

**A STUDY (i) ON THE MICELLIZATION BEHAVIOUR OF
SURFACTANTS IN AQUEOUS ELECTROLYTIC SOLUTIONS
AND (ii) ON THE INDICATOR EQUILIBRIA IN
MICROEMULSION MEDIA**



ABSTRACT

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NEHU**

**A THESIS
SUBMITTED
IN FULFILMENT OF THE REQUIREMENT FOR
THE DEGREE OF
DOCTOR OF PHILOSOPHY**

TO



**THE NORTH - EASTERN HILL UNIVERSITY
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In Chapter 1 a general introduction to the subject of study has been given along with the scope and scheme of the work. In Chapter 2 a broad outline of experimental techniques and the methods of data analysis adopted are given.

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on electrolyte concentration was analyzed. Dependence of cmc on coion concentration (acetate ion) has been detected in addition to its dependence on counterion concentration.

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In Chapter 6 we developed a computer program to calculate the surface potentials of ionic micelles by solving numerically the non - linearized Poisson - Boltzmann equation using the fourth - order Runge - Kutta method. The computer program was first tested by calculating surface potentials of known micellar systems. A complete agreement has been obtained with the reported values. Surface potentials of SDS in sodium acetate, sodium propionate and sodium chloride solutions were then computed using the data presented in Chapter 5.

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“ एतद् सर्वम् श्री गुरुगोविन्दचरणारविन्देषु समर्पितम् ”





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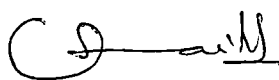
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CERTIFICATE

I certify that the thesis entitled "A Study (i) on the Micellization Behaviour of Surfactants in Aqueous Electrolytic Solutions and (ii) on the Indicator Equilibria in Microemulsion Media" submitted by Mr.Babul Chandra Paul for the Degree of Doctor of Philosophy of the North - Eastern Hill University, embodies the record of original investigation carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the Ph.D Degree. This work has not been submitted for any degree of any other University.

Place : Shillong

Date : 23/8/96


(Dr.K.Ismail)

Supervisor

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Shillong, Dated

23rd August, 1996.

Babulchandra Paul.

BABUL CHANDRA PAUL

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Chapter 1

General Introduction

1.1 SURFACTANTS

Molecules consisting of a nonpolar hydrophobic portion and a polar hydrophilic portion exhibit interesting behaviour at surfaces and interfaces. Such molecules are therefore called as surface-active agents or surfactants or amphiphiles. The polar hydrophilic part of a surfactant molecule is called the hydrophilic or lipophilic group and the nonpolar hydrophobic part is called the hydrophobic or lipophobic group. Often the hydrophilic part of the molecule is simply called the head and the hydrophobic part, consisting of a hydrocarbon chain with 8 or more carbon atoms, is called the tail. Surfactants are classified on the basis of the charge carried by the polar head group as anionic, cationic, nonionic or zwitterionic.

1.2 THERMODYNAMICS OF LOWERING OF SURFACE TENSION BY SURFACTANTS.

An equilibrium exists between the surfactant molecules at the surface or interface and those in the bulk solution. The change in surface Gibbs function, dG_{σ} at

constant temperature and pressure is given as

$$dG_{\sigma} = \gamma d\sigma + \sum_i \mu_i dn_{i\sigma} \quad (1.1)$$

where γ is the surface tension, $d\sigma$ is the change in the area of the surface, μ_i is the chemical potential of the i th component and $dn_{i\sigma}$ is the change in the amount of i th component at the interface. The Gibbs surface tension equation¹ in its general form is written as

$$d\gamma = - \sum_i \tau_i d\mu_i \quad (1.2)$$

is the change in surface or interfacial tension of the solvent and $d\mu_i$ is the change in chemical potential of the i th component. τ_i is the surface excess concentration of the i th component and is defined as

$$\tau_i = n_{i\sigma} / \sigma \quad (1.3)$$

$n_{i\sigma}$ and τ_i can be positive or negative. For a two-component system at constant temperature and pressure equation(1.2) reduces to

$$d\gamma = -\tau_1 d\mu_1 - \tau_2 d\mu_2 \quad (1.4)$$

Subscripts 1 and 2 refer to solvent and solute, respectively. A convenient choice of location of the arbitrarily chosen dividing surface of the two bulk phases is that at which the surface excess concentration of the solvent, τ_1 is zero. This is infact the

most realistic position since we are considering a surface layer of adsorbed solute. Eq (1.4) then becomes

$$d\gamma = -\tau_2 d\mu_2 = -\tau_2 RT d\ln a_2 \quad (1.5)$$

where a_2 is the activity of solute, R is the gas constant and T is the temperature. For dilute solutions τ_2 can be written as

$$\tau_2 = -(1/RT) (d\gamma/d\ln c_2) \quad (1.6)$$

where a_2 has been replaced by the concentration, c_2 . Since τ_2 is positive for surfactants, $d\gamma/d\ln c_2$ must be negative. Therefore accumulation of surfactants on the surface or interface lowers the surface tension. In surfactant solutions the surface tension initially decreases with increasing surfactant concentration and then attains a constant value above a critical concentration. Because of the ability of surfactants to lower interfacial tension, they are used as emulsifiers, detergents, dispersing agents, foaming agents, etc.

1.3 MICELLE FORMATION

One of the most characteristic properties of amphiphilic molecules is their capacity to aggregate in solutions. Near the concentration at which aggregation of

surfactants begins to occur sudden changes in many physical properties of surfactant solutions take place. The narrow concentration range over which changes in physical properties like surface tension, conductivity, viscosity, solubilization, osmotic pressure, etc take place is called the critical micelle concentration (cmc). The molecular aggregates that form above cmc are known as micelles. The micelles unlike other colloids are in dynamic equilibrium with the monomers in the solution.

1.4 HYDROPHOBIC INTERACTION

Frank and Evans² introduced the idea that water molecules form 'ice-bergs' around nonpolar solutes. In general terms it can be said that the water molecules become more ordered around the hydrophobic solute with an increase in hydrogen bonding in this region. Nonpolar solutes are also described to dissolve interstitially in water.³ The favourable free energy for transfer of a nonpolar solute from an aqueous to a hydrophobic environment results from a large positive entropy associated with the disordering of water molecules in the vicinity of nonpolar solutes. Such interaction between a nonpolar solute and

water molecules is termed as hydrophobic interaction or hydrophobic hydration. Statistical thermodynamic analysis of hydrophobic effects has been reported.^{4,5} The driving force for micellization results therefore from the transfer of nonpolar surfactant chains from an ordered aqueous environment to the hydrocarbon like environment of the micelle interior. In the absence of hydrophobic interaction a large negative entropy would otherwise have been expected for the transfer of surfactant molecules and counterions from aqueous solution to the confines of a small micelle. Accordingly, the entropy generated in the solvent medium actually drives the micellization process. This concept suggests that micellization process is not restricted only to aqueous medium. A more general term called the solvophobic interaction is therefore used for the interaction between solvent molecules and amphiphiles.^{4,6} It has been reported⁷ that solvents having $\gamma/V^{1/3} > 17 \text{ erg cm}^{-3}$ produce micellization. γ is the solvent surface tension as defined above and V is its molar volume.

1.5 STRUCTURE OF MICELLES

A general structure of a regular ionic micelle consists of a liquid core formed by the associated hydrocarbon chains with the fully ionized head groups projecting out into the water. Similar structure of micelle exists in polar non-aqueous solvents also. In nonpolar solvents the structure of micelle gets reversed and such a micelle is called a reverse micelle. Immediately surrounding the core is the Stern layer which contains the ionic head groups and a part of counterions (bound counterions). The Stern layer constitute the inner part of the electrical double layer surrounding the micelle. The outer layer which is a diffuse layer contains the remaining counterions (free counterions) and is termed as Gouy-Chapman layer. The average location of the interface between the core and the water has been reported⁸ to be 0.08 ± 0.04 nm above the α carbon atom of the associated alkyl chains. Appreciable amount of water has been reported^{9,10} to penetrate into the liquid-like hydrocarbon core.

