rate of CMC depression for all the dyes (dye 1 to dye 5) are calculated by plotting concentration of dye (C_a) against the depression in CMC's. The slope of the plot, i.e.,

$$\frac{d\,\mathrm{CMC}}{dC_a} = k$$

represents the rate of CMC depression. This is an important parameter and is used to calculate partition coefficient and interaction coefficient θ.[30,73] θ is a measure of the penetrability of the micelles by the amphiphilic additives.

The k values suggest that the rate of CMC depression is more for the dyes consisting of long chain of alkyl groups ($m_p = 10$). Table 16 and Figure 24 illustrate the data and plot of CMC depression rate, respectively. As the CMC of system depends on the hydrophobicity, so the trend is similar as it should be.

5.3 DIFFERENTIAL ABSORBANCE

Figures 25-29 shows the differential absorption spectra of all the dyes solutions, respectively in the presence of SDBS at certain concentration of dye (1.0×10^{-5} mol/dm^3). The differential absorbance, ΔA, increases with increasing surfactant cocentration (C_s). Figure 30 shows the differential absorbance, ΔA, of all the dyes solutions in the presence of various concentration (C_s) of SDBS at 25 °C. It is evident from the curves that ΔA is sustantially zero at the pre-micellar concentration of surfactant. As the concentration of SDBS increases, ΔA increases for each dye indicating an increase in the amount of solubilized dye in the surfactant micelles, as observed in other cases.[57,58]

Moreover, hydrophobic dye (dye 5) shows significant increase in ΔA than other dyes. The analysis for the amount of solubilized dye will be made at the wavelength, λ_{max} , where the highest peak observed in the spectra. The wavelength, λ_{max} , for the respective dye is shown in Tables 17-21. The shift of each peak with increasing C_s can be ignored within the experimental error (± 0.5 nm). λ_{max} is almost constant for a particular dye at various surfactant concentrations in micellar phase.[13,58,74]

The values of λ_{max} of these dyes fall in the visible region of the electromagnetic spectra, and we expect n—π^* type electronic transition which usually take place into visible region of the spectrum.[46] π—π^* and n—π^* transitions of organic additives usually occur in the region 200-700 nm of the visible spectrum due to the chromophoric groups in the molecule.[24]

It is evident from the data given in Tables 17-21 that λ_{max} first increases and then decreases with the increasing hydrophobicity of the dyes. When the dye hydrophobicity is very low as in case of dye 1, the dye molecule orients itself near the hydrophilic surface of the micelles. As the hydrophobicity increases, resulting in an increase in the interaction between the dialkyl chain of dye and hydrophobic part of the surfactant, the dye molecules more penetrate into the micelles. This results in an increase in the λ_{max} value, while going from dye 1 to dye 3.

When the hydrophobicity of dye is high as in the case of dye 4 and dye 5, the dye is penetrated deeply into the micelles with the anilino nitrogen present almost in the hydrocarbon core of the micelles with hindered lone pair. Which results in the decrease in λ_{max} values. The relation among the differential absorbance (ΔA), λ_{max}, $[Ca + Cs^{mo}]$ and concentration of SDBS (C_s), in presence of each dye at 25 °C are given in Tables 22-26.

5.4 PARTITION COEFFICIENT

The partition coefficient, K_x, of solubilizate between the bulk water and the micellar phase is an important factor not only in elucidating the mechanism of solubilization but also in understanding biological phenomenon, e.g., interaction between biological membranes and anesthetics.[11] Partition coefficient is basically the ratio of the mole fraction concentration of the additive in the micelle to its mole fraction in the surrounding aqueous solution. Higher value of the partition coefficient suggests that more of the additive is solubilized into the micelle as compared to the aqueous phase and vice versa.[7]

5.4.1 PARTITION COEFFICIENT BY DIFFERENTIAL ABSORBANCE

Partition coefficients of all the hemicyanine dyes have been calculated using the relationship proposed by Kawamura, Manabe and co-workers.[13] Partition coefficient,

K_c , for additive between the bulk water and the micellar phase is given by the relationship.

$$\frac{1}{\Delta A} = \frac{1}{K_c \, \Delta A_\infty \, (C_a + C_s^{mo})} + \frac{1}{\Delta A_\infty}$$

K_c is obtained from a plot of $1/\Delta A$ against $1/\,(C_a + C_s^{mo})$. The intercept and the slope of this plot give $\Delta A_\propto$ and K_c respectively. In above relationship ΔA, C_a represents differential absorbance and concentration of additive respectively. While $C_s^{mo} = C_s - CMC_o$. Here C_s is the total surfactant concentration and CMC_o is the CMC of SDBS in water at 25 °C.

The straight line plots of above equation for all the dyes are shown in Figure 31 and the data is given in Tables 22-26. Least square method is used for plotting the data. The values of K_c and K_x along with slopes and intercepts are given in the Table 27 where $K_x = K_c \times n_W$, where n_W is the number of moles of water per dm^3, i.e., 55.5 mol/dm^3.

Since the amino stilbazolium butyl sulfonate group is common, and the presence of dialkyl chain

$$[\ {>}N{-}C_6H_5{-}CH{=}CH{-}C_5H_4N^+{-}(CH_2)_4{-}SO_3^-\ ]$$

on the dyes contribute a major role in the process of solubilization in the micelles of SDBS. The value of the partition coefficient K_x increases as we replace lower alkyl groups with the higher ones, i.e., from methyl to pentyl dyes. For dyes having short hydrophobicity, the value of K_x are less and it is due to the less solubilization of these dyes into the micelles, which in turn depends upon less hydrophobic dialkyl group. In the case of dye 4 and dye 5, the values of K_x abruptly increases due to the more hydrophobic character of the dyes. however, dye 5 has the maximum value of partition coefficient.

The change in the partition coefficient of the water-micelle system is due to the type of interaction occurring inside the micelle. In the case of dye containing methyl group, i.e., dye 1, the hydrophilic character of dye is prevalent, so the dye orients itself near the stern layer of the micelle. Whereas in the case of dye 5, there is maximum hydrophobic character, so it deeply penetrates in the micelles. This shows that as the hydrophobic character is increased, the absorption of dyes increases and, in turn the partition coefficient also increases.

The results are also confirmed by the ΔG°_{p} values of the dyes (Table 28). The more hydrophobic dye 5 induces micellization, which is the out come of a strong interaction between the dipentyl groups of dye and the surfactant's hydrocarbon chain inside the micelles in aqueous solutions. It is assumed that each dye forms a complex with the surfactant molecules in the bulk of the solution prior to the penetration into the micelles,[40] when a dye molecule interacts with a surfactant molecule an insoluble salt is formed. At first the adhesion of dye surfactant complex to the micelle surface takes place, then the dye reorients into the inner hydrophobic portion of the micelle. This is observed in the case of anthraquinone dyes.[28,30] During this reorientation, the more hydrophobic dyes, i.e., dye 4 and dye 5 makes their way into the interior of micelles more actively. Sato and Kawasaki[75] suggested that the hydrophobic interactions between micelles and a cationic dye (3,3-diethyl thiocarbocyanine iodide) molecule play a very important role in the formation and solubilization of dye aggregates in the micelles.

5.4.2 PARTITION COEFFICIENT BY DIFFERENTIAL ABSORBANCE-CONDUCTANCE METHOD

The improved relationship including two new factors j and k by Kawamura and Manabe[13] is shown below

$$\frac{1}{\Delta A} = \frac{1}{K_c \Delta A_{\infty} [C_s^{mo} - kC_s + (1+k) C_s j]} + \frac{1}{\Delta A_{\infty}}$$

For this equation, it is necessary to determine the values k and j. k is determined from the slope of the plot between CMC versus C_s by conductivity method for all the five dyes. j is calculated from equation 14 by using ΔA_∞ obtained from the intercept of the plot of equation 19. k and j values are given in Tables 16,29.

The physical meaning of j is the fraction of the amount of solubilized dyes in that of added dyes. It is expected that, at a certain C_s , j is equal to zero in the nonmicellar region upto the CMC and increases with increasing C_s above the CMC. As C_s increases upto infinity, j approaches unity, since almost all added dye should be solubilized in the micelle.

The values of $1/\Delta A$, λ_{max} , $1/ [C_s^{mo} - kC_s + (1+k) C_s j]$ and concentrations of SDBS are reported in Tables 30-34 for all the dyes. By plotting $1/\Delta A$ versus $1/ [C_s^{mo} - kC_s + (1+k) C_s j]$, we get slope = $1/K_c\Delta A_\infty$ and intercept = $1/\Delta A_\infty$ and hence we can calculate K_c and K_x ($K_x = K_c \times n_w$). The values of K_c and K_x along with the slope and intercept are given in Table 35. Table 36 presents a summary of K_x obtained using equation 25 and corresponding ΔG°_p values.

5.5 THERMODYNAMIC PARAMETERS ΔG°_p AND $\Delta G^\circ(CH_2)$

5.5.1 STANDARD FREE ENERGY CHANGE OF SOLUBILIZATION (ΔG°_p)

Standard free energy change of transfer for all the dyes are shown in the Tables 28 and 36 using K_x calculated by Eq. 19 and 25. The values are calculated using a relationship

$$\Delta G^\circ_p = - RT \ln K_x$$

where R is gas constant, T is the absolute temperature and K_x is the partition coefficient.

It is observed that the value of ΔG°_{p} becomes more and more negative if we go from dye 1 to dye 5. It is a well known phenomenon that more negative value of ΔG°_{p} represent more stabilization of any system. We can say that in the system, the dye molecule will try to go to that part of the system where they have more negative free energy and system is more stable.

The free energy values of all the dyes suggest that with the increase of K_x, ΔG°_{p} become more and more negative. The ΔG°_{p} value for dye 1 is least and for dye 5 most negative. It means that dye 5 is the most stable system. It also confirm that K_x having more value causes a stabilized system. ΔG°_{p} value show that the dyes in bulk environment are less stable as in the micellar, so they incorporate themselves inside the micelle. The value of ΔG°_{p} show higher solubilization of dye 4 and dye 5 than dyes 1,2 and 3.

5.5.2 FREE ENERGY CHANGE PER METHYLENE GROUP $\Delta G^{\circ}(CH_2)$

Free energy change of transfer per methylene group $\Delta G^{\circ}(CH_2)$, from the bulk water to micelle is evaluated from the slope of the straight line as shown in Figure 33.

$$- \Delta G^{\circ}(CH_2) = RT \frac{d \ln K_x}{dm}$$

where K_x is partition coefficient obtained using equation 25, R is gas constant, T is the absolute temperature and m refers to m_p or m_n ,i.e., number of carbon atoms in dialkyl chain of the dye molecule. $\Delta G^{\circ}(CH_2)$ thus obtained for the dyes is -1.091 kJ/mole or -0.261 kcal/mole. Table 37 shows the calculation for $\Delta G^{\circ}(CH_2)$. $\Delta G^{\circ}(CH_2)$ in SDBS system was found to be - 0.261 kcal/mol while $\Delta G^{\circ}(CH_2)$ in SDS system was found to be - 0.251 kcal/mol.[68] The low value of $\Delta G^{\circ}(CH_2)$ suggest that system with SDBS is more favourable for solubilization.

The negative value of $\Delta G^{o}(CH_2)$ indicates that the solubilization of hemicyanine dyes into micelles is a spontaneous phenomenon. $\Delta G^{o}(CH_2)$ value suggest that methylene (CH_2) group in a molecule of dye contribute -1.091 kJ/mol energy during the process of solubilization in SDBS micelles. The energetic consideration may lead us to conclude that the shorter chain dyes are located at micellar surface region but the longer chain dyes may penetrate deeper and are incorporated into the hydrophobic core of the micelle.[76]

5.5.3 DEPENDENCE OF K_x ON NUMBER OF CARBON ATOMS IN DIALKYL CHAIN OF DYES

The dependence of partition coefficient (K_x) on the number of carbon atoms in the dialkyl chain (m_p) of all dyes is shown in Figure 34. K_x (partition coefficient) increases somewhat in a curve. The effect of (m_p) in dye 1 and dye 2 is not prominent but in the case of dye 3, dye 4 and dye 5, the graph shows almost linear change. Increasing the dialkayl chain, there is remarkable effect on K_x due to the more penetration ability of the dye molecules in the micelles. It is a well known phenomenon in the case of micelles that the less hydrophobic additives are oriented near the stern layer or the outer portion of the micelle, while in the case of more hydrophobic additives the orientation is expected near the outer portion of the core of the micelles. The K_x values are in a good agreement to the general phenomenon. Higher the K_x values, more will be the solubilization of dyes in the micelles and vice versa .

5.6 INTERACTION COEFFICIENT (θ)

Interaction coefficient (θ), describes the extent of interaction between the dye and surfactant molecules. Less value of θ indicates more interaction between the surfactant and the additive. θ is a function of the extent of the hydrocarbon-water contact region in the micelle. θ may be looked upon as a measure of the penetrability of the micelle by the amphiphilic additives.

The interaction parameter is calculated by using the equation[24]

$$-\frac{dCMC}{dC_s} = \frac{K_x \, . \, CMC_o \, . \, \theta}{n_w} \qquad (1)$$

where $-dCMC/d\,C_s$ is the slope obtained by plotting CMC's Vs. C_s. K_x is the partition coefficient, CMC_o is the CMC of SDBS in water at 25 ° C and n_w is the number of moles of water per dm^3 (55.5). Taking logrithm of above equation on both sides, we get,

$$\log\left(-\frac{dCMC}{d\,C_s}\right) = \ln K_x + \log\left(\frac{CMC_o\,\theta}{n_w}\right) \qquad (2)$$

The CMC data and K_x in Table 35 makes it possible to estimate θ from the line plotted in Figure 35. It is noted that based on Eq. 2, line has slope of unity. The value of θ comes out to be 0.84 and is given in Table 38.

According to Abu-Hamdiyyah,[8] θ is a function of surfactant chain length and independent of additive. Thus, once θ is known for a given surfactant, the partition coefficient of any amphiphilic additive may be estimated from its CMC lowering effect at low concentration.

TABLES

TABLE 1

Maximum spectral values of Dialkylamino stilbazoliam butyl sulfonate dyes in aqueous solution at 25 °C

No.	Additive	C_a x 10^5	A	λ_{max}
1	Dye 1	1.0	0.305	454.0
2	Dye 2	1.0	0.206	477.0
3	Dye 3	1.0	0.157	481.8
4	Dye 4	1.0	0.108	484.0
5	Dye 5	1.0	0.089	487.0

Additive	Dialkylamino stilbazoliam butyl sulfonate
C_a	Concentration of dye (mol / dm^3)
A	Maximum absorbance
λ_{max}	Wavelength of maximum absorbance (nm)

TABLE 2

Relation among A, λ_{max} and concentration of SDBS for Dimethylamino stilbazoliam butyl sulfonate-Water mixture at 25 °C

No.	$C_s \times 10^4$	A	λ_{max}	$\Delta E_T \times 10^{22}$
1	1.2	0.235	455.0	-9.26
2	2.1	0.236	456.0	-19.20
3	3.0	0.236	456.6	-24.93
4	4.2	0.289	457.0	-28.74
5	5.1	0.292	459.0	-47.70
6	6.9	0.295	467.0	-121.88
7	10.2	0.346	467.3	-124.62
8	15.0	0.354	467.6	-127.34
9	20.1	0.356	467.2	-123.70
10	25.2	0.372	467.5	-126.44
11	30.0	0.355	467.8	-129.16

C_a	Concentration of dimethylamino stilbazoliam butyl sulfonate dye $= 1 \times 10^{-5}$ mol / dm^3
C_s	Concentration of SDBS (mol / dm^3)
A	Maximum absorbance
λ_{max}	Wavelength at maximum absorbance (nm)
ΔE_T	Electronic transition energy (Joules)

TABLE 3

Relation among A, λ_{max} and concentration of SDBS for Diethylamino stilbazoliam butyl sulfonate-Water mixture at 25 °C

No.	$C_s \times 10^4$	A	λ_{max}	$\Delta E_T \times 10^{22}$
1	1.2	0.274	477.1	-0.87
2	2.1	0.276	477.6	-5.24
3	3.0	0.283	478.0	-8.72
4	4.2	0.288	479.0	-17.40
5	5.1	0.299	480.8	-32.94
6	6.9	0.311	491.2	-120.47
7	10.2	0.367	491.6	-123.76
8	15.0	0.378	491.9	-126.23
9	20.1	0.394	492.1	-127.87
10	25.2	0.395	492.3	-129.51
11	30.0	0.409	492.3	-128.69

C_a	Concentration of diethylamino stilbazoliam butyl sulfonate dye $= 1 \times 10^{-5}$ mol / dm^3
C_s	Concentration of SDBS (mol / dm^3)
A	Maximum absorbance
λ_{max}	Wavelength at maximum absorbance (nm)
ΔE_T	Electronic transition energy (Joules)

TABLE 4

Relation among A, λ_{max} and Concentration of SDBS for Dipropylamino stilbazoliam butyl sulfonate-Water mixture at 25 °C

No.	$C_s \times 10^4$	A	λ_{max}	$\Delta E_T \times 10^{22}$
1	1.2	0.351	482.1	- 2.57
2	2.1	0.330	483.0	-10.25
3	3.0	0.335	483.7	- 16.21
4	4.2	0.345	484.4	- 22.14
5	5.1	0.323	485.0	- 27.22
6	6.9	0.349	494.0	- 101.89
7	10.2	0.384	494.5	- 105.96
8	15.0	0.421	494.8	- 108.40
9	20.1	0.427	495.0	- 110.02
10	25.2	0.409	494.9	- 109.21
11	30.0	0.420	495.1	- 110.83

C_a	Concentration of dipropylamino stilbazoliam butyl sulfonate dye $= 1 \times 10^{-5}$ mol / dm^3
C_s	Concentration of SDBS (mol / dm^3)
A	Maximum absorbance
λ_{max}	Wavelength at maximum absorbance (nm)
ΔE_T	Electronic transition energy (Joules)

TABLE 5

Relation among A, λ_{max} and Concentration of SDBS for Dibutylamino stilbazoliam butyl sulfonate-Water mixture at 25 °C

No.	$C_s \times 10^4$	A	λ_{max}	$\Delta E_T \times 10^{22}$
1	1.2	0.436	482.1	16.19
2	2.1	0.455	482.3	14.48
3	3.0	0.466	482.4	13.62
4	4.2	0.467	482.6	11.91
5	5.1	0.448	483.1	7.65
6	6.9	0.455	490.0	- 50.29
7	10.2	0.479	490.4	- 53.60
8	15.0	0.486	490.3	- 52.77
9	20.1	0.490	490.7	- 56.08
10	25.2	0.489	490.6	- 55.25
11	30.0	0.494	490.6	- 55.25

C_a	Concentration of dibutylamino stilbazoliam butyl sulfonate dye $= 1 \times 10^{-5}$ mol / dm^3
C_s	Concentration of SDBS (mol / dm^3)
A	Maximum Absorbance
λ_{max}	Wavelength at maximum absorbance (nm)
ΔE_T	Electronic transition energy (Joules)

TABLE 6

Relation among A, λ_{max} and Concentration of SDBS for Dipentylamino stilbazolium butyl sulfonate-Water at 25 °C

No.	$C_s \times 10^4$	A	λ_{max}	$\Delta E_T \times 10^{22}$
1	1.2	0.408	474.6	106.64
2	2.1	0.398	476.2	92.57
3	3.0	0.403	478.5	55.22
4	4.2	0.461	480.5	39.78
5	5.1	0.479	482.3	20.64
6	6.9	0.499	488.9	-15.86
7	10.2	0.500	489.3	- 19.19
8	15.0	0.511	489.6	- 21.68
9	20.1	0.502	489.9	- 24.16
10	25.2	0.502	490.1	- 25.82
11	30.0	0.508	490.0	- 24.99

C_a	Concentration of dipentylamino stilbazoliam butyl sulfonate dye $= 1 \times 10^{-5}$ mol / dm^3
C_s	Concentration of SDBS (mol / dm^3)
A	Maximum absorbance
λ_{max}	Wavelength at maximum absorbance (nm)
ΔE_T	Electronic transition energy (Joules)

TABLE 7

Relation between experimental data and approximate number (n) of dye molecules incarporated per micelle of SDBS at 25 °C

Additive	A_o	A	A_m	ε_o $dm^3\ mol^{-1}\ cm^{-1}$	ε_m $dm^3\ mol^{-1}\ cm^{-1}$	$C_m \times 10^5$ mol / dm^3	n
Dye 1	0.279	0.295	0.356	27900	35600	0.210	1
Dye 2	0.231	0.311	0.395	23100	39500	0.488	2
Dye 3	0.137	0.349	0.421	13700	42100	0.746	3
Dye 4	0.093	0.455	0.490	9300	49000	0.912	3.6
Dye 5	0.083	0.499	0.502	8300	50200	0.993	4

TABLE 8

Determination of cell constant using KCl solution at 25 °C

$C_s \times 10^4$	Λ_m	G_o	K
5.62	147.44	755	0.1097
10.72	146.41	1327	0.1182
15.40	145.64	1819	0.1232
19.66	145.03	2272	0.1255
23.60	144.52	2723	0.1252
27.23	144.08	3092	0.1268
30.59	143.69	3439	0.1278
33.71	143.35	3671	0.1316
36.62	143.04	3941	0.1329
39.33	142.77	4207	0.1334
41.87	142.51	4467	0.1335
44.25	142.29	4713	0.1335
46.48	142.08	4881	0.1352
48.58	141.88	5067	0.1360
50.57	141.70	5277	0.1357
52.44	141.53	5431	0.1366
54.21	141.38	5597	0.1369
55.89	141.24	5789	0.1363
57.48	141.10	5922	0.1369
59.00	140.97	6057	0.1371

$K_{ave} = 0.1306$ cm^{-1}

C_s	Concentration of KCl (mol / dm^3)
Λ_m	Molar Conductance of KCl (S cm^2 / mol)
G_o	Specific Conductance (µS)
K	Cell Constant (cm^{-1})

TABLE 9

Relation between the specific conductance and concentration of surfactant (SDBS) in water at 25 °C

$C_s^{1/2} \times 10^4$	K	$C_s^{1/2} \times 10^4$	K
0.0	0.160	2.55	8.78
0.96	1.65	2.63	9.34
1.33	2.46	2.70	9.80
1.59	3.49	2.77	10.30
1.80	4.40	2.83	10.78
1.97	5.30	2.89	11.18
2.12	6.14	2.94	11.52
2.25	6.86	2.99	11.94
2.36	7.52	3.04	12.25
2.46	8.11	3.08	12.49

C_s Surfactant concentration (mol / dm^3)

K Specific conductance (μS / cm)

TABLE 10

Relation between specific conductance and concentration of SDBS for Dimethylamino stilbazoliam butyl sulfonate (Dye 1)

C_a x10^5 $C_s^{1/2}$ x 10^4	1.2 K	2.4 K	3.6 K	4.8 K
0.0	0.193	0.291	0.234	0.229
0.96	1.76	1.58	1.27	1.07
1.33	2.58	2.53	1.91	2.06
1.59	3.34	3.36	2.88	3.01
1.80	4.37	4.08	4.05	3.81
1.97	5.16	4.97	5.11	4.84
2.12	6.22	6.19	5.97	6.11
2.25	6.87	7.02	6.79	7.08
2.36	7.61	7.63	7.46	7.49
2.46	8.18	8.17	8.06	8.09
2.55	8.83	8.91	8.73	8.63
2.63	9.44	9.37	9.19	9.22
2.70	9.76	9.78	9.57	9.62
2.77	10.12	10.18	10.07	10.02
2.83	10.71	10.69	10.58	10.54
2.89	11.09	11.12	10.99	11.03
2.94	11.47	11.40	11.18	11.15
2.99	11.86	11.68	11.47	11.43
3.04	12.14	12.02	11.82	11.74
3.08	12.41	12.38	12.17	12.06

C_a	Concentration of dimethylamino stilbazoliam butyl sulfonate (mol /dm^3)
C_s	Surfactant concentration (mol /dm^3)
K	Specific conductance (µS/cm)

TABLE 11

Relation between specific conductance and concentration of SDBS for Diethylamino stilbazoliam butyl sulfonate (Dye 2)

$C_a \times 10^5$	1.2	2.4	3.6	4.8
$C_s^{1/2} \times 10^4$	K	K	K	K
0.0	0.247	0.209	0.217	0.202
0.96	1.34	1.42	1.22	1.38
1.33	2.31	2.39	1.97	2.19
1.59	3.12	3.21	2.89	3.14
1.80	4.07	4.01	3.94	4.23
1.97	4.83	4.78	4.54	4.94
2.12	6.04	5.95	5.61	5.80
2.25	6.77	6.71	6.57	6.62
2.36	7.38	7.48	7.36	7.31
2.46	8.23	8.37	8.22	7.88
2.55	8.86	9.00	8.98	8.43
2.63	9.34	9.39	9.32	8.87
2.70	9.71	9.82	9.77	9.39
2.77	10.16	10.37	10.17	9.82
2.83	10.72	10.96	10.59	10.31
2.89	11.13	11.32	10.83	10.64
2.94	11.56	11.56	11.16	10.79
2.99	11.73	12.11	11.42	11.10
3.04	12.15	12.52	11.81	11.42
3.08	12.42	12.81	11.96	11.67

C_a	Concentration of diethylamino stilbazoliam butyl sulfonate (mol / dm^3)
C_s	Surfactant concentration (mol / dm^3)
K	Specific conductance (µS/cm)

TABLE 12

Relation between specific conductance and concentration of SDBS for Dipropylamino stilbazoliam butyl sulfonate (Dye 3)

$C_a \times 10^5$	1.2	2.4	3.6	4.8
$C_s^{1/2} \times 10^4$	K	K	K	K
0.0	0.188	0.217	0.165	0.129
0.96	1.44	1.26	1.08	1.16
1.33	2.26	2.18	1.91	2.05
1.59	3.17	2.98	3.12	3.09
1.80	4.23	4.12	4.03	4.07
1.97	5.24	5.06	4.81	4.93
2.12	6.11	5.77	5.72	5.69
2.25	6.89	6.74	6.63	6.57
2.36	7.51	7.37	7.26	7.29
2.46	8.14	8.02	7.93	7.82
2.55	8.69	8.51	8.49	8.27
2.63	9.19	9.06	8.93	8.77
2.70	9.56	9.40	9.24	9.21
2.77	9.96	9.73	9.61	9.56
2.83	10.56	10.21	10.12	10.02
2.89	10.87	10.59	10.48	10.38
2.94	11.27	10.91	10.72	10.61
2.99	11.39	11.28	11.13	10.92
3.04	11.80	11.62	11.39	11.21
3.08	12.16	11.85	11.63	11.45

C_a	Concentration of dipropylamino stilbazoliam butyl sulfonate (mol / dm^3)
C_s	Surfactant concentration (mol / dm^3)
K	Specific conductance (µS/cm)

TABLE 13

Relation between specific conductance and concentration of SDBS for Dibutylamino stilbazoliam butyl sulfonate (Dye 4)

$C_a \times 10^5$ $C_s^{1/2} \times 10^4$	1.2 K	2.4 K	3.6 K	4.8 K
0	0.175	0.139	0.148	0.127
1.19	1.19	1.08	1.03	1.01
2.27	2.03	2.11	2.05	2.06
3.26	3.16	3.07	2.99	3.21
4.16	4.08	4.13	3.96	4.09
5.00	4.96	5.06	5.01	5.00
5.77	5.87	5.97	5.84	5.98
6.48	6.94	6.91	6.95	6.96
7.14	7.44	7.60	7.54	7.64
7.76	7.97	8.02	8.11	8.23
8.33	8.56	8.34	8.46	8.65
8.87	9.10	8.89	8.86	8.94
9.37	9.43	9.27	9.25	9.32
9.85	9.91	9.84	9.64	9.59
10.29	10.49	10.27	10.14	10.01
10.71	10.82	10.55	10.37	10.17
11.11	11.19	10.96	10.69	10.56
11.49	11.41	11.21	10.86	10.67
11.84	11.74	11.42	11.04	10.85
12.17	12.08	11.75	11.42	11.16

C_a	Concentration of dipropylamino stilbazoliam butyl sulfonate (mol / dm^3)
C_s	Surfactant concentration (mol / dm^3)
K	Specific conductance (μS/cm)

TABLE 14

Relation between specific conductance and concentration of SDBS for Dipentylamino stilbazoliam butyl sulfofate (Dye 5)

$C_a \times 10^5$ $C_s^{1/2} \times 10^4$	0.4 K	0.8 K	1.2 K	1.6 K
0.0	0.147	0.102	0.138	0.168
0.96	1.24	1.31	1.17	1.09
1.33	2.17	2.35	2.21	2.29
1.59	3.19	3.36	3.20	3.52
1.80	4.31	4.25	4.59	4.40
1.97	5.38	5.11	5.53	5.57
2.12	6.29	6.13	6.37	6.26
2.25	7.21	6.53	7.06	6.93
2.36	7.81	7.18	7.69	7.48
2.46	8.47	7.76	8.26	7.96
2.55	8.93	8.32	8.71	8.33
2.63	9.40	8.83	9.14	8.75
2.70	9.82	9.34	9.60	9.22
2.77	10.36	9.93	9.96	9.59
2.83	10.69	10.45	10.21	10.02
2.89	10.94	10.58	10.67	10.34
2.94	11.23	10.96	10.97	10.61
2.99	11.51	11.32	11.19	10.82
3.04	11.89	11.63	11.41	11.08
3.08	12.12	11.92	11.72	11.28

C_a	Concentration of dDipentylamino stilbazoliam butyl sulfonate (mol / dm^3)
C_s	Surfactant concentration (mol / dm^3)
K	Specific conductance (μ S/cm)

TABLE 15

Criticle micelle concentration of SDBS in the presence of Dialkylamino stilbazolium butyl sulfonate at 25 °C

$C_a \times 10^5$	CMC of Dye. $1x10^4$	CMC of Dye. $2x10^4$	CMC of Dye. $3x10^4$	CMC of Dye. $4x10^4$	$C_a \times 10^5$	CMC of Dye.$5x10^4$
0	6.3	6.3	6.3	6.3	0	6.3
1.2	6.28	6.27	6.25	6.22	0.4	6.06
2.4	6.27	6.25	6.23	6.12	0.8	5.82
3.6	6.25	6.24	6.21	6.05	1.2	5.55
4.8	6.24	6.22	6.20	5.98	1.6	5.32

C_a	Concentration of respective dye (mol / dm^3)
CMC	Critical micelle concentration of SDBS (mol / dm^3)
Dye	Dialkylamino stilbazolium butyl sulfonate

TABLE 16

Rate of CMC depression for SDBS with Dialkylamino stilbazoliam butyl sulfonate at 25 °C

No.	Additive	m_n	$-\Delta CMC/\Delta C_a$	$\log(-\Delta CMC/\Delta C_a)$
1	Dye 1	2	0.125	−0.903
2	Dye 2	4	0.158	−0.801
3	Dye 3	6	0.200	−0.699
4	Dye 4	8	0.675	−0.171
5	Dye 5	10	6.175	0.791

Dye	Dialkylamino stilbazoliam butyl sulfonate
m_n	Number of carbon atoms in dye hydrocarbon chain
$-\Delta CMC/\Delta C_a$	Slope of CMC Vs. C_a plot

TABLE 17

Relation among differential absorbance, ΔA, λ_{max} and concentration, C_s, of SDBS for Dye 1 at 25 °C

No.	$C_s \times 10^4$	ΔA	λ_{max}
1	18.0	0.023	507.7
2	27.0	0.033	507.3
3	36.0	0.044	507.9
4	45.0	0.051	507.5
5	54.0	0.056	507.4
6	63.0	0.062	507.4
7	72.0	0.062	507.1
8	81.0	0.064	507.5
9	90.0	0.068	507.4

C_s	Concentration of SDBS (mol / dm^3)
C_a	Concentration of dimethylamino stilbazoliam butyl sulfonate (mol / dm^3)
ΔA	Differential absorbance
λ_{max}	Wavelength at maximum absorbance (nm)

TABLE 18

Relation among differential absorbance, ΔA, λ_{max} and concentration, C_s, of SDBS for Dye 2 at 25 °C

No.	$C_s \times 10^4$	ΔA	λ_{max}
1	18.0	0.039	521.7
2	27.0	0.047	521.5
3	36.0	0.066	521.8
4	45.0	0.078	521.5
5	54.0	0.080	521.6
6	63.0	0.092	521.8
7	72.0	0.095	521.6
8	81.0	0.096	521.6
9	90.0	0.105	521.6

C_s	Concentration of SDBS (mol / dm^3)
C_a	Concentration of diethylamino stilbazoliam butyl sulfonate (mol / dm^3)
ΔA	Differential absorbance
λ_{max}	Wavelength at maximum absorbance (nm)

TABLE 19

Relation among differential absorbance, ΔA, λ_{max} and concentration, C_s, of SDBS for Dye 3 at 25 °C

No.	$C_s \times 10^4$	ΔA	λ_{max}
1	18.0	0.050	522.4
2	27.0	0.077	522.8
3	36.0	0.090	522.7
4	45.0	0.099	523.0
5	54.0	0.100	523.1
6	63.0	0.110	522.8
7	72.0	0.120	522.8
8	81.0	0.124	522.7
9	90.0	0.132	522.9

C_s	Concentration of SDBS (mol / dm^3)
C_a	Concentration of dipropylamino stilbazoliam butyl sulfonate (mol / dm^3)
ΔA	Differential absorbance
λ_{max}	Wavelength at maximum absorbance (nm)

TABLE 20

Relation among differential absorbance, ΔA, λ_{max} and concentration, C_s, of SDBS for Dye 4 at 25 °C

No.	$C_s \times 10^4$	ΔA	λ_{max}
1	18.0	0.118	518.2
2	27.0	0.144	518.6
3	36.0	0.160	518.7
4	45.0	0.188	518.6
5	54.0	0.192	518.5
6	63.0	0.193	518.8
7	72.0	0.195	518.3
8	81.0	0.198	518.4
9	90.0	0.200	518.3

C_s	Concentration of SDBS (mol / dm^3)
C_a	Concentration of dibutylamino stilbazoliam butyl sulfonate (mol / dm^3)
ΔA	Differential absorbance
λ_{max}	Wavelength at maximum absorbance (nm)

TABLE 21

Relation among differential absorbance, ΔA, λ_{max} and concentration, C_s, of SDBS for Dye 5 at 25 °C

No.	$C_s \times 10^4$	ΔA	λ_{max}
1	18.0	0.402	492.8
2	27.0	0.414	492.9
3	36.0	0.415	492.4
4	45.0	0.418	492.5
5	54.0	0.418	492.8
6	63.0	0.418	492.3
7	72.0	0.420	492.0
8	81.0	0.428	491.9
9	90.0	0.432	492.6

C_s	Concentration of SDBS (mol / dm^3)
C_s	Concentration of dipentylamino stilbazoliam butyl sulfonate (mol /dm^3)
ΔA	Differential absorbance
λ_{max}	Wavelength at maximum absorbance (nm)