1.6 MICELLAR SHAPE

Since micelles are dynamic structures with a liquid core it is probably unrealistic to regard them as rigid structures with a precise shape. It is, however, instructive to consider an average micellar shape. Hartley¹¹ proposed that micelles are spherical with the charged groups situated at the micellar surface. Small-angle neutron scattering experiments on sodium dodecyl sulfate and other ionic micelles^{12,13} support the Hartley model of a spherical micelle. As the ion concentration is increased, the shape of ionic micelles changes in the sequence spherical - cylindrical - hexagonal - lamellar.¹⁴⁻¹⁶ The concentration range where a sphere to cylindrical (or rod) transition takes place is referred to as the second cmc.¹⁷

1.7 THERMODYNAMICS OF MICELLE FORMATION

Two main approaches to the thermodynamic analysis of the micellization process have gained wide acceptance.^{1,16,18} In the phase-separation approach the micelles are considered to form a separate phase at the cmc, while in the mass-action approach micelles and unassociated monomers are considered to be in association-dissociation

equilibrium. The two models merge asymptotically with increasing micellar aggregation number. Besides these two approaches thermodynamics of small systems developed by Hill¹⁹ has also been applied to the aggregation of solutes.^{16,20} Application of mass-action law to small thermodynamic systems has been critically assessed recently by Blumenfeld et al.²¹ and by Sokirko.²² The phase-separation and the mass-action models are briefly discussed below.

1.7.1 PHASE-SEPARATION MODEL

In this approach the micelle is treated as a separate phase although there are problems associated with the application of the phase rule to micellar phase. In order to calculate the thermodynamic parameters for the micellization the standard states need to be defined first. The hypothetical standard state for the surfactant in the aqueous phase is taken to be the solvated monomer at unit mole fraction with the properties of the infinitely dilute solution. For the surfactant in the micellar state, the micellar state itself is considered to be the standard state.^{23,24}

If μ_s and μ_m are the chemical potentials of the unassociated surfactant in the aqueous phase and of the associated surfactant in the micellar phase, respectively, and since the two phases are in equilibrium at and above the cmc

$$\mu_s = \mu_m \quad (1.7)$$

For a non-ionized surfactant

$$\mu_s = \mu_s^0 + RT \ln a_s \quad (1.8)$$

μ_s^0 corresponds to the chemical potential at the standard state. It is assumed that the concentration of free monomers is low and this permits one to replace the activity a_s of surfactant monomers by its mole fraction, x_s . Eq 1.8 is therefore written as

$$\mu_s = \mu_s^0 + RT \ln x_s \quad (1.9)$$

Since micellar phase is treated as a separate hydrocarbon phase the mole fraction of the associated surfactant in this phase is equal to one and we obtain

$$\mu_m = \mu_m^0 \quad (1.10)$$

If ΔG_m^0 is the standard free energy change for transfer of one mole of amphiphile from solution to micellar phase, then

$$\begin{aligned} \Delta G_m^0 &= \mu_m^0 - \mu_s^0 \\ &= \mu_m - \mu_s + RT \ln x_s \end{aligned}$$

$$= RT \ln x_s \quad (1.11)$$

Assuming that the concentration of free surfactant in the presence of micelle is constant and equal to the cmc value, x_{cmc} , we get

$$\Delta G_m^0 = RT \ln x_{cmc} \quad (1.12)$$

Since the number of moles of free surfactant, n_s , is small compared to the number of moles of water, n_{H_2O} ,

$$x_{cmc} \approx n_s / n_{H_2O} \quad (1.13)$$

Eq 1.12 therefore also takes the form

$$\Delta G_m^0 = RT(\ln cmc - \ln 55.55) \quad (1.14')$$

In the case of ionic surfactants ΔG_m^0 must also include the free energy change for the transfer of β moles of counter ion from its standard state to the micelle. β is the number of moles of counterion per mole of the associated monomer in the micellar phase. If one mole of micelle consist of n moles of surfactant and $(n-z)$ moles of counterion,

$$\beta = (n - z)/n \quad (1.14)$$

β is termed as the counterion binding constant. Therefore for ionic surfactants eq 1.12 is written as

$$\Delta G_m^0 = RT \ln x_s + \beta RT \ln x_x \quad (1.15)$$

x_x is the mole fraction of counterion. At the cmc when the micellar phase is just formed, in the absence of added

electrolyte it can be approximated that

$$x_s = x_x = x_{cmc} \quad (1.16)$$

and eq 1.15 becomes

$$\Delta G_m^0 = (1 + \beta) RT \ln x_{cmc} \quad (1.17)$$

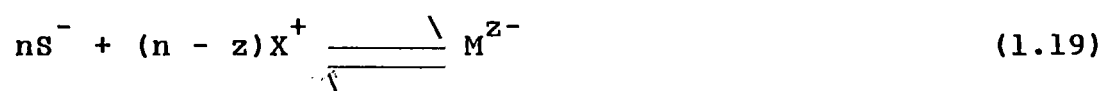
If it is considered that the micellar phase is composed of the charged aggregate of monomers together with an equivalent number of counterions to make the micellar phase electrically neutral, we get

$$\Delta G_m^0 = 2RT \ln x_{cmc} \quad (1.18)$$

One of the main criticisms of the phase-separation model is that it predicts that the activity of the monomers above the cmc remains constant. However, the monomer activity has been reported^{25,26} to decrease with increasing surfactant concentration above the cmc.

1.7.2 MASS - ACTION MODEL

According to this model in the case of ionic surfactants micelles are assumed to be in equilibrium with the unassociated surfactant ions and counterions. Further it is assumed that micelles are effectively monodispersed. The equilibrium is represented as



where S^- represents the single detergent ions, X^+ represents the counterions, M^{z-} represents micelles, n is the aggregation number and z is the charge on the micelle. Applying mass-action law to the above equilibrium, the corresponding equilibrium constant, K , can be written as

$$K = a_m / \left[a_s^n a_x^{n-z} \right] \quad (1.20)$$

a_s , a_x and a_m are activities of the surfactant monomers, counterions and of micelles, respectively. Presuming ideal behaviour, eq 1.20 takes the form

$$K = C_m / \left[C_s^n C_x^{n-z} \right] \quad (1.21)$$

where C_s , C_x and C_m are the concentrations of monomers, counterions and micelles, respectively. Phillips²⁷ accounted for the nonideality by considering an effective charge on micelle equal to $n-p$ instead of $n-z$. The standard free energy of micellization per mole of monomeric surfactant is given by

$$\Delta G_m^0 = -(RT/n) \ln K \quad (1.22')$$

Substituting for K from eq 1.21, we obtain

$$\Delta G_m^0/RT = -(1/n) \ln C_m + \ln C_s + [(n-z)/n] \ln C_x \quad (1.22)$$

Eq 1.22 can be rewritten as

$$\ln C_s = \left[(\Delta G_m^0/RT) + (1/n) \ln C_m \right] - \left[(n-z)/n \right] \ln C_x \quad (1.23)$$

Near the cmc, C_s may be approximated to cmc and the value of C_m will be very low. Under this condition,²⁸ we can write

$$(\Delta G_m^0/RT) + (1/n) \ln C_m \approx \Delta G_m^0/RT \quad (1.24)$$

For instance, if $C_m = 0.1 \text{ mol dm}^{-3}$ and $n=50$,

$(1/n) \ln C_m = -0.046$ whereas $\Delta G_m^0/RT$ is reported^{24,27} to have a value of about -10 to -15 . With these approximations eq 1.23 is modified to

$$\ln c_{mc} = (\Delta G_m^0/RT) - \beta \ln C_x \quad (1.25)$$

where $\beta = (n-z)/n$ as defined in eq 1.14. In the absence of added electrolyte C_x is approximated to c_{mc} whereas in the presence of an added electrolyte $C_x = C_{add} + c_{mc}$, C_{add} being the concentration of counterion supplied by the added electrolyte. Eq (1.25) is sometimes referred as the Corrin-Harkins relation.²⁹ If mole fraction units are used, eq 1.25 becomes

$$\ln x_{cmc} = \left(\Delta G_m^0/RT \right) - \beta \ln x_x \quad (1.26)$$

In the absence of added electrolyte eq 1.26 reduces to

$$\Delta G_m^0/RT = (1+\beta) \ln x_{cmc} \quad (1.27)$$

It can be noted that eqs 1.26 and 1.27 are identical to eqs 1.15 and 1.17 derived from the phase-separation model. Phillips,²⁷ on the other hand, employed a different approach to obtain an expression similar to eq 1.25. Phillips first defined c_{mc} as the concentration at which

$$\left[d^3 \phi / dC^3 \right]_{C=c_{mc}} = 0 \quad (1.28)$$

where ϕ is any property of a surfactant solution having dependence on concentration, C. It was shown by Phillips²⁷ that near cmc, in the absence of added electrolyte,

$$\text{cmc}/C_m \approx 4n^2 \quad (1.29)$$

and, in the presence of added electrolyte,

$$\text{cmc}/C_m \approx 2n^2 \quad (1.30)$$

For practical purposes it was assumed²⁷ over the entire range of electrolyte concentration that

$$\text{cmc}/C_m \approx 3n^2 \quad (1.31)$$

Substituting eq 1.31 in eq 1.22, we obtain

$$\Delta G_m^0/RT = (1/n)\ln 3n^2 + [(n-1)/n]\ln \text{cmc} + [(n-z)/n]\ln C_x \quad (1.32)$$

In eq 1.32 if we use the approximations,

$(\Delta G_m^0/RT) - (1/n)\ln 3n^2 \approx \Delta G_m^0/RT$ and $(n-1)/n \approx 1$, Phillips approach also gives the same expression as eq 1.25.

1.8 MICELLIZATION PARAMETERS

The frequently referred micellization parameters are cmc, aggregation number, counterion binding constant, free energy of micellization, molecular weight of micelle, Kraft temperature, surface potential and core radius. Attempts have been made to determine these parameters from the various physicochemical studies made on micellar solutions. Out of

103233



these the most significant parameter which has been widely studied and discussed is the cmc.

1.9 CRITICAL MICELLE CONCENTRATION

As mentioned above the narrow concentration range over which surfactant solutions show an abrupt change in physical properties is called the cmc. A variety of experimental methods have been used to determine the cmc and mostly it is taken directly as the concentration at which the property under measurement shows a singularity when plotted versus surfactant concentration. Therefore slight variations exist in the values of cmc of a particular surfactant determined from different properties. In order to minimize the arbitrariness involved in the determination of cmc several definitions of cmc have been proposed.^{30,31} Phillips²⁷ defined the cmc as the concentration corresponding to the maximum change in the gradient of a solution property versus concentration curve and is represented as already given above by eq 1.28. This definition has now been widely accepted.^{16,32,33} A schematic illustration of cmc determination according to the definition of Phillips²⁷ is shown in Fig 1.1.

1.10 FACTORS AFFECTING THE CMC OF IONIC SURFACTANTS

1.10.1 Nature of the hydrophobic group

For ionic amphiphiles increase in the number of carbon atoms in unbranched hydrocarbon chains leads to a decrease in the cmc.²³ The dependence of cmc on the number of carbon atoms in the chain, n_c , for compounds with the same head group is expressed by the empirical equation

$$\ln \text{cmc} = A - Bn_c \quad (1.33)$$

where A and B are constants for a given homologous series.³⁴

As a general rule, for ionic surfactants the cmc is halved when the length of the straight hydrocarbon chain is increased by one methylene group.²³ For chains of greater length than 16 carbon atoms eq 1.33 no longer holds and further increase in chain length often has no appreciable effect on the cmc, probably due to the coiling of the long chains in solution.³⁵ A phenyl group when introduced into a straight hydrocarbon chain is roughly equivalent in its effect on the cmc to three and half methylene groups.²³

1.10.2 NATURE OF THE HYDROPHILIC GROUP

There is a pronounced difference between the cmcs of ionic and nonionic surfactants with identical hydrophobic moieties indicating the influence of hydrophilic group on cmc. The lower cmcs of the nonionic surfactants are a consequence of the lack of electrical work necessary in forming the micelles. The more ionized groups present in the surfactants, the higher the cmc due to the increase in electrical work required to form the micelles.²³

1.10.3 NATURE OF THE COUNTERION

In ionic surfactants cmc decreases as the ionic radius of the counterion increases. A change in counterion to one of greater polarizability or valence also decreases cmc.^{23,35,36}

1.10.4 EFFECT OF ADDITIVES

Addition of electrolytes to ionic surfactants causes a decrease in cmc^{29,37} which is generally explained by eq 1.25. Both increase and decrease of cmc are observed on addition of nonelectrolytes like urea, amides and alcohols.^{36,38-42}

1.10.5 EFFECT OF TEMPERATURE

The cmc of ionic surfactants usually passes through a minimum with increasing temperature. For sodium dodecyl sulfate in water the minimum in cmc occurs around 298K.⁴³ This is normally explained in terms of the diminish in the ordered properties of solvent by increasing the temperature and the positive entropy change of micellization becoming negative above the temperature of minimum cmc. Recently La Mesa⁴⁴ used the reduced variables treatment to explain the temperature dependence of cmc. Muller,⁴⁵ on the other hand, using a thermodynamic treatment obtained a better analytical expression to describe the temperature dependence of cmc.

1.10.6 EFFECT OF PRESSURE

With pressure cmc of ionic surfactants increases upto 100MPa followed by a cmc decrease at higher pressures.⁴⁶⁻⁵³ Such behaviour has been rationalized in terms of solidification of the micellar interior,⁴⁶ dielectric constant increase of water⁴⁷ and other aspects related to water structure.^{48,49} La Mesa⁴⁴ applied the

reduced variables treatment to discuss also the effect of pressure on cmc.

1.11 MICROEMULSIONS

Microemulsions represent an intermediate state between micellar solutions and true emulsions. They are readily distinguished from emulsions (sometimes also called a macroemulsion) by their transparency and more fundamentally by the fact that they represent single thermodynamically stable solution phases. Microemulsions although transparent are microheterogeneous dispersions consisting of dispersed and dispersing media. The dispersed media exist in the form of droplets having diameters in the range 10-100nm. In emulsions the droplets have diameters in the range 100-1000nm whereas typical micelles have diameters less than 10nm. For example, sodium dodecyl sulfate micelle with aggregation number equal to 65 has a diameter of about 4nm. Depending upon the type of dispersed and dispersing media microemulsions are classified as water-in-oil (w/o) and oil-in-water (o/w) microemulsions. The change-over region from one type of microemulsion to the other is called a bicontinuous phase or a phase-inversion region. The two

liquids, oil and water, are immiscible and chemically unreactive and form systems characterized by a minimal thermodynamic stability. Addition of surfactant to a mixture of oil and water stabilizes the system by decreasing the free energy of oil-water interface as can be understood from eq 1.1. Microemulsions are known to exhibit isotropic nature and in many cases well defined droplets are reported to be not present.⁵⁴ Due to this finding, Danielsson and Lindman⁵⁵ defined a microemulsion as a system of water, oil and amphiphile which is a single optically isotropic and thermodynamically stable liquid solution. Microemulsions are also formed by using polar nonaqueous liquids instead of water.^{56,57}