TABLE 22

Relation among λ_{max} , $1/\Delta A$, $1/(C_a + C_s^{mo})$ and concentration of SDBS in Dimethylamino stilbazoliam butyl sulfonate -Water mixture at 25 °C

No.	$C_s \times 10^4$	ΔA	λ_{max}	$(C_a+C_s^{mo}) \times 10^4$	$1/\Delta A$	$1/(C_a+C_s^{mo})$
1	18.0	0.023	507.7	11.8	43.68	847.46
2	27.0	0.033	507.3	20.8	30.30	480.77
3	36.0	0.044	507.9	29.8	22.73	335.57
4	45.0	0.051	507.5	38.8	19.61	257.73
5	54.0	0.056	507.4	47.8	17.86	209.20
6	63.0	0.062	507.4	56.8	16.13	176.05
7	72.0	0.062	507.1	65.8	16.13	151.97
8	81.0	0.064	507.5	74.8	15.62	133.68
9	90.0	0.068	507.4	83.8	14.70	119.33

C_a	Concentration of dimethylamino stilbazoliam butyl sulfonate dye $= 1.0 \times 10^{-5}$ mol / dm^3
ΔA	Maximum differential absorbance
λ_{max}	Wavelength at maximum absorbance (nm)
C_s	Concentration of SDBS (mol / dm^3)
C_s^{mo}	$= C_s - CMC_o$ (mol / dm^3)

TABLE 23

Relation among λ_{max} , $1/\Delta A$, $1/(C_a + C_s^{mo})$ and concentration of SDBS in Diethylamino stilbazoliam butyl sulfonate-Water mixture at 25 °C

No.	$C_s \times 10^4$	ΔA	λ_{max}	$(C_a+C_s^{mo}) \times 10^4$	$1/\Delta A$	$1/(C_a+C_s^{mo})$
1	18.0	0.039	521.7	11.8	25.64	847.46
2	27.0	0.047	521.5	20.8	20.83	480.77
3	36.0	0.066	521.8	29.8	15.15	335.57
4	45.0	0.078	521.5	38.8	12.82	257.73
5	54.0	0.080	521.6	47.8	12.50	209.20
6	63.0	0.092	521.8	56.8	10.87	176.05
7	72.0	0.095	521.6	65.8	10.53	151.97
8	81.0	0.096	521.6	74.8	10.42	133.68
9	90.0	0.105	521.6	83.8	9.52	119.33

C_a	Concentration of diethylamino stilbazoliam butyl sulfonate dye $= 1.0 \times 10^{-5}$ mol / dm^3
ΔA	Maximum differential absorbance
λ_{max}	Wavelength at maximum absorbance (nm)
C_s	Concentration of SDBS (mol / dm^3)
C_s^{mo}	$= C_s - CMC_o$ (mol / dm^3)

TABLE 24

Relation among λ_{max}, $1/\Delta A$, $1/(C_a + C_s^{mo})$ and concentration of SDBS in Dipropylamino stilbazoliam butyl sulfonate-Water mixture at 25 °C

No.	$C_s \times 10^4$	ΔA	λ_{max}	$(C_a+C_s^{mo}) \times 10^4$	$1/\Delta A$	$1/(C_a+C_s^{mo})$
1	18.0	0.050	522.4	11.8	20.0	847.46
2	27.0	0.077	522.8	20.8	12.99	480.77
3	36.0	0.090	522.7	29.8	11.11	335.57
4	45.0	0.099	523.0	38.8	10.10	257.73
5	54.0	0.100	523.1	47.8	10.0	209.20
6	63.0	0.110	522.8	56.8	9.09	176.05
7	72.0	0.120	522.8	65.8	8.33	151.97
8	81.0	0.124	522.7	74.8	8.06	133.68
9	90.0	0.132	522.9	83.8	7.58	119.33

C_a	Concentration of dipropylamino stilbazoliam butyl sulfonate dye $= 1.0 \times 10^{-5}$ mol / dm^3
ΔA	Maximum differential absorbance
λ_{max}	Wavelength at maximum absorbance (nm)
C_s	Concentration of SDBS (mol / dm^3)
C_s^{mo}	$= C_s - CMC_o$ (mol / dm^3)

TABLE 25

Relation among λ_{max}, $1/\Delta A$, $1/(C_a + C_s^{mo})$ and concentration of SDBS in Dibutylamino stilbazoliam butyl sulfonate-Water mixtureat at 25 °C

No.	$C_s \times 10^4$	ΔA	λ_{max}	$(C_a+C_s^{mo}) \times 10^4$	$1/\Delta A$	$1/(C_a+C_s^{mo})$
1	18.0	0.118	518.2	11.8	8.47	847.46
2	27.0	0.144	518.6	20.8	6.94	480.77
3	36.0	0.160	518.7	29.8	6.25	335.57
4	45.0	0.188	518.6	38.8	5.32	257.73
5	54.0	0.192	518.5	47.8	5.21	209.20
6	63.0	0.193	518.8	56.8	5.18	176.05
7	72.0	0.195	518.3	65.8	5.13	151.97
8	81.0	0.198	518.4	74.8	5.05	133.68
9	90.0	0.200	518.3	83.8	5.00	119.33

C_a	Concentration of dibutylamino stilbazoliam butyl sulfonate dye $= 1.0 \times 10^{-5}$ mol / dm^3
ΔA	Maximum differential absorbance
λ_{max}	Wavelength at maximum absorbance (nm)
C_s	Concentration of SDBS (mol / dm^3)
C_s^{mo}	$= C_s - CMC_o$ (mol / dm^3)

TABLE 26

Relation among λ_{max} , $1/\Delta A$, $1/(C_a + C_s^{mo})$ and concentration of SDBS in Dipentylamino stilbazoliam butyl sulfonate-Water mixture at 25 °C

No.	$C_s \times 10^4$	ΔA	λ_{max}	$(C_a+C_s^{mo}) \times 10^4$	$1/\Delta A$	$1/(C_a+C_s^{mo})$
1	18.0	0.402	492.8	11.8	2.49	847.46
2	27.0	0.414	492.9	20.8	2.42	480.77
3	36.0	0.415	492.4	29.8	2.41	335.57
4	45.0	0.418	492.5	38.8	2.39	257.73
5	54.0	0.418	492.8	47.8	2.39	209.20
6	63.0	0.418	492.3	56.8	2.39	176.05
7	72.0	0.420	492.0	65.8	2.38	151.97
8	81.0	0.428	491.9	74.8	2.34	133.68
9	90.0	0.432	492.6	83.8	2.31	119.33

C_a	Concentration of dipentylamino stilbazoliam butyl sulfonate dye $= 1.0 \times 10^{-5}$ mol / dm^3
ΔA	Maximum differential absorbance
λ_{max}	Wavelength at maximum absorbance (nm)
C_s	Concentration of SDBS (mol / dm^3)
C_s^{mo}	$= C_s - CMC_o$ (mol / dm^3)

TABLE 27

The values of $1/\Delta A_\infty$ (Intercept), $1/K_c\,\Delta A_\infty$ (Slopes) and Partition coefficients of Dialkylamino stilbazoliam butyl sulfonate dyes in SDBS solution at 25 °C

Additive	$1/\Delta A_\infty$ **(Intercept)**	$1/K_c\,\Delta A_\infty$ **(Slope)**	K_c^{a}	K_x^{a}
Dye 1	9.726	0.04021	241.88	13424
Dye 2	7.331	0.02297	319.12	17713
Dye 3	5.899	0.01631	361.07	20039
Dye 4	4.354	0.004959	877.99	48729
Dye 5	2.333	0.0001929	12094.35	671236

$1/\Delta A_\infty$	Represents $1/\Delta A$ at infinity value of C_s
K_c^{a}	Partition coefficient ($K_c = K_x / n_w$) $dm^3\,mol^{-1}$
K_x^{a}	Partition coefficient

TABLE 28

Partition coefficient (K_x^a) of Dialkylamino stilbazoliam butyl sulfonate dyes between the aqueous and miceller phase and free energy change of penetration ΔG^o_p at 25 °C

No.	Additive	K_x^a	ΔG^o_p
1	Dye 1	13424	-23.55
2	Dye 2	17713	-24.24
3	Dye 3	20039	-24.54
4	Dye 4	48729	-26.74
5	Dye 5	671236	-33.24

Additive	Dialkylamino stilbazoliam butyl sulfonate
K_x^a	Partition coefficient obtained using Eq. 19
ΔG^o_p	Free energy change of penetration of dyes (kJ/ mol)

TABLE 29

Table for *j* values for all dyes

$C_s \times 10^4$	Dye 1 *j*	Dye 2 *j*	Dye 3 *j*	Dye 4 *j*	Dye 5 *j*
18.0	0.224	0.286	0.294	0.514	0.938
27.0	0.321	0.344	0.453	0.627	0.966
36.0	0.428	0.484	0.530	0.697	0.968
45.0	0.496	0.572	0.583	0.818	0.975
54.0	0.545	0.586	0.589	0.836	0.975
63.0	0.603	0.674	0.648	0.840	0.975
72.0	0.603	0.696	0.707	0.850	0.980
81.0	0.622	0.704	0.730	0.862	0.998
90.0	0.661	0.770	0.777	0.871	1.008

C_s Surfactant concentration (mol / dm^3)

j $= \Delta A / \Delta A_\infty$

TABLE 30

Relation among λ_{max}, $1/\Delta A$, $1/[C_s^{mo} - kC_a + (1+k)C_a j]$ and concentration of SDBS for Dimethylamino stilbazoliam butyl sulfonate-Water mixture at 25 °C

No.	$C_s \times 10^4$	ΔA	λ_{max}	$[C_s^{mo} - kC_a + (1+k) C_a j] \times 10^4$	$1 / \Delta A$	$1 / [C_s^{mo} - kC_a + (1+k) C_a j]$
1	18.0	0.023	507.7	11.73	43.68	852.51
2	27.0	0.033	507.3	20.74	30.30	482.16
3	36.0	0.044	507.9	29.75	22.73	336.13
4	45.0	0.051	507.5	38.76	19.61	257.99
5	54.0	0.056	507.4	47.76	17.86	209.38
6	63.0	0.062	507.4	56.76	16.13	176.18
7	72.0	0.062	507.1	65.76	16.13	152.07
8	81.0	0.064	507.5	74.77	15.62	133.74
9	90.0	0.068	507.4	83.77	14.70	119.37

C_a	Concentration of dimethylamino stilbazoliam butyl sulfonate dye $= 1.0 \times 10^{-5}$ mol / dm^3
ΔA	Maximum differential absorbance
λ_{max}	Wavelength at maximum absorbance (nm)
C_s^{mo}	$= C_s - CMC_o$ (mol / dm^3)
k	$= (dCMC / dC_a)$; Slope of CMC Vs. C_a plot
j	$= \Delta A / \Delta A_\infty$

TABLE 31

Relation among λ_{max}, $1/\Delta A$, $1/[C_s^{mo} - kC_a + (1+k)C_a j]$ and concentration of SDBS for Diethylamino stilbazoliam butyl sulfonate-Water mixture at 25 °C

No.	$C_s \times 10^4$	ΔA	λ_{max}	$[C_s^{mo} - kC_a + (1+k)C_a j] \times 10^4$	$1/\Delta A$	$1/[C_s^{mo} - kC_a + (1+k)C_a j]$
1	18.0	0.039	521.7	11.74	25.64	851.79
2	27.0	0.047	521.5	20.74	20.83	482.16
3	36.0	0.066	521.8	29.76	15.15	336.02
4	45.0	0.078	521.5	38.76	12.80	257.99
5	54.0	0.080	521.6	47.76	12.50	209.38
6	63.0	0.092	521.8	56.77	10.87	176.15
7	72.0	0.095	521.6	65.77	10.53	152.04
8	81.0	0.096	521.6	74.78	10.42	133.72
9	90.0	0.105	521.6	83.78	9.52	119.36

C_a	Concentration of diethylamino stilbazoliam butyl sulfonate dye $= 1.0 \times 10^{-5}$ mol / dm^3
ΔA	Maximum differential absorbance
λ_{max}	Wavelength at maximum absorbance (nm)
C_s^{mo}	$= C_s - CMC_0$ (mol / dm^3)
k	$= (dCMC / dC_a)$; Slope of CMC Vs. C_a plot
j	$= \Delta A / \Delta A_\infty$

TABLE 32

Relation among λ_{max} , $1/\Delta A$, $1/(C_s^{mo} - kC_a+(1+k)C_a j)$ and concentration of SDBS for Dipropylamino stilbazoliam butyl sulfonate-Water mixture at 25 °C

No.	$C_s \times 10^4$	ΔA	λ_{max}	$[C_s^{mo} - kC_a + (1+k)C_a j] \times 10^4$	$1 / \Delta A$	$1 / [C_s^{mo} - kC_a+(1+k)C_a j]$
1	18.0	0.050	522.4	11.74	20.0	851.79
2	27.0	0.077	522.8	20.76	12.99	481.70
3	36.0	0.090	522.7	29.76	11.11	336.02
4	45.0	0.099	523.0	38.77	10.10	257.93
5	54.0	0.100	523.1	47.77	10.0	209.34
6	63.0	0.110	522.8	56.77	9.09	176.15
7	72.0	0.120	522.8	65.78	8.33	152.02
8	81.0	0.124	522.7	74.78	8.06	133.72
9	90.0	0.132	522.9	83.78	7.58	119.36

C_s	Concentration of Dipropylamino stilbazoliam butyl sulfonate dye $=1.0 \times 10^{-5}$ mol / dm^3
ΔA	Maximum differential absorbance
λ_{max}	Wavelength at maximum absorbance (nm)
C_s^{mo}	$= C_s - CMC_o$ (mol / dm^3)
k	$= (dCMC / dC_a)$; Slope of CMC Vs. C_a plot
j	$= \Delta A / \Delta A_\infty$

TABLE 33

Relation among λ_{max}, $1/\Delta A$, $1/[C_s^{mo} - kC_a + (1+k)C_a j]$ and concentration of SDBS for Dibutylamino stilbazoliam butyl sulfonate-Water mixture at 25 °C

No.	$C_s \times 10^4$	ΔA	λ_{max}	$[C_s^{mo} - kC_a + (1+k)C_a j] \times 10^4$	$1/\Delta A$	$1/[C_s^{mo} - kC_a + (1+k)C_a j]$
1	18.0	0.118	518.2	11.78	8.47	848.90
2	27.0	0.144	518.6	20.79	6.94	481.00
3	36.0	0.160	518.7	29.79	6.25	335.68
4	45.0	0.188	518.6	38.79	5.32	257.80
5	54.0	0.192	518.5	47.79	5.21	209.25
6	63.0	0.193	518.8	56.79	5.18	176.09
7	72.0	0.195	518.3	65.80	5.13	151.98
8	81.0	0.198	518.4	74.80	5.05	133.69
9	90.0	0.200	518.3	83.80	5.00	119.33

C_a	Concentration of Dibutylamino stilbazoliam butyl sulfonate dye $= 1.0 \times 10^{-5}$ mol / dm^3
ΔA	Maximum differential absorbance
λ_{max}	Wavelength at maximum absorbance (nm)
C_s^{mo}	$= C_s - CMC_o$ (mol / dm^3)
k	$= (dCMC / dC_a)$; Slope of CMC Vs. C_a plot
j	$= \Delta A / \Delta A_\infty$

TABLE 34

Relation among λ_{max}, $1/\Delta A$, $1/[C_s^{mo} - kC_a+(1+k)C_a j\ ]$ and concentration of SDBS for Dipentylamino stilbazoliam butyl sulfonate-Water mixture at 25 °C

No.	$C_s \times 10^4$	ΔA	λ_{max}	$[\ C_s^{mo} - kC_a+ (1+k)C_a j] \times 10^4$	$1/\Delta A$	$1/[C_s^{mo} - kC_a + (1+k)C_a\ j]$
1	18.0	0.402	492.8	11.83	2.49	845.31
2	27.0	0.414	492.9	20.82	2.42	480.31
3	36.0	0.415	492.4	29.82	2.41	335.34
4	45.0	0.418	492.5	38.81	2.39	257.66
5	54.0	0.418	492.8	47.81	2.39	209.16
6	63.0	0.418	492.3	56.81	2.39	176.02
7	72.0	0.420	492.0	65.81	2.38	151.95
8	81.0	0.428	491.9	74.80	2.34	133.69
9	90.0	0.432	492.6	83.80	2.31	119.33

C_a	Concentration of Dipentylamino stilbazoliam butyl sulfonate dye $=1.0 \times 10^{-5}$ mol / dm^3
ΔA	Maximum differential absorbance
λ_{max}	Wavelength at maximum absorbance (nm)
C_s^{mo}	$= C_s - CMC_o$ (mol / dm^3)
k	= (dCMC /dC$_a$); Slope of CMC Vs. C$_a$ plot.
j	$= \Delta A / \Delta A_{\infty}$

TABLE 35

The values of $1/\Delta A_\infty$ (Intercept), $1/K_c\ \Delta A_\infty$ (Slopes) and Partition coefficients of Dialkylamino stilbazoliam butyl sulfonate dyes in SDBS solution at 25 °C

Additive	**$1/\Delta A_\infty$ (Intercept)**	**$1/K_c\ \Delta A_\infty$ (Slope)**	**K_c^b**	**K_x^b**
Dye 1	9.720	0.04018	241.91	13426
Dye 2	7.355	0.02284	322.02	17872
Dye 3	5.933	0.01614	367.60	20402
Dye 4	4.337	0.004982	870.53	48314
Dye 5	2.333	0.0001935	12056.85	669155