1.11.1 COSURFACTANTS

Although microemulsions can be formed using oil, water and a surfactant such three-component microemulsions are very much limited. Generally, a fourth component known as cosurfactant is required to be added for the formation of microemulsion. To our knowledge, sodium bis (2-ethylhexyl) sulfosuccinate (Aerosol OT) is the only surfactant known to form microemulsion without the use of any cosurfactant. One

of the most fundamental properties of microemulsions is the interfacial tension between the oil and water phases. Considering the microemulsion to consist of droplets, for a typical droplet of diameter 10nm the interfacial area in a 1cm^3 dispersed phase would be 600m^2 . Spontaneous formation of a microemulsion requires the free energy of formation to be negative, but the generation of such a huge interfacial area makes a large positive contribution to the free energy of formation if the interfacial tension has a finite value (eq 1.1). To overcome this thermodynamic restriction Schulman et al.⁵⁸ postulated that in microemulsions the interfacial tension is zero or even negative and that one of the main roles of the cosurfactant was to reduce the interfacial tension to such low values. Therefore, a cosurfactant must enhance the adsorption of surface-active agents on the interface or must get adsorbed by itself alongwith the surfactant on the interface. Short chain alcohols are commonly used as cosurfactants. Cosurfactants other than alcohols are also being used.⁵⁹ It is also predicted on the basis of thermodynamic considerations that use of mixed surfactants, especially of different nature, would largely decrease the interfacial tension.⁶⁰ Formation of

microemulsions using mixed surfactants is indeed reported recently.^{61,62} Cosurfactants greatly influence the behaviour of microemulsions.^{63,64}

1.11.2 THEORIES OF MICROEMULSION FORMATION

The theories of microemulsion are classified into three main categories. They are: (1) interfacial or mixed film theories, (2) solubilization theories, and (3) thermodynamic theories. In mixed film theories^{58,65} the interfacial region is considered to be a liquid film and treated as a two dimensional third phase in equilibrium with both water and oil. The total interfacial tension is shown to be controlled by a two dimensional spreading pressure of the film.⁶⁰ In solubilization theories⁶⁶ microemulsions are treated as swollen micellar systems with oil or water solubilized in normal or reversed micelles. In the thermodynamic theories of microemulsion two different approaches, one due to Ruckenstein et al.⁶⁷⁻⁶⁹ and the other due to Overbeek,⁷⁰ are used for the calculation of free energy of formation of microemulsions.

1.12 ELECTRICAL CONDUCTANCE OF MICELLAR SOLUTIONS AND MICROEMULSIONS

Conductivity measurements provide valuable informations concerning the structural behaviour of micellar solutions and microemulsions. In micellar solutions below cmc the conductance behaviour is similar to that of a normal electrolytic solution. Conductance method has been widely used to estimate the micellisation parameters.^{71,72}

Microemulsions exhibit special conductance behaviours. W/O microemulsions show percolation in conductance above a threshold volume fraction of water.^{60,73} The percolative conduction in a microemulsion is explained in the light of an expression originally proposed to explain the conductance behaviour of conductor-insulator composite materials.⁷⁴ Moulik and coworkers^{75,76} have critically examined the theories of percolation conduction in microemulsions and used the conductivity data to evaluate several structural features of w/o microemulsions. The conductance behaviour of w/o microemulsions below the percolation threshold is interpreted in terms of a charge fluctuation model.⁷⁷⁻⁸⁰ Conductance of o/w microemulsions, on

the other hand, follows a different behaviour and is explained generally by the Bruggeman equation.⁸¹ Moulik and coworkers⁸² on the basis of their conductance study on a variety of o/w microemulsions established the effect of hydration of surfactants on the conductance of microemulsions. It has been shown by Clause et al.⁶³ that using conductance data of microemulsions the regions of bicontinuous phase can be located in their phase diagrams.

1.13 ACID-BASE EQUILIBRIA OF INDICATORS IN MICELLAR SOLUTIONS AND MICROEMULSIONS

The pK of indicators in ionic micellar medium differ from that in aqueous medium. The factors which contribute to the shift in pK are (1) the electrical potential, ψ on the micellar surface and (2) the lower dielectric constant at the surface of micelle compared to that of bulk solution. Accordingly pK of an indicator in an ionic micellar solution is written as^{83,84}

$$pK = pK^i - F\psi / (2.303RT) \quad (1.34)$$

pK is the intrinsic pK and F is the Faraday constant. The pK shifts of indicators in micellar solutions have been studied elaborately.⁸³⁻⁸⁷ However, relatively very few studies have

been made on the acid-base equilibria of indicators in microemulsions.⁸⁸⁻⁹¹ pK of a dye in microemulsion depends on various factors: (1) the location of residence of the dye - it may be either at the interface or in the bulk phase (water or oil) or partitioned between both the phases, (2) the effective pH and dielectric constant at the site of residence and (3) the interfacial electrical potential (in the case of ionic surfactants and if interface is the site of residence). These factors can alter the dissociation equilibrium of an indicator and a straightforward analysis of the results can be rather difficult. More studies on the indicator equilibria in microemulsions are therefore needed for rationalizing and quantifying the pK shift of dyes in microemulsions.

1.14 SCOPE AND SCHEME OF THE PRESENT WORK

The factors which affect the cmc are discussed above (section 1.10). The added electrolyte decreases the cmc of ionic surfactants which is generally explained as due to the decrease in the repulsive force between the head groups of an ionic micelle caused by the increased concentration of counterion. Although cmcs of ionic

surfactants are measured in several electrolytic solutions, such measurements in buffer solutions consisting of mixed electrolytes have not been made systematically. Cmc's of surfactants in buffer solutions are required especially during the spectral studies of indicator equilibria in micellar media. Furthermore, the variation of cmc with electrolytic concentration has been explained hitherto in terms of counterion effect only. Although the influence of coion on cmc has been detected by some workers,^{92,93} no attempt has been made to rationalize the coion effect on cmc.

Accordingly in the first part of this work which deals with studies in micellar solutions we have measured the cmc values of sodium dodecyl sulfate in sodium acetate-acetic acid buffer, a commonly used buffer solution. This work is discussed in chapter 3. In chapter 4 we have examined the effect of acetate and propionate coions on the cmc of sodium dodecyl sulfate. The conductance method has been used throughout for the cmc determination. In chapter 5 in order to estimate the micellization parameters the conductance data of surfactant solutions in the absence and presence of electrolytes have been analyzed using a model⁷²

which accounts for the ion-ion interactions. In chapter 6 an attempt has been made to compute the surface potentials of ionic micelles.

The second part of this work deals with studies in microemulsion medium. The importance of studying indicator equilibria in microemulsions has been highlighted in section 1.13. Therefore with a view to rationalize and throw more light on the pK shift of dyes in microemulsions, we have made spectral studies on the acid-base equilibria of methyl red and neutral red indicators in microemulsion media. This work has been presented in chapter 7.