$1/\Delta A_\infty$	Represents $1/\Delta A$ at infinity value of C_s
K_c^b	Partition coefficient ($K_c = K_x / n_w$) $dm^3\ mol^{-1}$
K_x^b	Partition coefficient

TABLE 36

Partition coefficient (K_x^b) of dialkylamino stilbazoliam butyl sulfonate dyes between the aqueous and miceller phase andfree energy change of penetration ΔG°_p at 25 °C

No.	Additive	K_x^b	ΔG°_p
1	Dye 1	13426	-23.55
2	Dye 2	17872	-24.26
3	Dye 3	20402	-24.58
4	Dye 4	48314	-26.72
5	Dye 5	669155	-33.23

Additive	Dialkylamino stilbazoliam butyl sulfonate dyes
K_x^b	Partition coefficient obtained using Eq. 25
ΔG°_p	Free energy change of penetration of dyes (kJ/ mol)

TABLE 37

Free energy transfer per CH_2 molecule at 25 °C

No. of methyl groups (m_p)	$\ln K_x^b$	$d\ln K_x^b / dm_p$	$\Delta G^\circ (CH_2)$ kJ/mol	$\Delta G^\circ (CH_2)$ kCal/mol
2	9.500	0.4405	- 1.091	-0.261
4	9.790			
6	9.920			
8	10.78			
10	13.41			

K_x^b	Partition coefficient by differential absorbance & conductance method
m_p	Number of alkyl carbon chain groups in the dyes
$\Delta G^\circ (CH_2)$	Free energy of transfer per methylene molecule
$d\ln K_x^b / dm_p$	Slope of $\ln K_x^b$ Vs. m_p plot

TABLE 38

Calculation for interaction coefficient (θ)

log (- k)	log K_x	Intercept	θ
- 0.903	4.13	- 5.022	0.84
- 0.801	4.25		
- 0.699	4.31		
- 0.171	4.68		
0.791	5.82		

K_x	Partition coefficient obtained using Eq. 25
k	= ($dCMC/dC_a$); Slope of CMC Vs. C_a plot
θ	Interaction coefficient

FIGURES

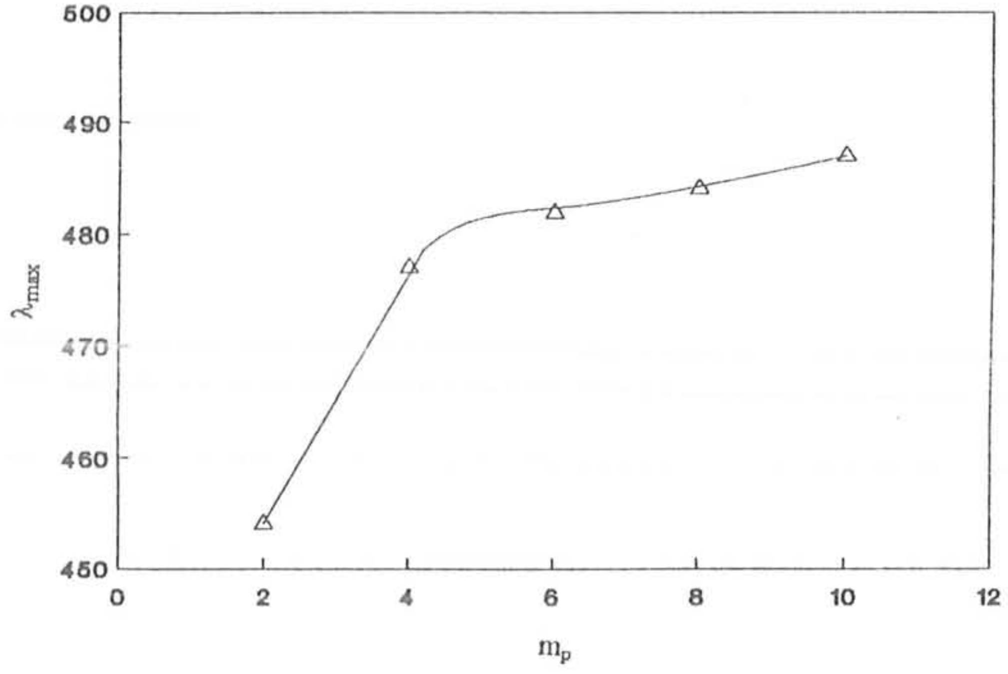


Figure 1. Relation between maximum wavelength (λ_{max}) and number of carbon atoms (m_p) in dye molecule.

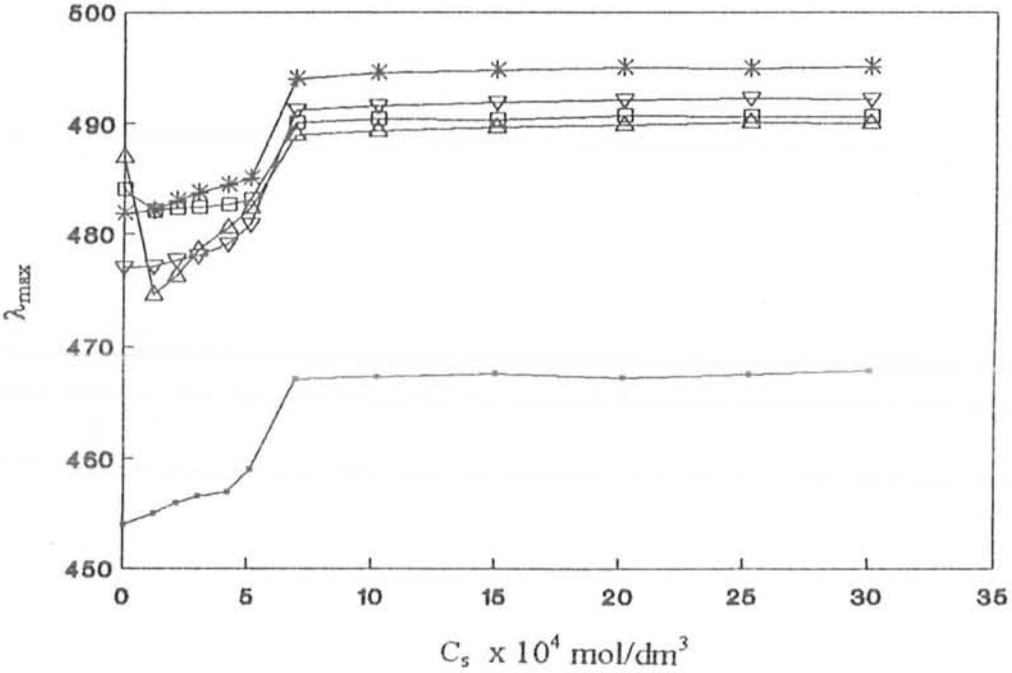


Figure 2. Relation between maximum wavelength (λ_{max}) and concentration (C_s) of SDBS at 25 °C.

(▪) Dye 1; (▽) Dye 2; (✱) Dye 3; (□) Dye 4; (△) Dye 5.

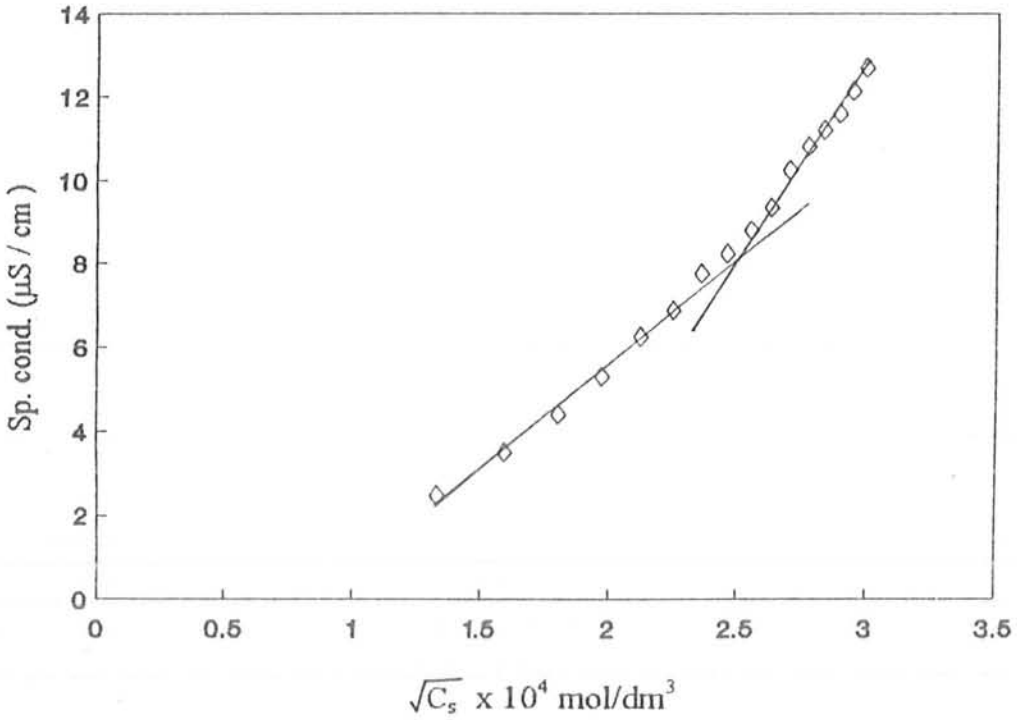


Figure 3. Relation between specific conductance and concentration of SDBS at 25 °C.

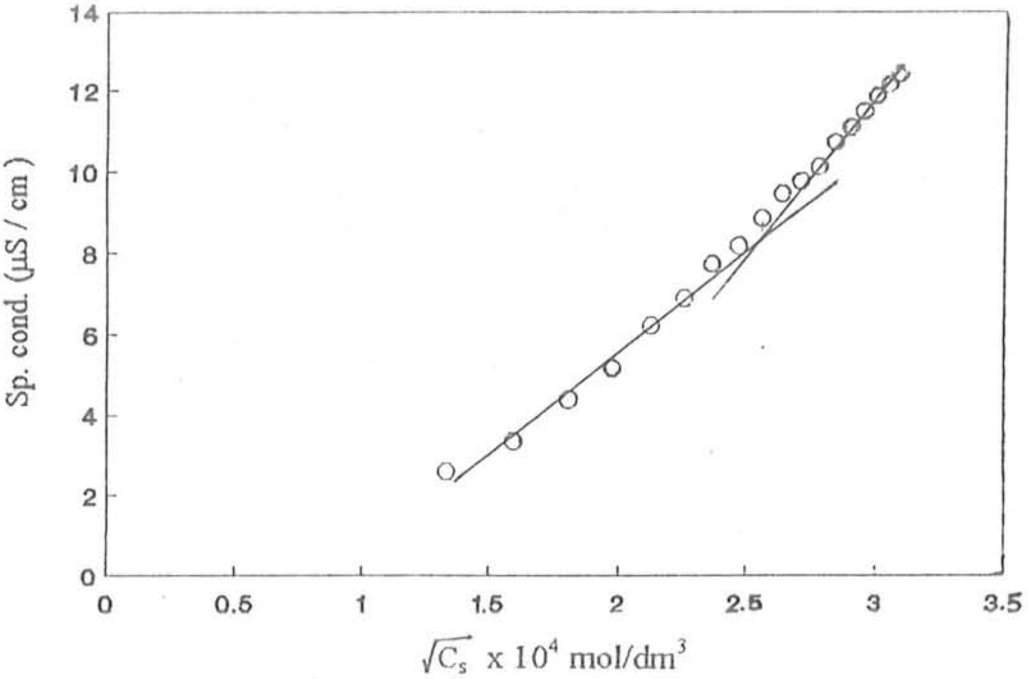


Figure 4. Relation between specific conductance and concentration of SDBS in presence of dye 1 at 25 °C. $C_a = 1.2 \times 10^{-5}$ mol/dm^3.

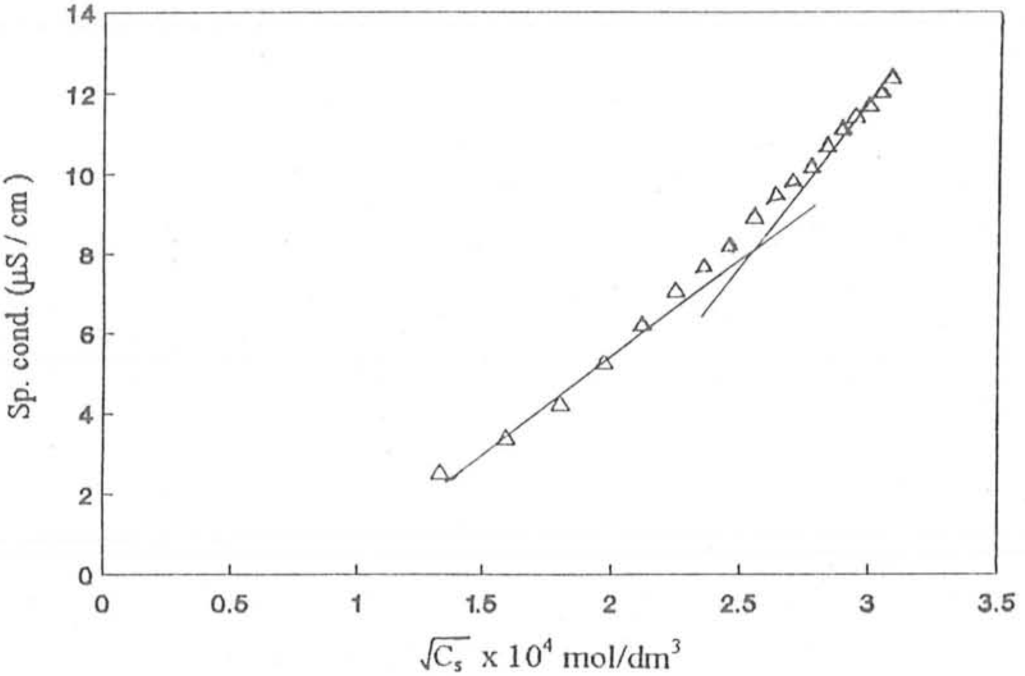


Figure 5. Relation between specific conductance and concentration of SDBS in presence of dye 1 at 25 °C. $C_a = 2.4 \times 10^{-5}$ mol/dm^3.

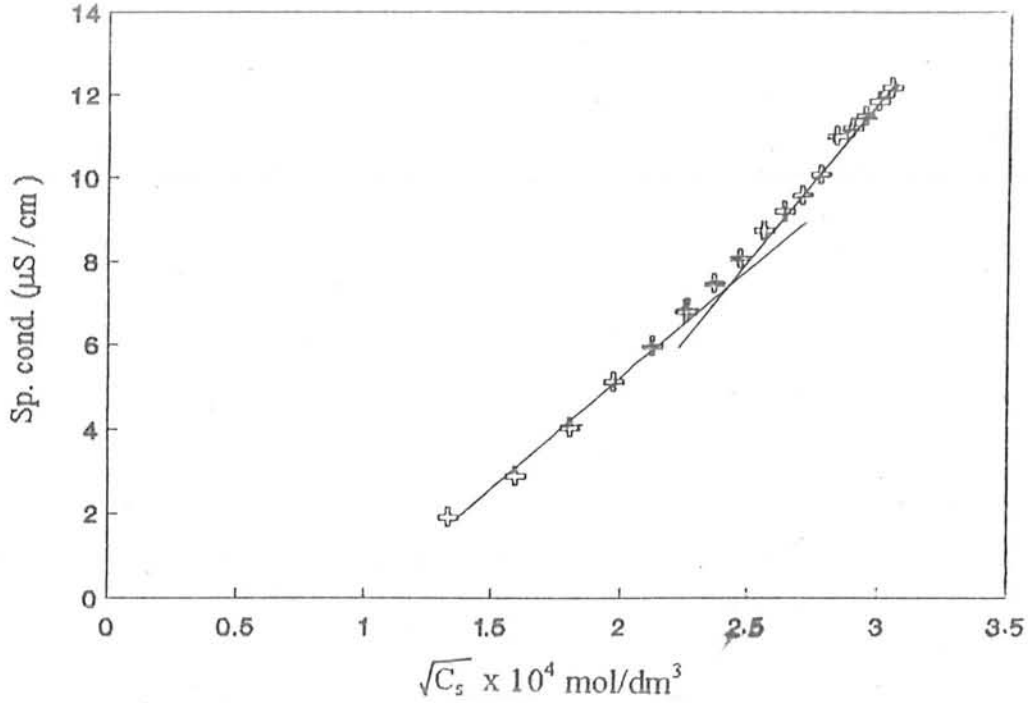


Figure 6. Relation between specific conductance and concentration of SDBS in presence of dye 1 at 25 °C. $C_a = 3.6 \times 10^{-5}$ mol/dm^3.

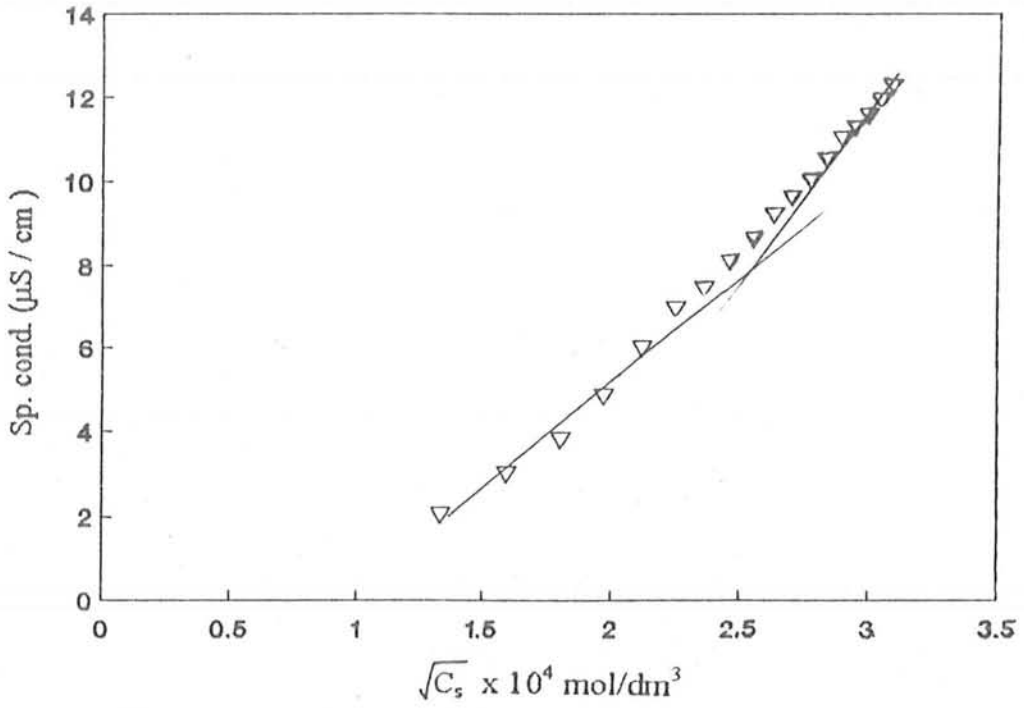


Figure 7. Relation between specific conductance and concentration of SDBS in presence of dye 1 at 25 °C. $C_a = 4.8 \times 10^{-5}$ mol/dm^3.

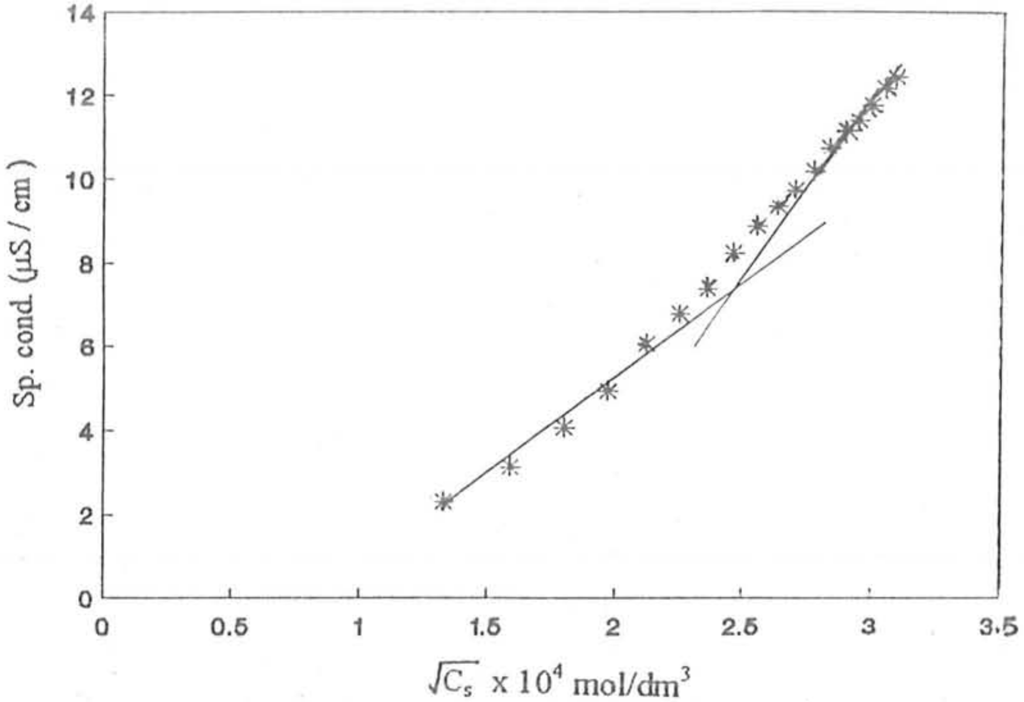


Figure 8. Relation between specific conductance and concentration of SDBS in presence of dye 2 at 25 °C. $C_a = 1.2 \times 10^{-5}$ mol/dm^3.

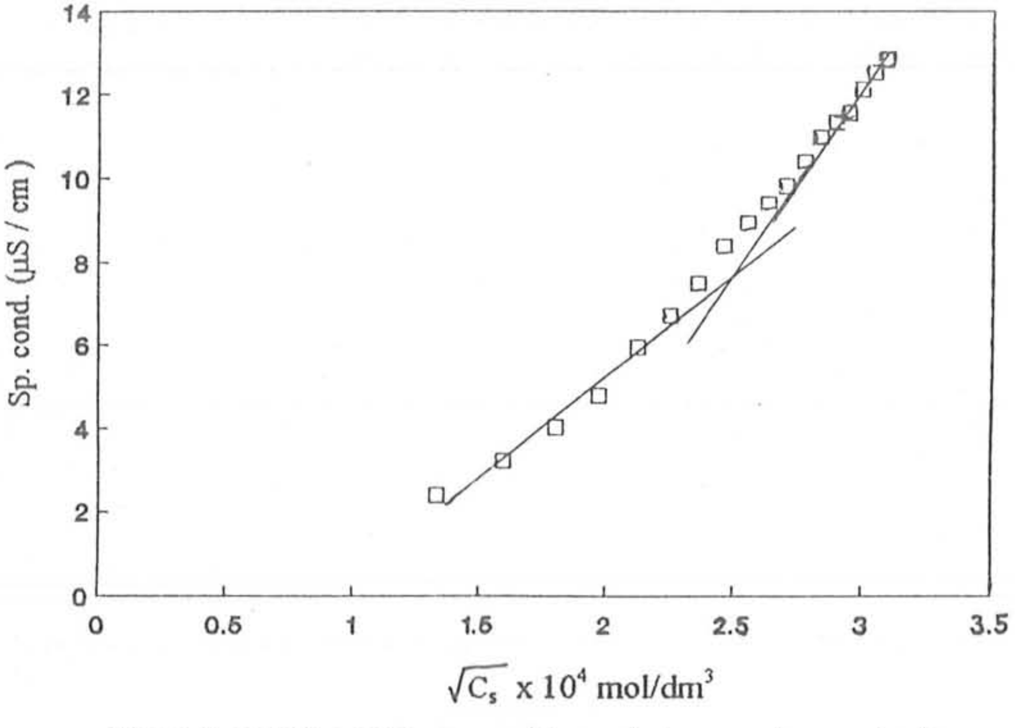


Figure 9. Relation between specific conductance and concentration of SDBS in presence of dye 2 at 25 °C. $C_a = 2.4 \times 10^{-5}$ mol/dm^3.

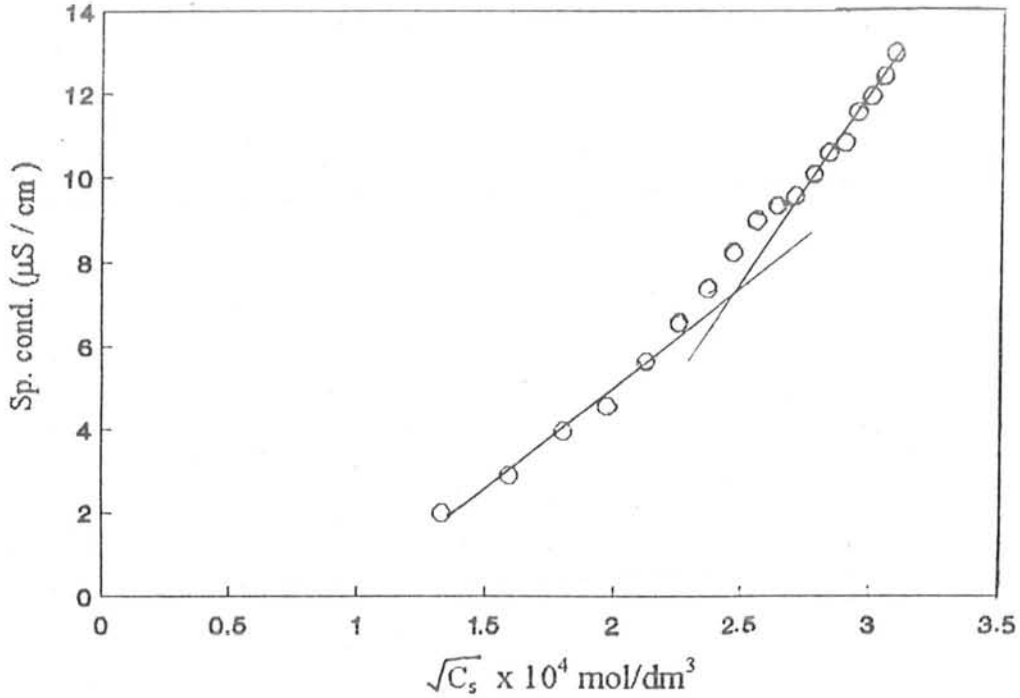


Figure 10. Relation between specific conductance and concentration of SDBS in presence of dye 2 at 25 °C. $C_s = 3.6 \times 10^{-5}$ mol/dm^3.

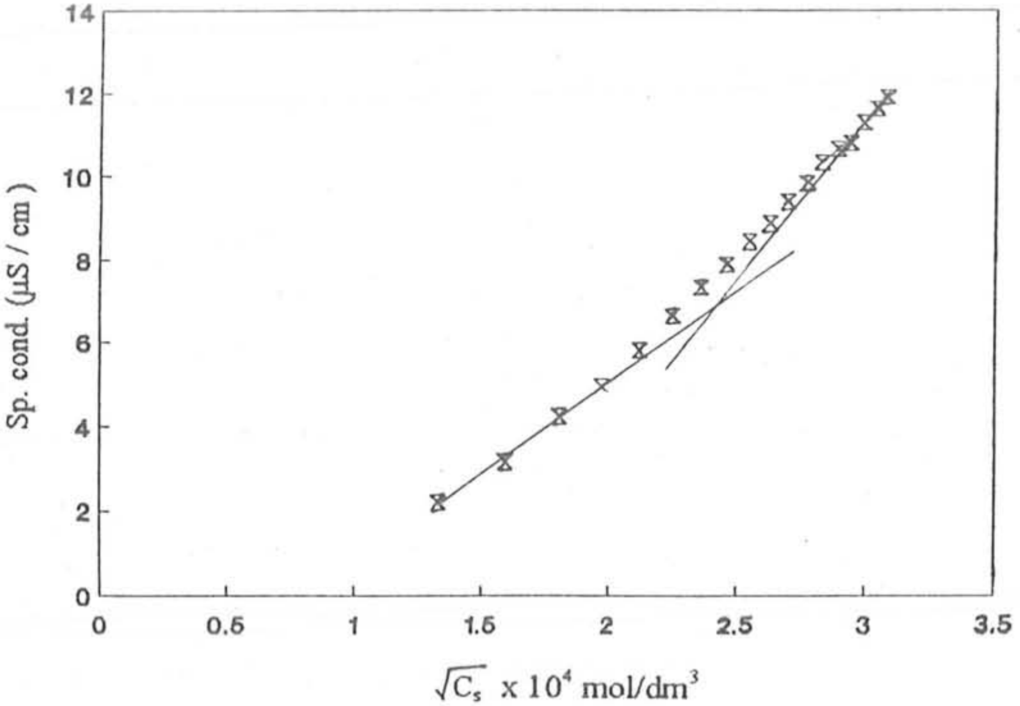


Figure 11. Relation between specific conductance and concentration of SDBS in presence of dye 2 at 25 °C. $C_s = 4.8 \times 10^{-5}$ mol/dm^3.

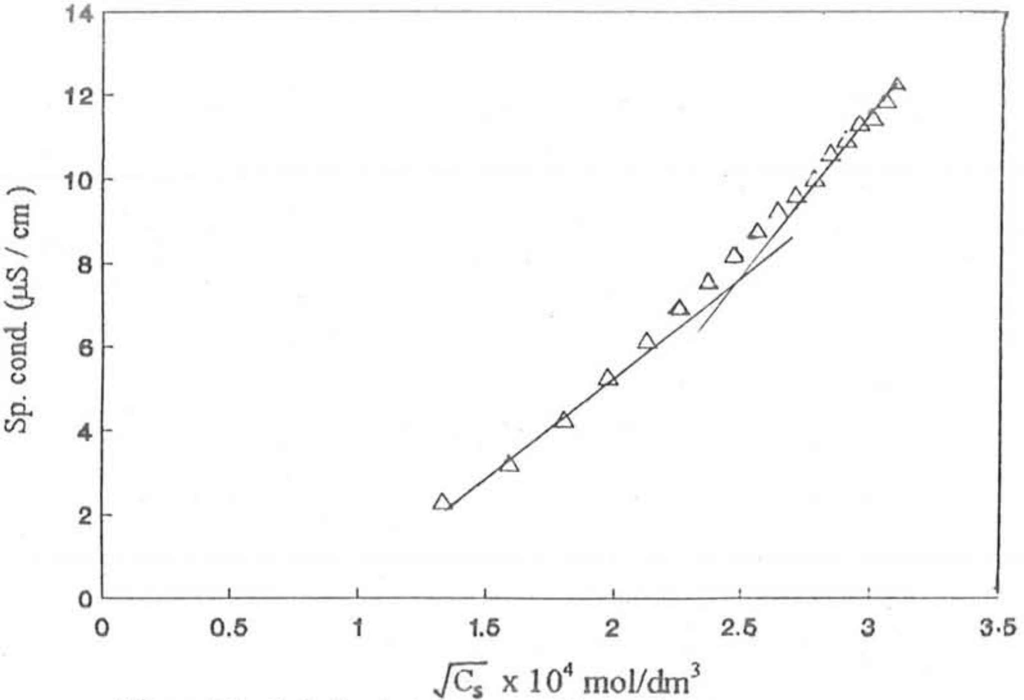


Figure 12. Relation between specific conductance and concentration of SDBS in presence of dye 3 at 25 °C. $C_a = 1.2 \times 10^{-5}$ mol/dm^3.

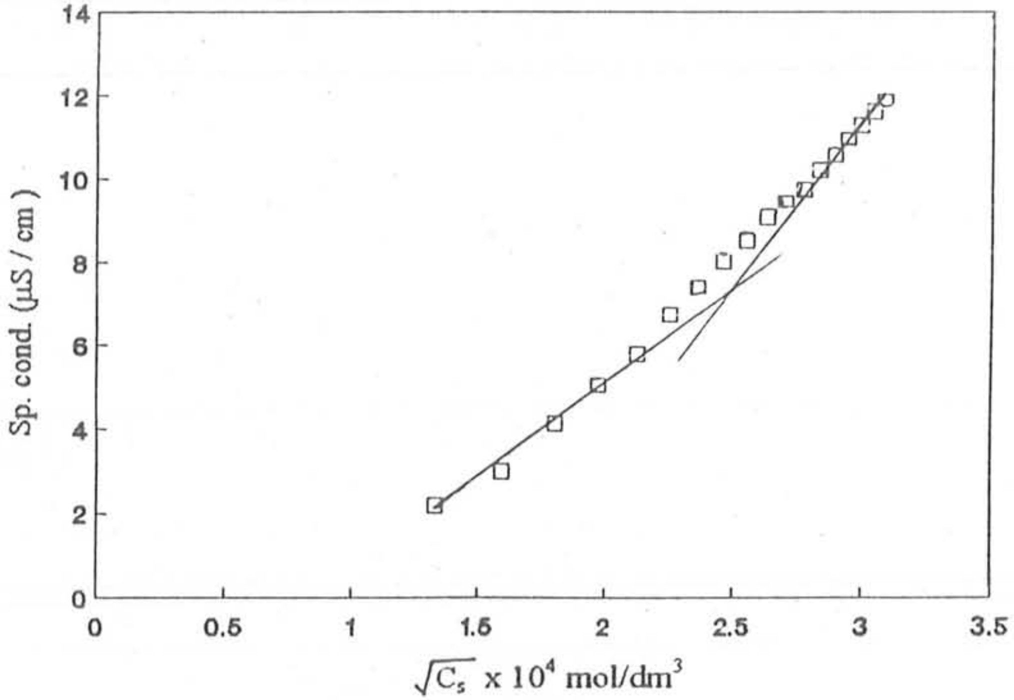


Figure 13. Relation between specific conductance and concentration of SDBS in presence of dye 3 at 25 °C. $C_a = 2.4 \times 10^{-5}$ mol/dm^3.