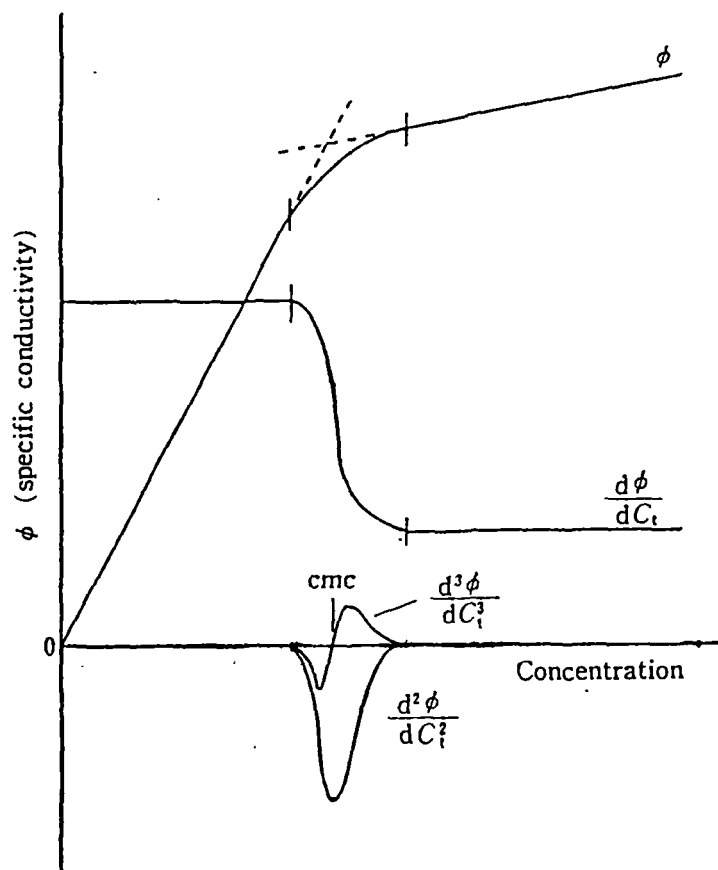


Fig 1.1 Schematic illustration of cmc determination according to the definition of Phillips²⁷ (taken from ref.16).

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Chapter 2

Experimental Techniques and Data Analysis

2.1 CONDUCTANCE MEASUREMENT

All conductance measurements were made at 1kHz using Wayne Kerr B905 Automatic Precision Bridge. This LCR meter has 0.01ns resolution and measures conductance with an accuracy of 0.05%. It also has an averaging facility and averages 2 ('Average'1) to 128 ('Average'9) measurements in a time span of about 670 ms to 36s. We have used throughout 'Average'9 option and therefore each conductance reading corresponds to an average of 128 measurements. The bridge works basically on the principle of Ohm's law. Matching currents are passed through the standard resistor and the solution under test. The corresponding two voltages produced, whose values depend upon the impedences at the standard resistor and the test solution, are measured, resolved and computed to give the desired information on the display. All functions of the instrument are under the direct control of a microprocessor.

A dip-type conductivity cell having platinized platinum electrodes was used for conductance measurement. The cell constant was determined using standard KCl solution.

2.2 SAMPLE PREPARATION

Details of the chemicals used are given in the respective chapters. Mostly molal solutions of surfactants and electrolytes were prepared. Weighing was done in a Shimadzu Libror AEL-200 electronic analytical balance having 0.1 mg readability. Since there could be a maximum error of ± 0.1 mg in weighing, the error limit in the concentrations of the solutions has been estimated to be $\pm 0.4 \times 10^{-5}$ mol.kg⁻¹.

Doubly distilled water having conductivity about $2 \mu\text{S.cm}^{-1}$ has been used throughout for preparing solutions and microemulsions.

2.3 SPECTROSCOPIC MEASUREMENTS

Visible absorption spectra of indicators in microemulsion media were recorded using Hitachi Model 330 and Beckmann DU -650 spectrophotometers. 1 cm quartz cells were used for holding the samples. For maintaining the temperature of the samples thermostated water was circulated around the cell holder.

2.4 TEMPERATURE CONTROL

The temperature of the test solutions was

controlled using an Insref IRI 015A thermostat equipped with a digital proportional temperature controller. The digital temperature display of the thermostat was first calibrated against a reference mercury thermometer. Water has been used as bath liquid. Using this thermostat temperature can be controlled with a thermal stability of $\pm 0.05^{\circ}\text{C}$

2.5 DATA ANALYSIS

All the data fittings to the different analytical expressions (details given in the respective chapters) and computation of surface potentials (chapter 6) were done using a PCS 486DX 100MHz computer.

PART 1

**A STUDY ON THE MIGELLIZATION
BEHAVIOUR OF SURFACTANTS IN
AQUEOUS ELECTROLYTIC SOLUTION**

Chapter 3

Micellization of Sodium Dodecyl Sulfate in Sodium Acetate-Acetic Acid Buffer

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B.C.Paul and K.Ismail, Bull. Chem. Soc. Jpn., 66, 703 (1993)

3.1 INTRODUCTION

It is well known that additives influence the micellization characteristics of surfactants. In general, electrolytes decrease the cmc, whereas nonelectrolytes may cause increase or decrease of cmc. For making pH dependent studies on micellar solutions, surfactants are normally taken in buffer solutions. For example, surface potentials of ionic micelles are estimated experimentally by making spectral studies of indicator dyes in buffered micellar solutions of varying pH.¹⁻³ In such studies the surfactant concentration is always taken to be well above the cmc. Since buffer solutions consist of mixed electrolytes, the cmc of surfactants is dependent on the pH of the solution. Moreover surfactants are known to have second cmc's whose values are also affected by the added electrolytes.⁴⁻⁸ Information about the exact values of first and second cmc's of various surfactants in buffered media of varying pH is going to be useful (i) in choosing the concentration range of surfactants for the type of spectral studies mentioned above and (ii) in the proper interpretation of the spectral data. Values of cmc of surfactants in different buffered

solutions as a function of pH are not well-documented. With this aim in mind we have reported here cm_{cl} and cm_{c2} of sodium dodecyl sulfate (SDS) in aqueous sodium acetate (NaAc) and acetic acid (AcH) buffer solutions (one of the frequently used buffer solutions) as functions of pH and temperature using conductance method.

3.2 EXPERIMENTAL SECTION

SDS (SISCO, extra pure grade) was recrystallized from its ethanol solution and dried under vacuum. Sodium acetate (SD, analytical grade) and glacial acetic acid (Merck, analytical grade) were used without further purification. Buffer solutions of various pH were prepared by mixing appropriate amounts of 0.2M sodium acetate solution, 0.2M acetic acid solution and conductivity water according to the standard buffer table.⁹ The temperature control and the electrical conductance measurements of solutions were made as described in chapter 2. A cell of cell constant 121.11 m^{-1} was used. Solutions of SDS in the buffers of various pH were prepared by weight. The pH's of the buffer solutions were checked by a Systronics Model 335 digital pH-meter using glass and calomel electrodes and

agreed within ± 0.01 with the expected pH values. The effect of SDS on the pH of the solution was ignored.¹⁰

3.3 RESULTS AND DISCUSSION

To check the purity of SDS we first measured the electrical conductance of aqueous solution of SDS at 25°C (Table 3.1) and the cmcl was found to be 0.0082 mol kg⁻¹ which is in good agreement with the reported value.¹¹

The measured specific conductivity (k) data (Table 3.2) of SDS in NaAc + AcH buffer solutions of various pH when plotted against concentration (m) form three linear plots exhibiting thereby three different concentration regions. A typical plot of this is shown in Fig.3.1 for SDS solution of pH = 4.8 at 25°C. Such a linear dependence of k on m is well well known in aqueous surfactant solutions.^{4,12,13} The experimental values of k of SDS solutions at different pH values and temperatures are therefore least-squares fitted to the linear equation

$$k = a + bm \quad (3.1)$$

in the three concentration regions separately and the corresponding values of intercepts, a and slopes, b are

listed in Table 3.3. The values of cm_{cl} and cmc_2 were estimated from the least-squares fitted values of a and b for the three linear plots of k vs. m and are listed in Table 3.4.