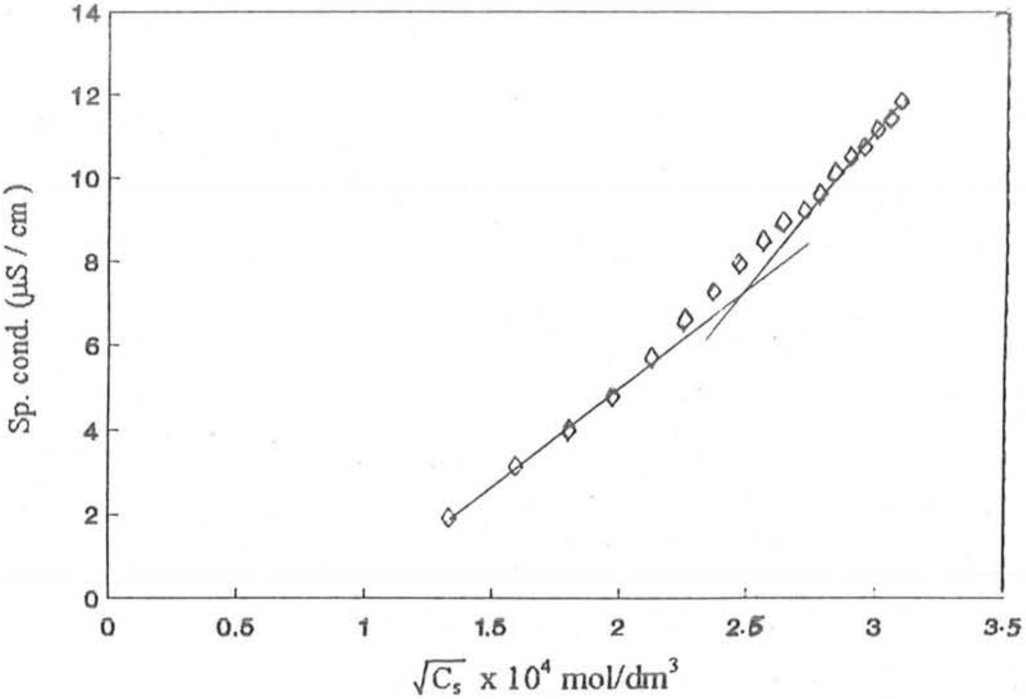


Figure 14. Relation between specific conductance and concentration of SDBS in presence of dye 3 at 25 °C. $C_a = 3.6 \times 10^{-5}$ mol/dm^3.

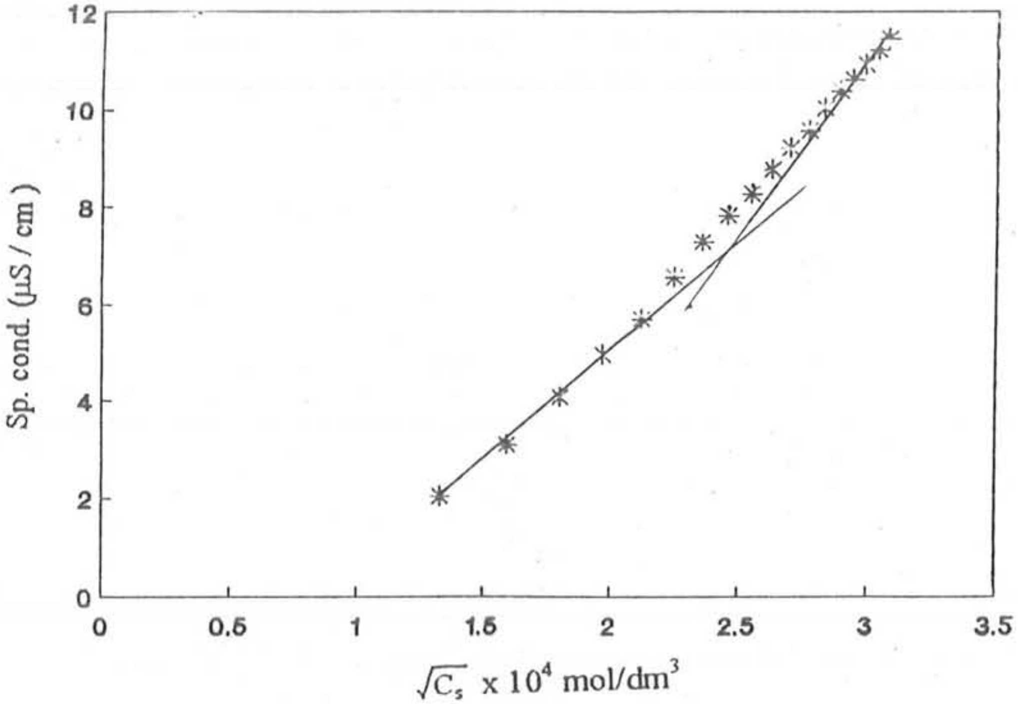


Figure 15. Relation between specific conductance and concentration of SDBS in presence of dye 3 at 25 °C. $C_a = 4.8 \times 10^{-5}$ mol/dm^3.

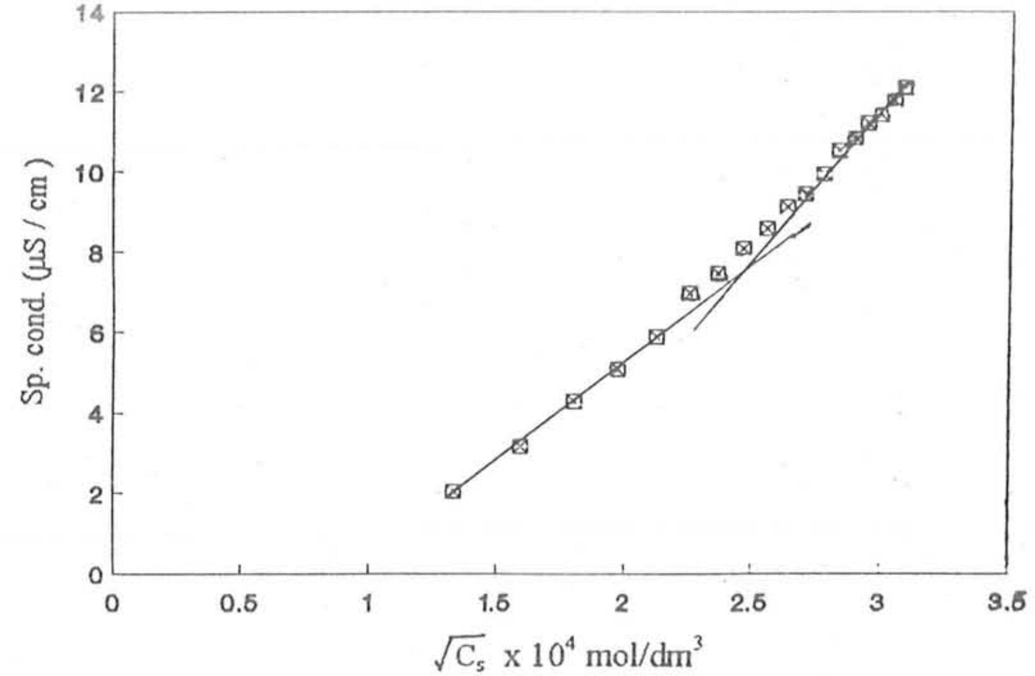


Figure 16. Relation between specific conductance and concentration of SDBS in presence of dye 4 at 25 °C. $C_s = 1.2 \times 10^{-5}$ mol/dm^3.

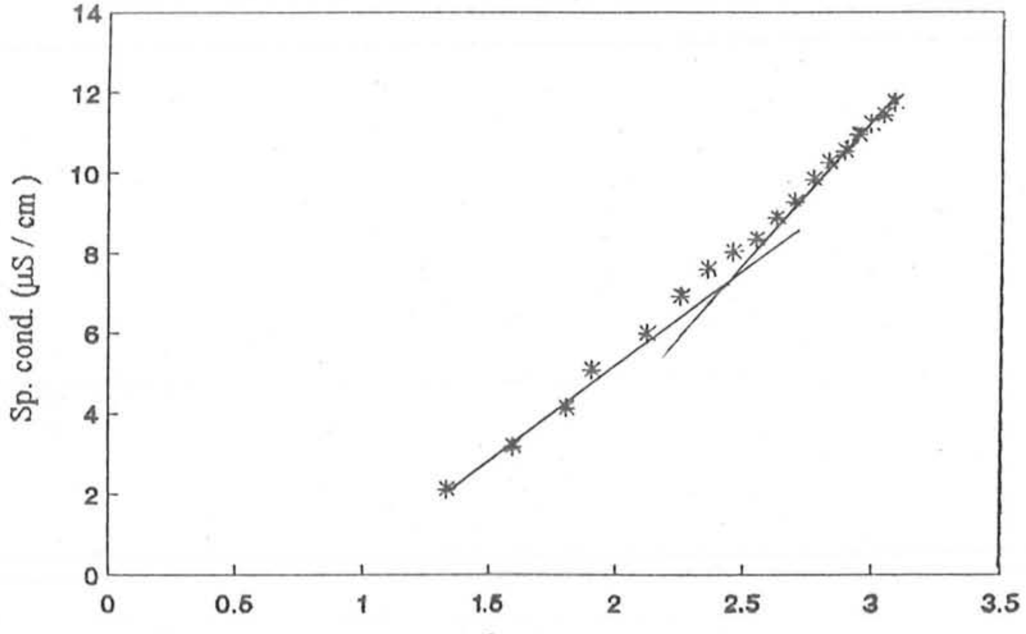


Figure 17. Relation between specific conductance and concentration of SDBS in presence of dye 4 at 25 °C. $C_s = 2.4 \times 10^{-5}$ mol/dm^3.

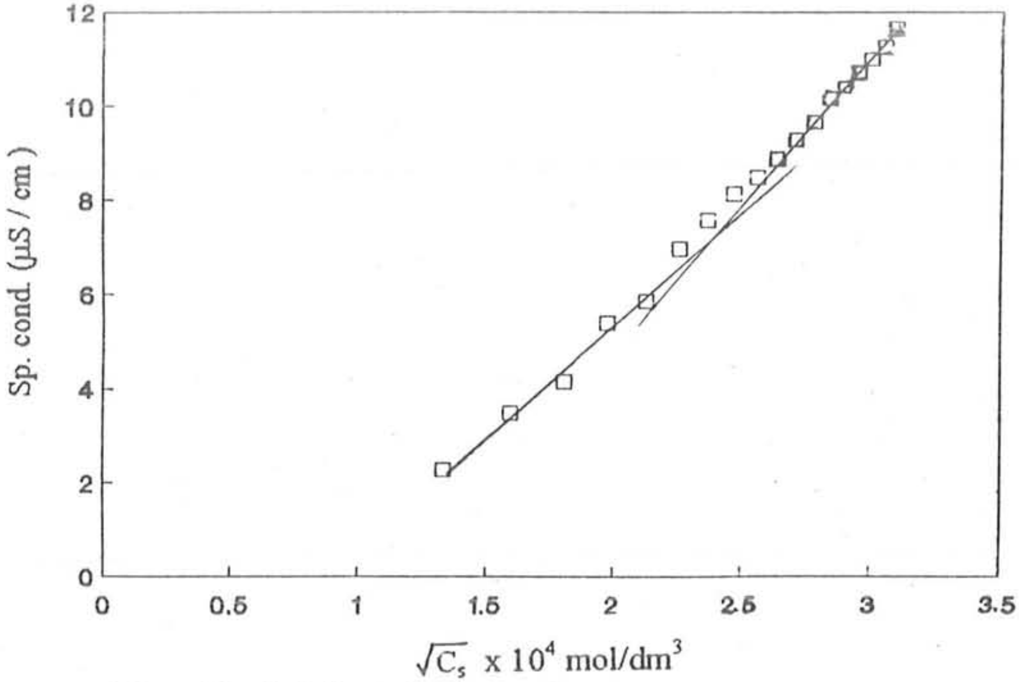


Figure 18. Relation between specific conductance and concentration of SDBS in presence of dye 4 at 25 °C. $C_a = 3.6 \times 10^{-5}$ mol/dm^3.

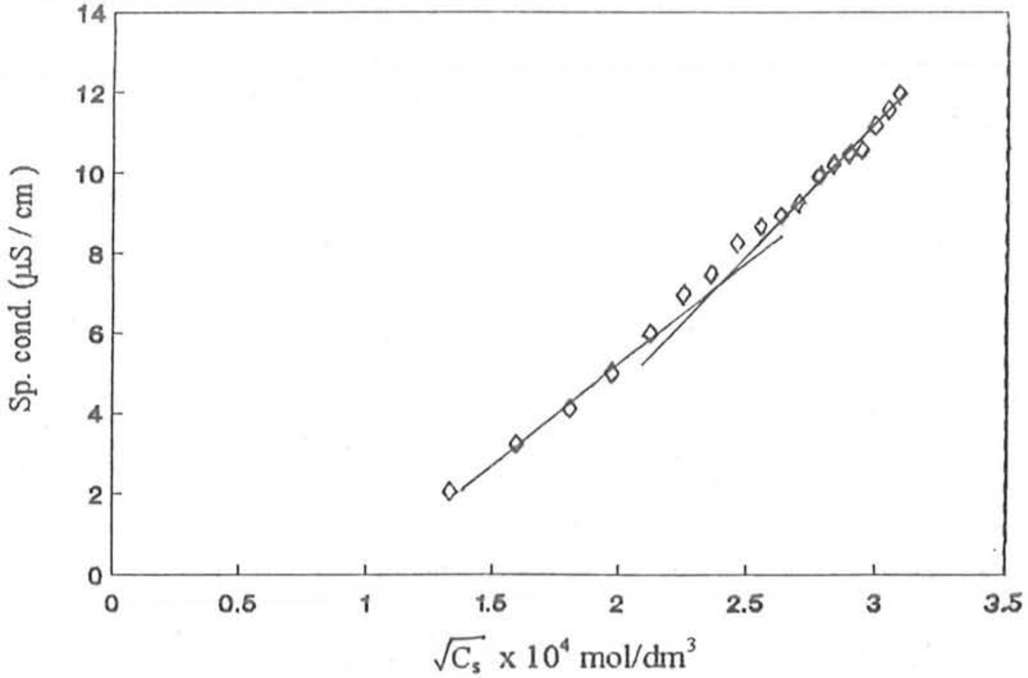


Figure 19. Relation between specific conductance and concentration of SDBS in presence of dye 4 at 25 °C. $C_a = 4.8 \times 10^{-5}$ mol/dm^3.

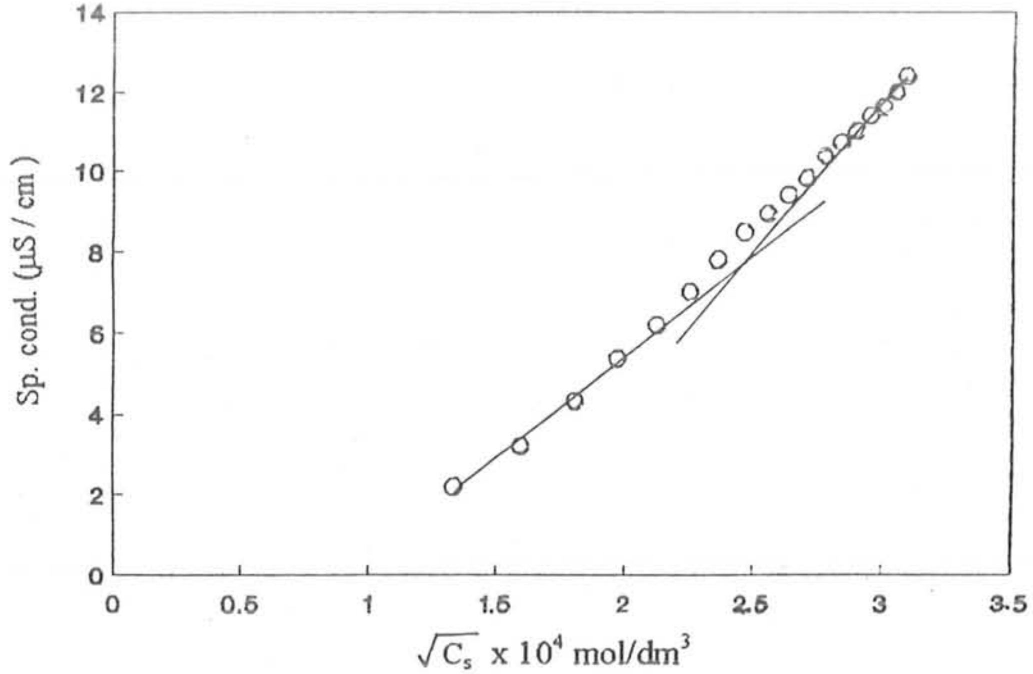


Figure 20. Relation between specific conductance and concentration of SDBS in presence of dye 5 at 25 °C. $C_a = 0.4 \times 10^{-5}$ mol/dm^3.

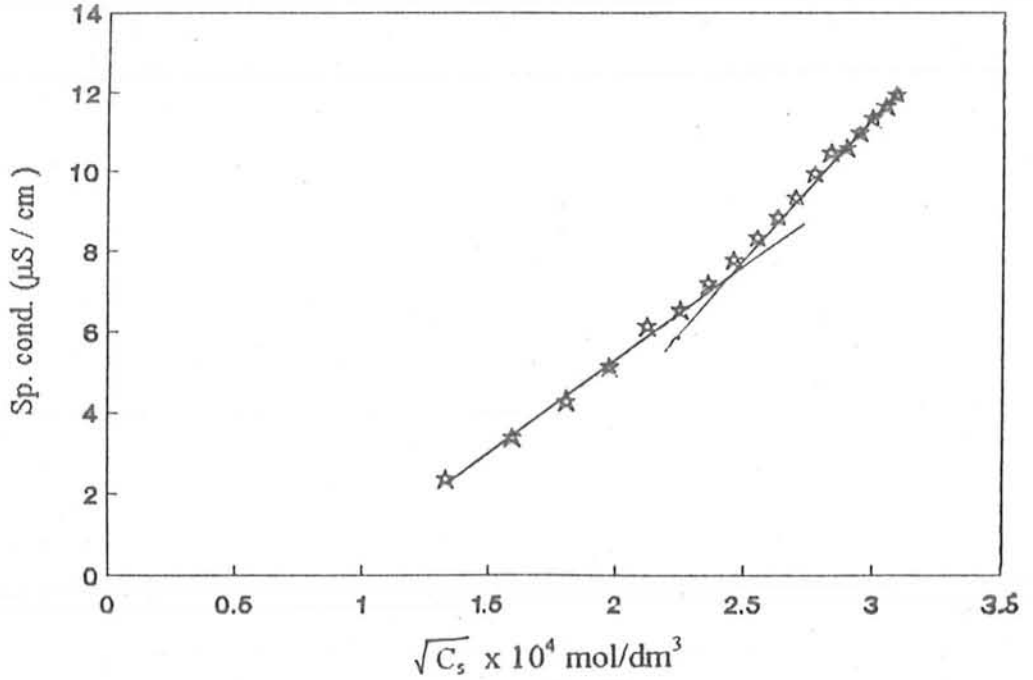


Figure 21. Relation between specific conductance and concentration of SDBS in presence of dye 5 at 25 °C. $C_a = 0.8 \times 10^{-5}$ mol/dm^3.