The variation of cm_{cl} with pH at $25^{\circ}C$ is shown in Fig.3.2. Below $40^{\circ}C$ cm_{cl} decreases with increase in pH upto pH=5.2 and increases with pH thereafter. At temperatures $\geq 40^{\circ}C$ the decrease in cm_{cl} with increasing pH is found to be upto pH = 5.6 (Table 3.4). The lowering of cm_{cl} with increasing pH can be attributed to the increase in the Na^{+} ion concentration in the solution due to the increasing amount of NaAc as also is the case observed by the addition of NaCl to SDS solution.^{14,15} However, for SDS solution no increase in cm_{cl} with increase in counterion concentration is reported upto 0.8M ($M = mol\ dm^{-3}$) NaCl concentration.¹⁵ In the present system upto pH=6.0 the total concentration of Na^{+} ion is much less (about 0.1M) than 0.8M and therefore the increase in cm_{cl} with increase in pH above pH=5.2 or 5.6 is not due to the Na^{+} ion. It cannot be due to H^{+} ion also because at pH>5.2 the H^{+} ion concentration is much lower. Therefore it appears that the increase in cm_{cl} may be due to the co-ion, in this case acetate ion. Structurally SDS

micelle is reported to undergo sphere - rod transition around 0.45M NaCl concentration¹⁵ and the nature of the co-ions was found to affect the molecular weight of the large nonspherical micelle.¹⁶ From the reported¹⁷ values of cmcl for 1-hexadecylpyridinium bromide (HDPB) in aqueous solution with added electrolytes it seems that co-ion has an influence on the cmcl value of this cationic surfactant also. Reported cmcl value of HDPB (6.86×10^{-4} M in H₂O) decreases initially in KCl, NaCl and HCl solutions and then it starts increasing somewhere between 0.01M and 0.1M KCl, 0.1M and 1M NaCl, and 0.2M and 1M HCl.¹⁷ The decrease of cmcl value is attributable to the counterion (Cl⁻ ion) binding whereas its increase can only be due to the effect of co-ion (K⁺/Na⁺/H⁺).

The variation of cmcl with pH below pH=5.2 (5.6 above 35^oC) is explained in the light of the expression

$$\log(\text{cmcl}) = A - \beta \log [C^+] \quad (3.2)$$

suggested by Phillips¹⁴ and also by Mukerjee et al.¹⁸ In eq.3.2 β is the counterion binding constant and $[C^+]$ is the total counterion concentration. A is a constant related to the equilibrium constant of the equilibrium

$$nS^- + n\beta C^+ \rightleftharpoons \frac{\backslash}{\backslash} M^{n(1-\beta)-} \quad (3.3)$$

where S^- is the dodecyl sulfate monomer, n is the aggregation number and M is the micellar species. In the present solution $[C^+]$ is equal to the total Na^+ ion concentration and is given by

$$[C^+] = cmcl + [Na^+]_b \quad (3.4)$$

where Na^+_b is the concentration of the Na^+ ion contributed by the buffer solution. Romsted and Zanette¹⁰ have also used eq.3.2 to describe successfully the effect of added electrolyte on $cmcl$. The plot of $\log(cmcl)$ vs. $\log[C^+]$ at 25°C is shown in Fig.3.3 and is linear in the region where $pH \leq 5.2$. The least-squares fitted value of the slope of this linear plot is 0.72 which is in good agreement with the value of counterion binding constant reported for aqueous SDS solution.^{11,13} The value of $A = -3.59$ is also in good agreement with the value reported for SDS + NaCl solutions.¹⁹ From the present study it is evident that eq.3.2 is not applicable all the time, instead there is a counterion concentration limit for the applicability of this equation. In order to examine the counterion concentration limit for the applicability of eq.3.2 we also plotted in Fig.3.3 the reported^{14,15} values of $\log(cmcl)$ against Na^+ ion concentration for SDS in NaCl solutions. From this plot

(Fig.3.3) it may be seen that there is a deviation from eq.3.2 in the region 0.4 - 0.5M NaCl concentration where a structural transition of the SDS micelle is reported to occur.¹⁵ $\log(\text{cmcl})$ values corresponding to NaCl concentration¹⁵ lying above 0.45M fall on a separate straight line (Fig.3.3). Therefore a deviation from Eq.3.2 envisages a structural transition of the micelles taking place. It may further be noted from Fig.3.3 that the plots of $\log(\text{cmcl})$ vs. $\log[\text{C}^+]$ in the low Na^+ ion concentration region (upto $\sim 0.08\text{M}$) corresponding to both SDS in NaCl solution and SDS in NaAc + AcH buffer solution almost overlap thereby indicating that the variation in cmcl with pH ($\text{pH} \leq 5.2$) observed in the present study is solely due to the Na^+ ion. This also suggests that the increase in cmcl with pH above $\text{pH} = 5.2$ is not due to the Na^+ ion because, if it is so, no deviation in the plot of $\log(\text{cmcl})$ vs. $\log[\text{C}^+]$ would be expected upto $[\text{Na}^+] \approx 0.45\text{M}$. Therefore from this analysis it is ascertained that the variation in cmcl with pH above $\text{pH} = 5.2$ is governed by the acetate co-ion. It can only be concluded from the present study that the acetate co-ion does not favour micelle formation unlike Na^+ counterion. In order to further verify this conclusion we

measured the cmcl of SDS in acetic acid solution of pH = 1.79 by conductance method (Table 3.5) at 25^oC. We observed cmcl of 0.006M. On the other hand, the cmcl of SDS in HCl solution of same pH at 25^oC is estimated to be 0.0019M from the reported data.²⁰ Therefore it is evident that acetate ion hinders significantly the micelle formation unlike halide co-ions. Although the decrease in cmcl with increasing counterion concentration is normally attributed to the electrostatic effect, at the moment we do not know the actual reason for the observed dependence of cmcl on co-ion concentration. The co-solvent (acetic acid) effect as a probable explanation for the increase in cmcl may not be ruled out also.

Furthermore, eq.3.2 can also be modified to the form

$$\log(\text{cmcl}) = (1+\beta)\log(\text{cmcl})_0 - \beta\log[C^+] \quad (3.5)$$

where $(\text{cmcl})_0$ is the cmcl of SDS in aqueous solution without the presence of buffer or added electrolyte. Substituting the measured value of $(\text{cmcl})_0 = 0.0082\text{M}$ and $\beta = 0.72$, we get $(1+\beta)\log(\text{cmcl})_0 = -3.588$ which is in excellent agreement with the value of A obtained above. Recently De Vijlder⁸ used an empirical equation of the form

$$\log(\text{cmcl}) = \log(\text{cmcl})_o + (a_{\pm})^{1/2} \quad (3.6)$$

for describing the variation of cmcl with the concentration of added uni-univalent electrolyte. In eq.3.6 a_{\pm} is the mean activity of the added electrolyte. Comparison of eqs.3.5 and 3.6 provides an empirical relation between $\log[(\text{cmcl})_o/[C^+]]$ and the mean activity of the added electrolyte.

From Table 3.4 it is apparent that for SDS solutions having $\text{pH} \leq 5.2$ cmcl decreases with increasing temperature and passes through a minimum in the temperature region from 25 to 30°C. This observation is in accordance with the temperature dependence of cmcl reported for aqueous SDS solution.¹² For SDS solutions of $\text{pH} = 5.6$ and 6.0 no regular trend in the temperature dependence of cmcl is observed. It may however be pointed out that the uncertainties in the values of cmcl at $\text{pH} = 5.6$ and 6.0 are relatively more than those at other pH's. This is because the precision of cmcl determination is found to be dependent on the difference in the respective values of a and b in the $m \leq \text{cmcl}$ and $\text{cmcl} < m \leq \text{cmc2}$ regions of concentration and this difference decreases with increasing pH. Plots of $\log(\text{cmcl})$ vs. $1/T$ for SDS solutions of $\text{pH} \leq 5.2$ form two

straight lines as shown in Fig.3.4. We therefore estimated the enthalpy change due to micelle formation, ΔH_m^0 for SDS solutions of $\text{pH} \leq 5.2$ from the expression¹²

$$\Delta H_m^0 = 2.303R[d\log(\text{cmcl})/d(1/T)] \quad (3.7)$$

where R is the gas constant and the values of $d\log(\text{cmcl})/d(1/T)$ were obtained by the least-squares fittings. The values of ΔH_m^0 estimated thus in the two temperature regions are listed in Table 3.6. ΔH_m^0 has positive values below 25°C and negative values above 35°C . Positive ΔH_m^0 values indicate that below 25°C entropy factor is the driving force to micellization. We also estimated the standard free energy change per mole of micelle formed, ΔG^0 from the expression¹⁴

$$\Delta G^0 = 2.303RT(\log(\text{cmcl}) + \beta\log[C^+]) \quad (3.8)$$

The standard state is chosen as that of mole fraction unity. Expressing therefore the concentrations in mole fractions and substituting the value 0.72 for β we calculated $\Delta G^0/RT$ at 25°C for SDS solutions of different pH and the values are listed in Table 3.6. These values of $\Delta G^0/RT$ are in agreement with the value reported by Phillips¹⁴ for solution of SDS in NaCl solutions. ΔG^0 is found to have negligible effect on pH upto $\text{pH} = 5.2$ and on temperature. Negligible dependence of

ΔG° on pH below pH = 5.2 shows that ΔG° is virtually independent of electrolyte concentration as observed by others.¹⁴ However, above pH=5.6 ΔG° tends to show a dependence on pH or electrolytic concentration and its value appears to become higher than that below pH = 5.2.

The values of cmc2 estimated for SDS solutions of different pH are given in Table 3.4. These values of cmc2 are however less precise because cmc2 value generally depends on the concentration region ($m > \text{cmc2}$) covered in the conductance measurement and the plot of k vs. m becomes curved when the concentration is extended to high m . We also measured cmc2 for aqueous SDS solution at 25°C using data given in Table 3.1 which was found to be $0.062 \text{ mol.kg}^{-1}$ and is in agreement with the reported value.⁴ No regular trend is observed in the dependence of cmc2 on temperature or pH. However, the slope, b_3 of the k vs. m plot in the region $m > \text{cmc2}$ decreases at all temperatures with increasing pH or NaAc amount. For SDS in NaCl solution the slope, b_3 is, on the other hand, reported to increase with increasing concentration of NaCl.⁴ The opposite trend in the variation of b_3 with the addition of NaCl and NaAc solutions therefore suggests that the acetate co-ion also affects the second

micellization process. The slope, b_3 is found to be always greater than the slope of k vs. m plot in the region $cmc1 < m \leq cmc2$ as reported for aqueous SDS solutions.⁴

Table 3.1 Specific Conductance(k) of Aqueous Solution of SDS at

25°C

Conc. of SDS x 10 ⁴ / mol kg ⁻¹		Conc. of SDS x 10 ⁴ / mol kg ⁻¹	
k x 10 ⁴ / s m ⁻¹		k x 10 ⁴ / s m ⁻¹	
24.0	173.58	35.0	253.37
41.0	296.24	53.0	383.18
59.4	429.26	62.51	451.02
65.52	471.75	68.59	493.10
71.55	513.45	74.65	535.28
75.78	542.1	77.55	554.89
80.41	571.97	83.09	585.5
85.89	597.40	88.53	606.61
91.26	615.71	92.96	619.1
93.85	623.41	96.54	631.57
98.95	638.45	102.0	647.08
184.2	856.5	229.5	971.5
441.4	1529.9	716.6	2269.9
972.5	2964.9	2462.4	7323.3

Table 3.2 Specific Conductance (k) of SDS in Sodium Acetate + Acetic Acid Buffer of Different pH at Various Temperatures

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/mS m ⁻¹						
	15°C	20°C	25°C	30°C	35°C	40°C	45°C
	pH = 3.6						
0.0052	0.6230	0.6998	0.7783	0.8582	0.9409	1.0166	1.1099
0.0108	0.6244	0.7011	0.7796	0.8606	0.9422	1.0227	1.1116
0.0267	0.6464	0.7263	0.8076	0.8909	0.9768	1.0667	1.1474
0.0537	0.6507	0.7303	0.8131	0.8969	0.9832	1.0706	1.1611
0.0751	0.6599	0.7406	0.8248	0.9099	0.9978	1.0852	1.1791
0.1073	0.6781	0.7615	0.8468	0.9362	1.0263	1.1170	1.2065
0.2679	0.7641	0.8588	0.9567	1.0571	1.1599	1.2640	1.3732
0.5267	0.9013	1.0143	1.1308	1.2518	1.3750	1.5010	1.6289
0.7612	0.9677	1.0888	1.2145	1.3489	1.4898	1.6379	1.7928
1.0573	1.0264	1.1559	1.2930	1.4373	1.5909	1.7520	1.9259
2.6212	1.3392	1.5197	1.7097	1.9121	2.1263	2.3476	2.5854
4.6816	1.7556	2.0050	2.2664	2.5435	2.8350	3.1382	3.4578
7.3808	2.3127	2.6502	3.0048	3.3780	3.7735	4.1820	4.6143
10.5933	2.9994	3.4467	3.9190	4.4135	4.9329	5.4673	6.0312
27.5610	6.8089	7.8577	8.9634	10.1140	11.3178	12.5471	13.8369

Table 3.2 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/mS m ⁻¹						
	15°C	20°C	25°C	30°C	35°C	40°C	45°C
	pH = 4.0						
0.0040	1.2591	1.4199	1.5850	1.7572	1.9323	2.1127	2.2926
0.0089	1.2626	1.4215	1.5867	1.7588	1.9349	2.1138	2.3018
0.0228	1.2688	1.4297	1.5968	1.7704	1.9477	2.1280	2.3118
0.0467	1.2789	1.4415	1.6087	1.7813	1.9601	2.1417	2.3333
0.0639	1.2947	1.4588	1.6311	1.8065	1.9890	2.1755	2.3645
0.0945	1.3024	1.4685	1.6400	1.8180	2.0003	2.1865	2.3577
0.2324	1.3742	1.5500	1.7306	1.9161	2.1096	2.3028	2.5035
0.4590	1.4745	1.6625	1.8581	2.0631	2.2749	2.4940	2.7214
0.6853	1.5185	1.7121	1.9169	2.1296	2.3497	2.5772	2.8207
0.9449	1.5748	1.7773	1.9883	2.2105	2.4440	2.6862	2.9421
2.3783	1.8442	2.0917	2.3488	2.6199	2.9048	3.2000	3.5113
4.8044	2.3179	2.6390	2.9787	3.3310	3.7054	4.0913	4.4969
7.4043	2.8299	3.2335	3.6601	4.1060	4.5719	5.0601	5.5727
11.3552	3.6594	4.1993	4.7623	5.3519	5.9710	6.6163	7.2860
31.5396	8.1726	9.4285	10.7474	12.1172	13.5596	15.0262	16.5680

Table 3.2 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/mS m ⁻¹						
	15°C	20°C	25°C	30°C	35°C	40°C	45°C
	pH = 4.4						
0.0060	2.4784	2.7921	3.1202	3.4566	3.8060	4.1602	4.5271
0.0134	2.4830	2.7971	3.1244	3.4595	3.8086	4.1649	4.5263
0.0332	2.4842	2.7979	3.1244	3.4605	3.8060	4.1596	4.5276
0.0666	2.5118	2.8272	3.1582	3.4976	3.8476	4.1768	4.5354
0.0928	2.5235	2.8449	3.1764	3.5211	3.8734	4.2348	4.5945
0.1325	2.5490	2.8718	3.2062	3.5515	3.9045	4.2696	4.6105
0.3329	2.6265	2.9575	3.3004	3.6594	4.0289	4.4042	4.7982
0.6637	2.6888	3.0307	3.3872	3.7604	4.1428	4.5390	4.9441
0.9459	2.7361	3.0845	3.4528	3.8286	4.2247	4.6266	5.0496
2.0545	2.9265	3.3058	3.7027	4.1134	4.5419	4.9820	5.4349
4.1183	3.2985	3.7365	4.1989	4.6783	5.1754	5.6863	6.2203
6.9297	3.8060	4.3289	4.8744	5.4470	6.0361	6.6490	7.2800
9.7415	4.3512	4.9658	5.6088	6.2772	6.9724	7.6893	8.4439
13.2368	4.9212	5.6233	6.3620	7.1322	7.9352	8.7636	9.6271
37.2832	10.1019	11.6315	13.2314	14.8991	16.6261	18.4016	20.2437