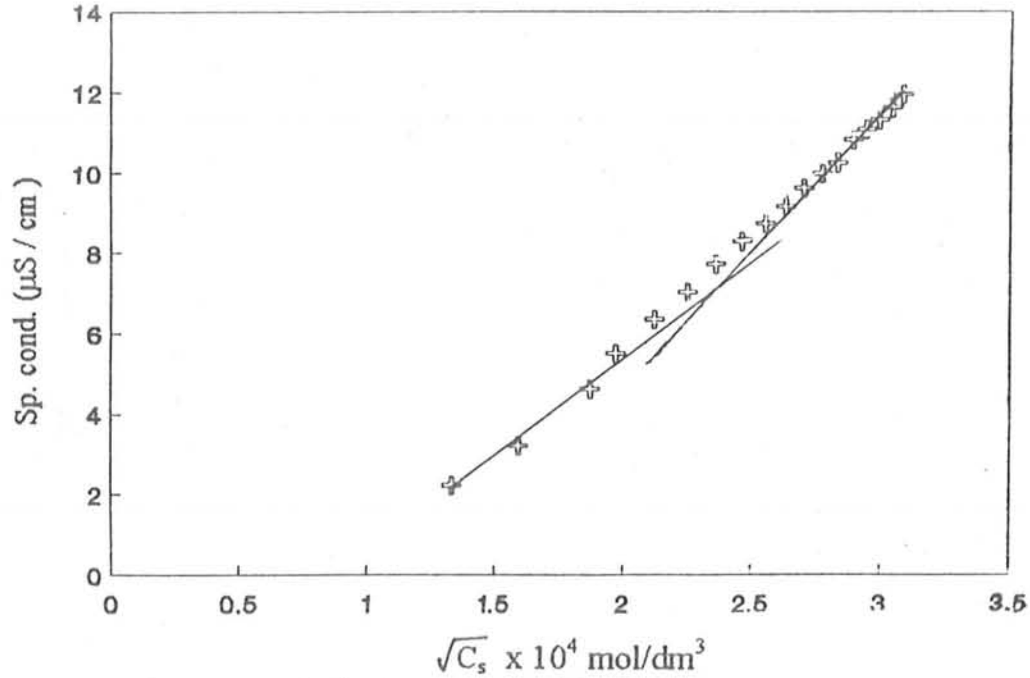


Figure 22. Relation between specific conductance and concentration of SDBS in presence of dye 5 at 25 °C. $C_a = 1.2 \times 10^{-5}$ mol/dm^3.

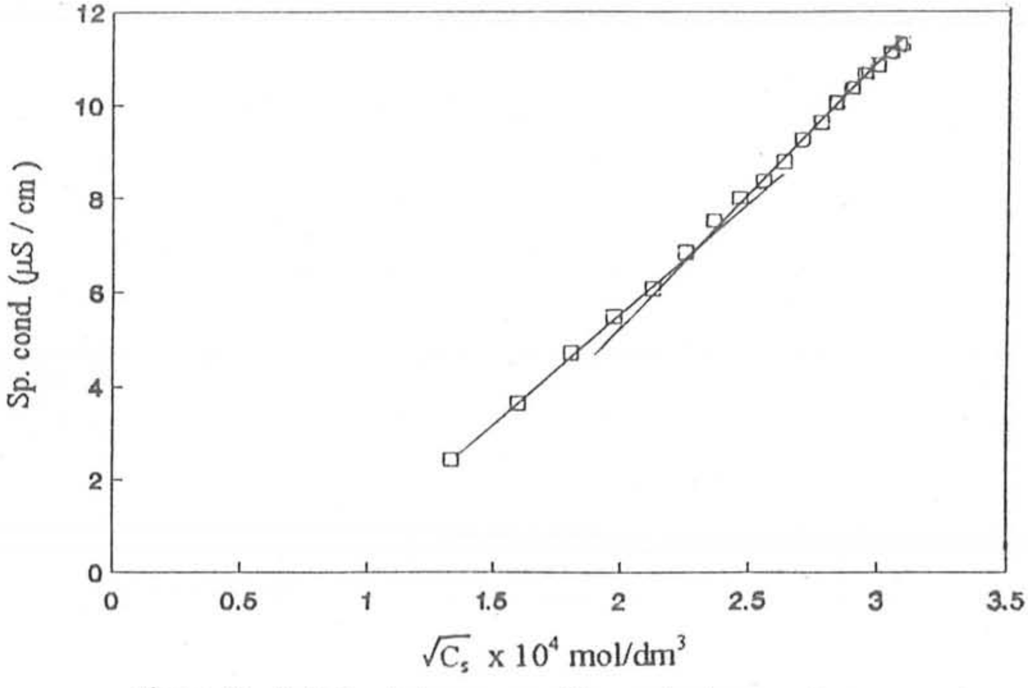


Figure 23. Relation between specific conductance and concentration of SDBS in presence of dye 5 at 25 °C. $C_a = 1.6 \times 10^{-5}$ mol/dm^3.

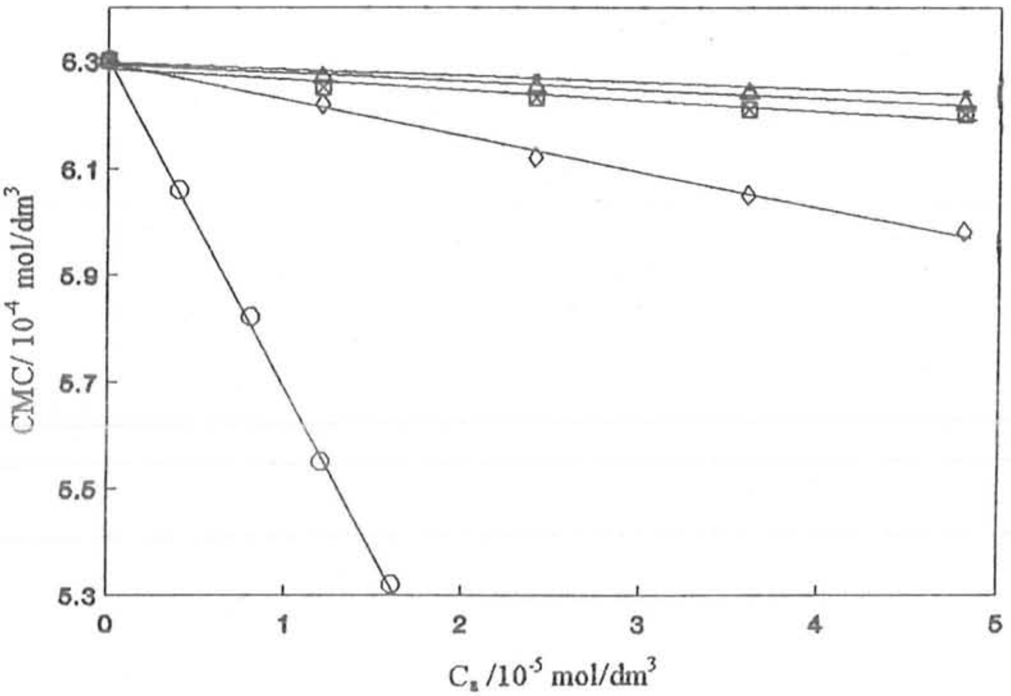


Figure 24. CMC of SDBS as a function of C_s : (▪) $m_p = 2$; (△) $m_p = 4$; (⊠) $m_p = 6$; (◊) $m_p = 8$; (○) $m_p = 10$.

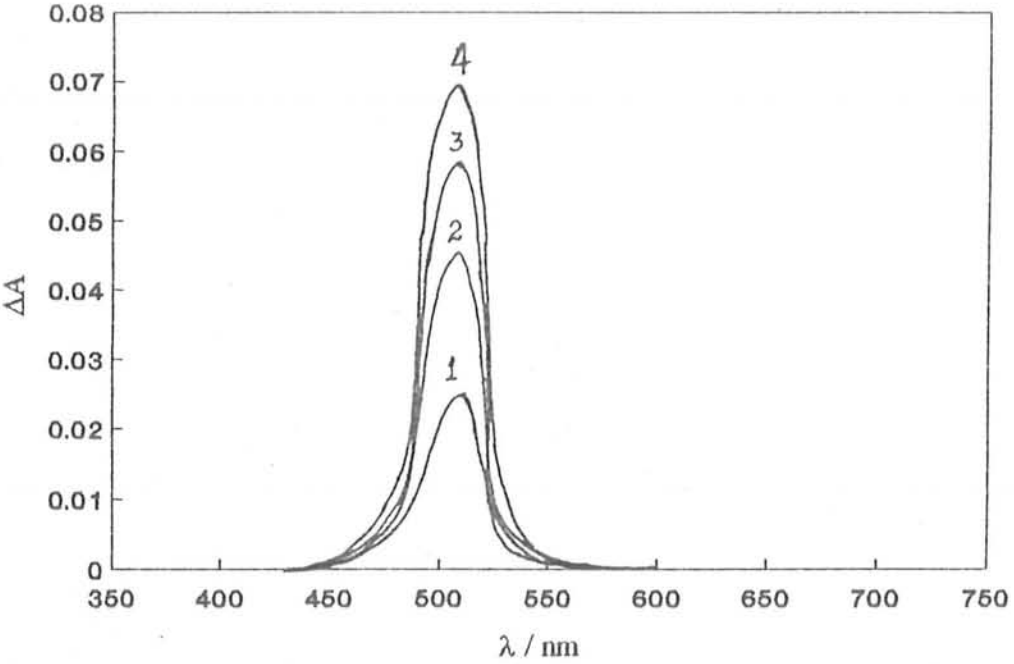


Figure 25. Differential absorption spectra of dye 1 (1.0×10^{-5} mol/dm^3) in SDBS. Concentration of SDBS, C_s = (1) 18.0, (2) 36.0, (3) 54.0, and (4) 90.0 x 10^4 mol/dm^3.

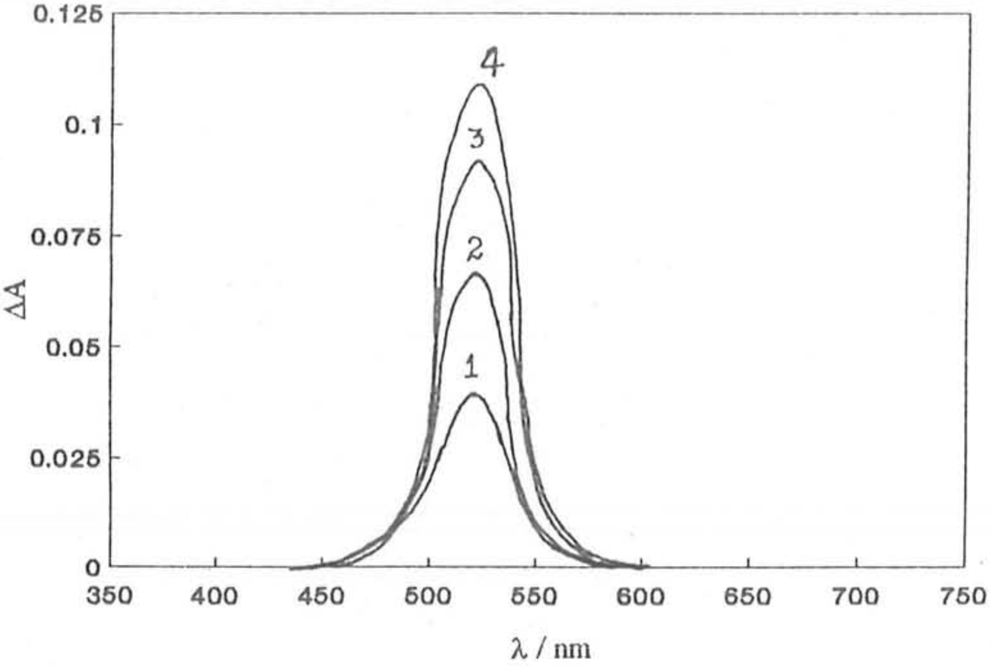


Figure 26. Differential absorption spectra of dye 2 (1.0×10^{-5} mol/dm^3) in SDBS. Concentration of SDBS, C_s = (1) 18.0, (2) 36.0, (3) 63.0, and (4) 90.0 x 10^4 mol/dm^3.

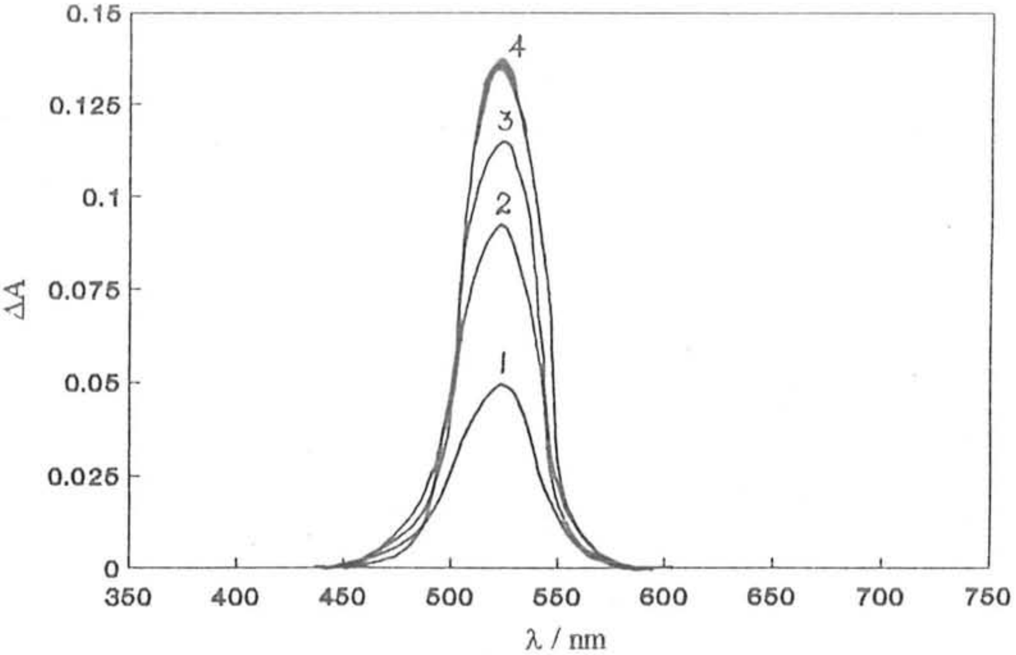


Figure 27. Differential absorption spectra of dye 3 (1.0×10^{-5} mol/dm^3) in SDBS. Concentration of SDBS, C_s = (1) 18.0, (2) 36.0, (3) 63.0, and (4) 90.0×10^4 mol/dm^3.

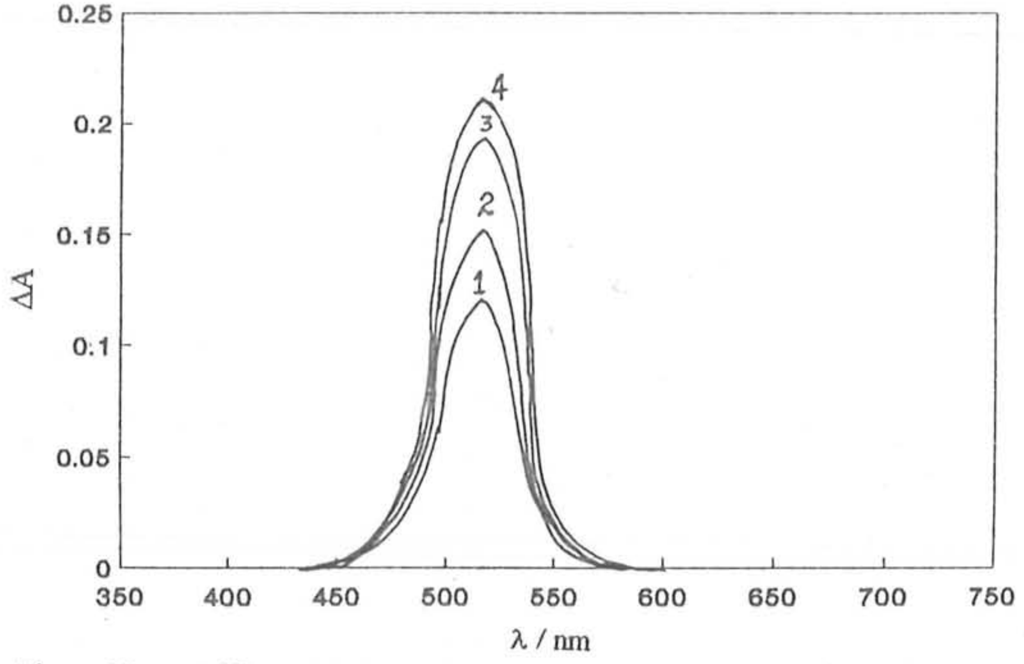


Figure 28. Differential absorption spectra of dye 4 (1.0×10^{-5} mol/dm^3) in SDBS. Concentration of SDBS, C_s = (1) 18.0, (2) 27.0, (3) 45.0, and (4) 90.0×10^4 mol/dm^3.

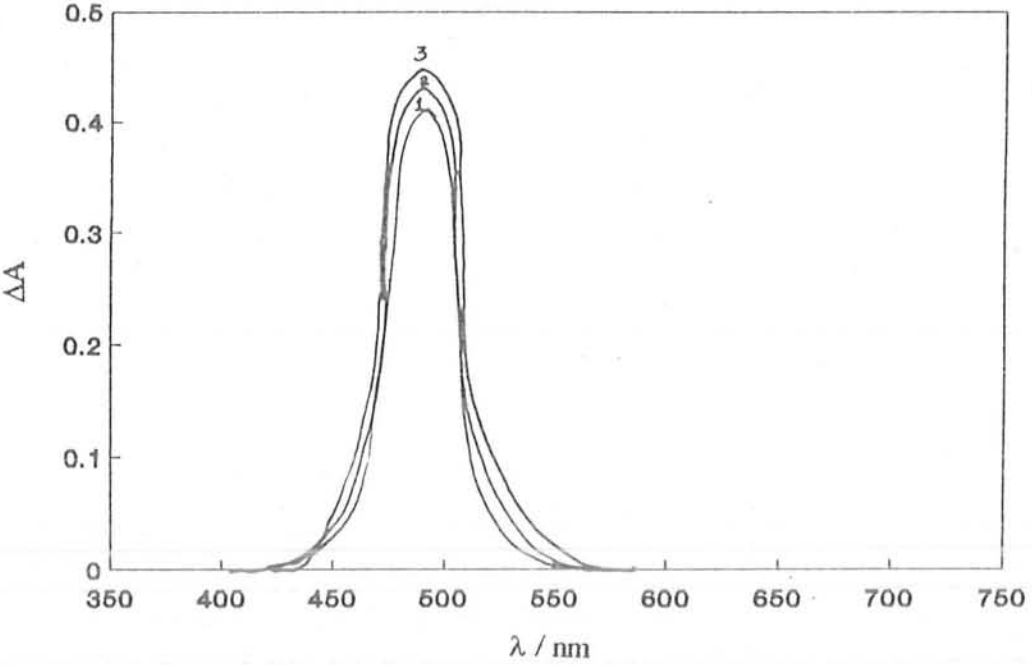


Figure 29. Differential absorption spectra of dye 5 (1.0×10^{-5} mol/dm^3) in SDBS. Concentration of SDBS, C_s = (1) 18.0, (2) 63.0, and (3) and 90.0×10^4 mol/dm^3

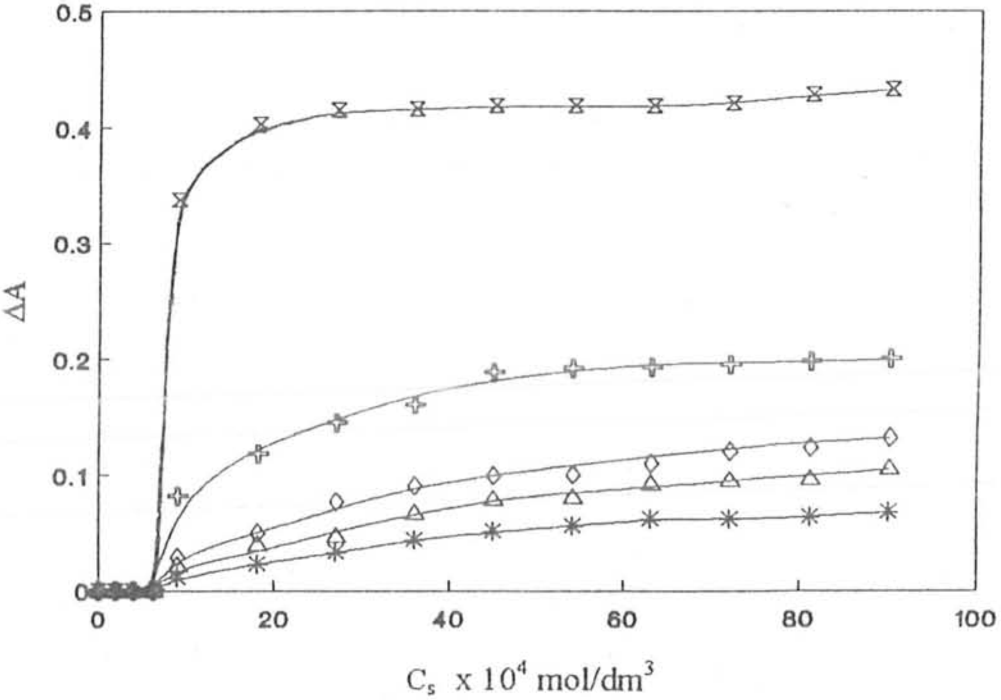


Figure 30. Relation between differential absorbance (ΔA) for dialkylamino stilbazolium butyl sulfonate and concentration of SDBS (C_S) at 25 °C. $C_a = 1.0 \times 10^{-5}$ mol/dm^3.

(✱) Dye 1; (△) Dye 2; (◇) Dye 3; (✙) Dye 4; (⧖) Dye 5.

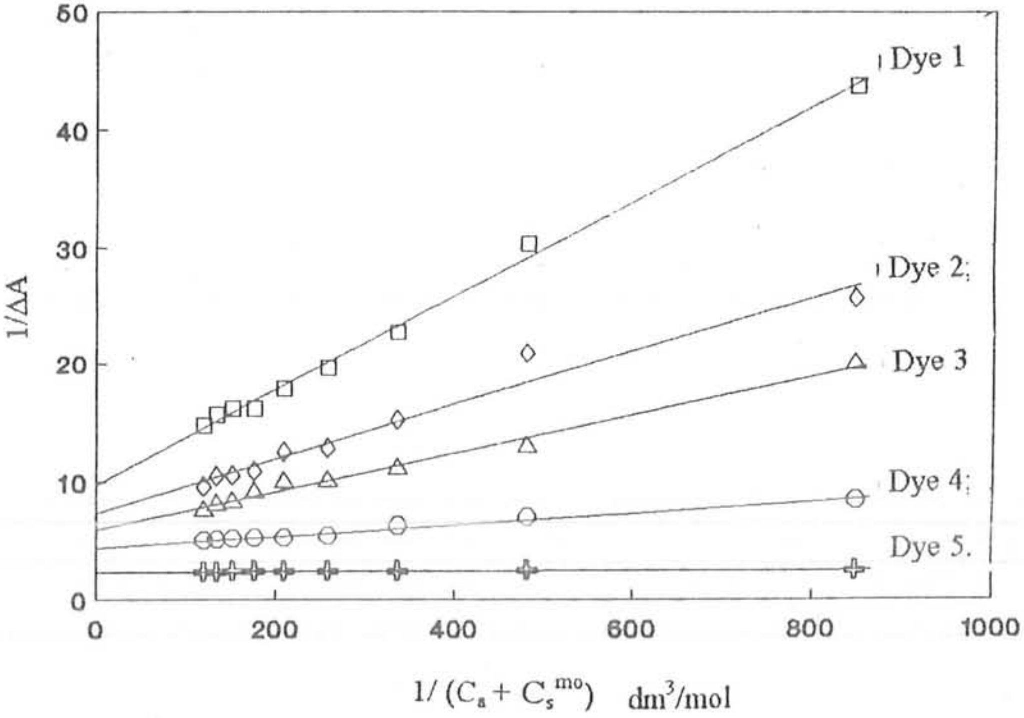


Figure 31. Relation between $1/\Delta A$ and $1/(C_a + C_s^{mo})$ for dialkylamino stilbazolium butyl sulfonate-water in SDBS solution at 25 °C. $C_a = 1.0 \times 10^{-5}$ mol/dm^3

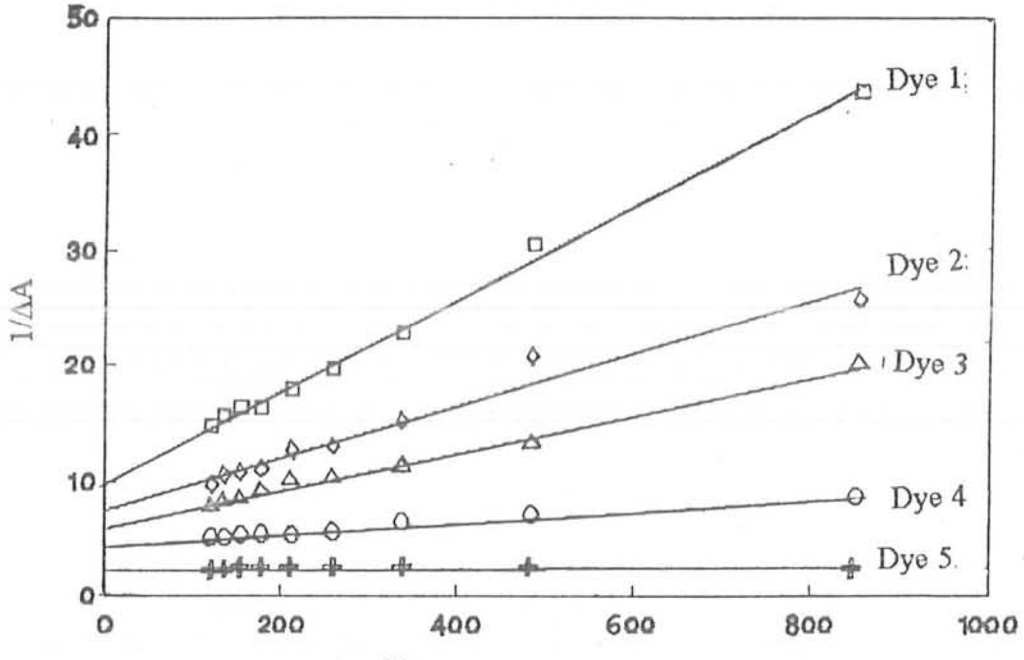


Figure 32. Relation between 1/ΔA and 1/ $[C_s^{mo} - kC_a + (1+k)\ C_a\, j\ ]$ for dialkylamino stilbazolium butyl sulfonate-water in SDBS solution at 25 °C. $C_a = 1.0 \times 10^{-5}$ mol/dm^3

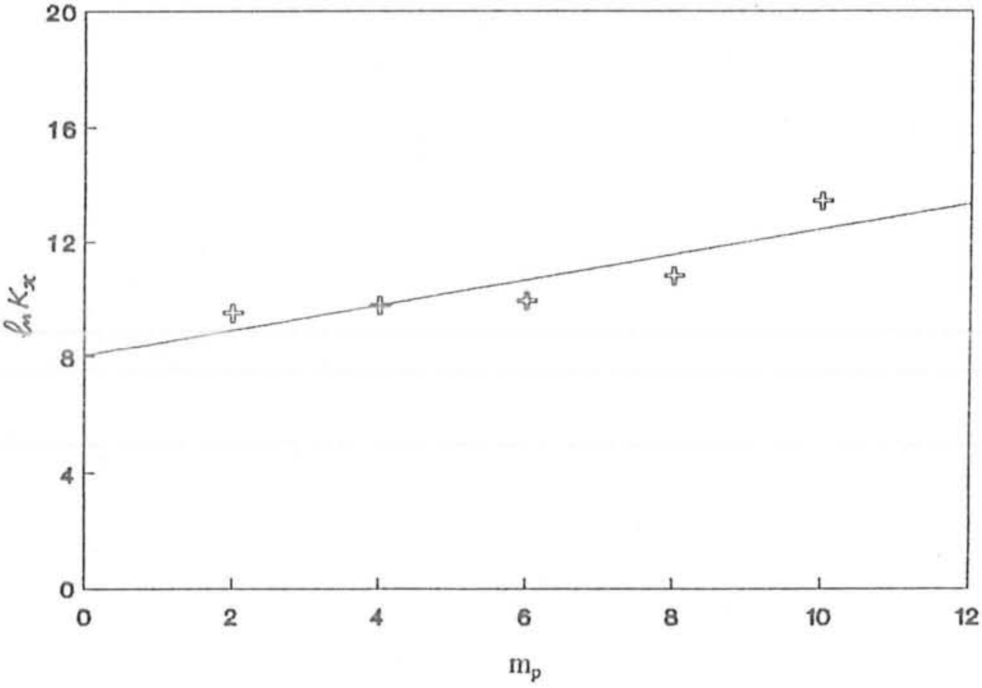


Figure 33. Dependence of ln K_x of hemicyanine dyes between water and SDBS micelles on dialkyl chain length (m_p) at 25 °C.

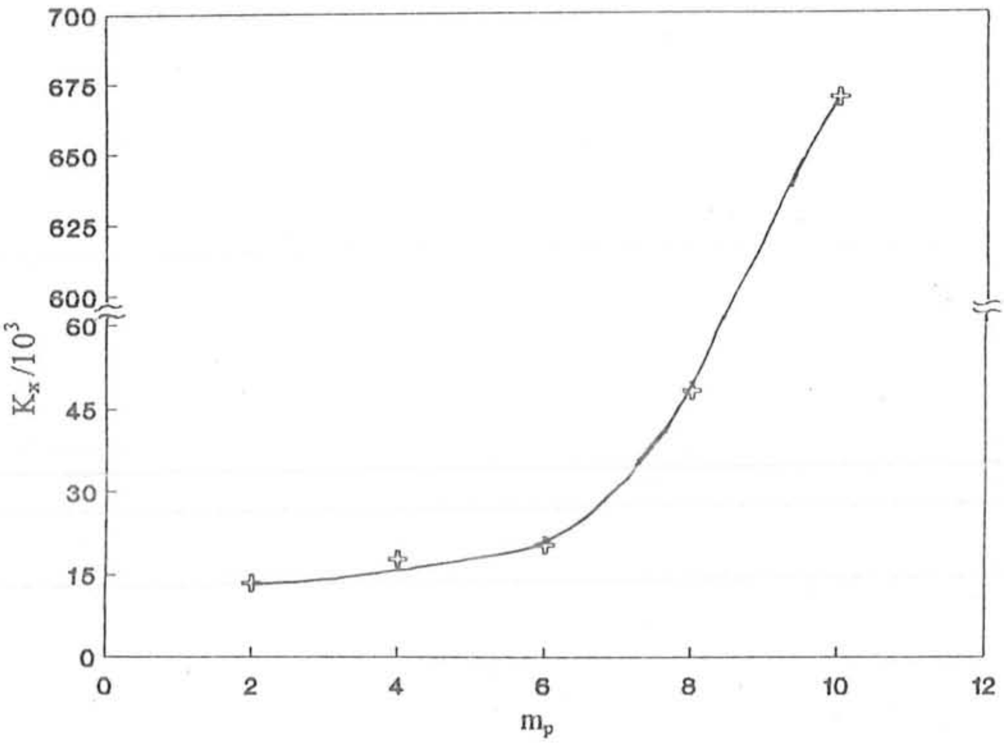


Figure 34. Dependence of K_x of hemicyanine dyes between water and SDBS micelles on m_p at 25 °C.

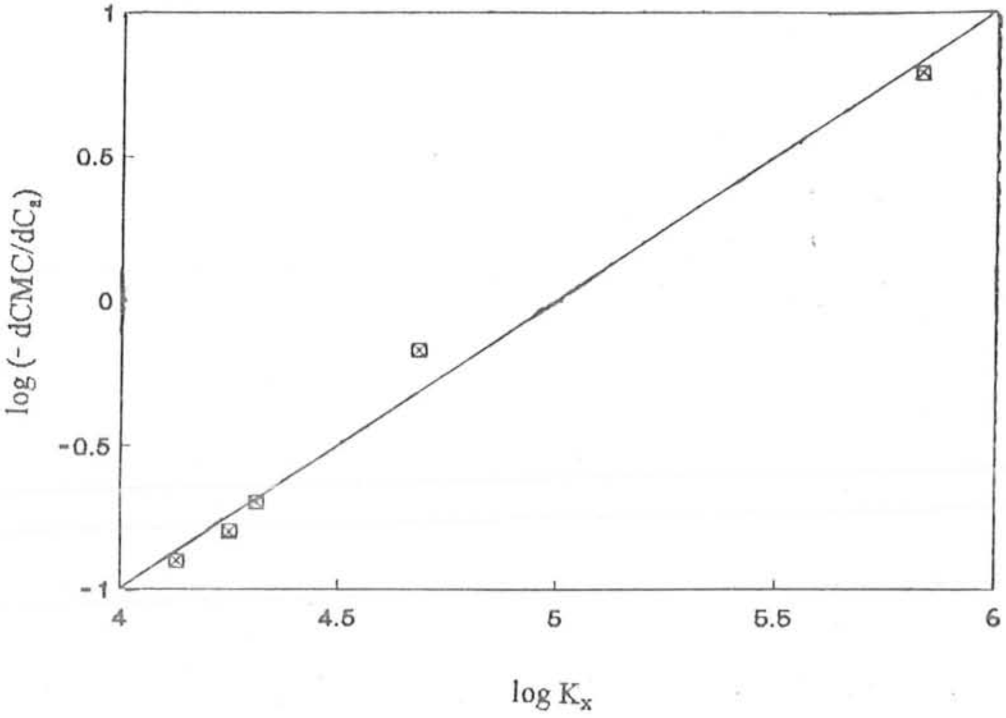


Figure 35. Plot of log (- dCMC/dC$_s$) and log (K$_x$)

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REFERENCES

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