Table 3.2 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/mS m ⁻¹						
	15°C	20°C	25°C	30°C	35°C	40°C	45°C
	pH = 4.8						
0.0167	3.6791	4.1431	4.6304	5.1260	5.6403	6.1670	6.6853
0.0400	3.6909	4.1569	4.6409	5.1415	5.6558	6.1851	6.7144
0.0589	3.7012	4.1650	4.6498	5.1512	5.6639	6.1815	6.7241
0.0927	3.7271	4.1960	4.6845	5.1869	5.7060	6.2336	6.7677
0.1802	3.7627	4.2397	4.7339	5.2399	5.7608	6.2941	6.8403
0.2984	3.7886	4.2646	4.7595	5.2691	5.8001	6.3438	6.8973
0.5038	3.8250	4.3089	4.8131	5.3341	5.8693	6.4213	6.9917
0.7807	3.8782	4.3709	4.8843	5.4089	5.9616	6.5206	7.1007
1.5013	4.0036	4.5164	5.0481	5.5998	6.1730	6.7568	7.3611
3.0077	4.2649	4.8163	5.3950	5.9943	6.6102	7.2424	7.9085
6.0910	4.8133	5.4614	6.1318	6.8307	7.5513	8.2900	9.0603
10.0755	5.5522	6.3159	7.1104	7.9388	8.8023	9.6901	10.6093
14.3670	6.3862	7.2848	8.2210	9.2032	10.2133	11.2524	12.3170
25.2738	8.5831	9.8366	11.1543	12.5132	13.9266	15.3859	16.8986
56.3940	14.8422	17.0536	19.3826	21.7794	24.2719	26.8309	29.4627

Table 3.2 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/mS m ⁻¹						
	15°C	20°C	25°C	30°C	35°C	40°C	45°C
	pH = 5.2						
0.0601	4.7393	5.3369	5.9555	6.5933	7.2436	7.9194	8.5468
0.0762	4.7499	5.3395	5.9621	6.6005	7.2533	7.9303	8.5940
0.1182	4.7637	5.3645	5.9851	6.6260	7.2776	7.9570	8.6376
0.2884	4.8000	5.4024	6.0290	6.6720	7.3393	8.0212	8.7369
0.4889	4.8460	5.4527	6.0882	6.7483	7.4217	8.1132	8.8290
0.6790	4.8846	5.4984	6.1379	6.7967	7.4738	8.1653	8.8811
1.0588	4.9355	5.5600	6.2118	6.8839	7.5743	8.2779	9.0119
1.9541	5.0925	5.7448	6.4189	7.1201	7.8468	8.5710	9.3352
4.8271	5.6008	6.3305	7.0971	7.8916	8.7006	9.5302	10.4083
9.8940	6.5097	7.3890	8.3034	9.2541	10.2411	11.2379	12.2770
16.8907	7.8104	8.9017	10.0365	11.2173	12.4417	13.6964	15.0226
24.3926	9.2698	10.5996	11.9815	13.4155	14.9015	16.4384	18.0504
41.8589	12.7021	14.5091	16.5317	18.5518	20.6555	22.8040	25.0252
77.4615	18.8812	21.6982	24.6364	27.6593	30.7477	33.9220	37.2562

Table 3.2 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/mS m ⁻¹						
	15°C	20°C	25°C	30°C	35°C	40°C	45°C
	pH = 5.6						
0.0291	5.3330	5.9925	6.6768	7.3866	8.1132	8.8556	9.6223
0.0697	5.3368	6.0009	6.6902	7.3987	8.1278	8.8847	9.6610
0.0992	5.3490	6.0202	6.7120	7.4193	8.1544	8.9065	9.6792
0.1477	5.3606	6.0362	6.7313	7.4556	8.1847	8.9477	9.7240
0.3492	5.4087	6.0870	6.7871	7.5137	8.2537	9.0203	9.8088
0.5866	5.4467	6.1318	6.8355	7.5658	8.3191	9.0894	9.8875
0.8172	5.4827	6.1706	6.8876	7.6239	8.3869	9.1633	9.9711
1.3204	5.5706	6.2711	7.0002	7.7584	8.5347	9.3292	10.1624
2.4828	5.7684	6.5061	7.2739	8.0515	8.8665	9.6937	10.5742
6.6824	6.4915	7.3502	8.2343	9.1536	10.1055	11.0720	12.0893
13.6487	7.7620	8.8278	9.9311	11.0780	12.2528	13.4833	14.7210
23.7499	9.6816	11.0586	12.4926	13.9738	15.5022	17.0827	18.6862
36.4443	12.1644	13.9302	15.7662	17.6822	19.6563	21.6680	23.7172
56.9322	15.9455	18.3108	20.7693	23.3284	25.9347	28.6791	31.4271
104.4518	22.6683	25.9081	29.3549	33.1614	36.9849	40.7139	44.8510

Table 3.2 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/mS m ⁻¹						
	15 ^o C	20 ^o C	25 ^o C	30 ^o C	35 ^o C	40 ^o C	45 ^o C
	pH = 6.0						
0.0284	5.8179	6.5388	7.2860	8.0551	8.8423	9.6513	10.4725
0.0782	5.8156	6.5412	7.2909	8.0696	8.8605	9.6671	10.4943
0.1240	5.8354	6.5642	7.3163	8.0866	8.8871	9.6986	10.5294
0.2152	5.8638	6.5933	7.3490	8.1265	8.9319	9.7458	10.5863
0.5129	5.9153	6.6575	7.4193	8.2162	9.0373	9.8536	10.7147
0.9689	5.9893	6.7398	7.5222	8.3252	9.1548	10.0074	10.8758
1.4343	6.0737	6.8403	7.6324	8.4523	9.2868	10.1503	11.0429
2.1147	6.1972	6.9820	7.7959	8.6388	9.5024	10.3744	11.2984
3.1972	6.3825	7.1855	8.0369	8.9126	9.8076	10.7268	11.6739
9.4302	7.4689	8.4608	9.4878	10.5536	11.6533	12.8087	13.9411
20.2143	9.4794	10.7910	12.1692	13.5911	15.0589	16.5547	18.1013
34.8065	12.2734	14.0343	15.8740	17.7900	19.6999	21.6982	23.7814
58.2131	16.5256	18.9684	21.4936	24.0926	26.8164	29.5571	32.3730
91.1504	21.4245	24.4838	27.8265	31.2575	34.7589	38.3813	42.0715
139.5051	25.8051	29.2931	33.0221	37.0588	41.2989	45.6601	49.9462

Table 3.3 Least - Squares Fitted Values of the Parameters of eq 3.1 (Correlation Coefficient ≥ 0.999)

t/°C	m ≤ cmc1		cmc1 < m ≤ cmc2		m > cmc2	
	a x 10 ²	b	a x 10 ²	b	a x 10 ²	b
	(a in S m ⁻¹ and b in S m ⁻¹ mol ⁻¹ kg)					
pH = 3.6 (m ^h) = 0.276 mol kg ⁻¹)						
15.0	6.197	5.357	8.139	2.010	6.211	2.245
20.0	6.954	6.065	9.091	2.338	6.929	2.599
25.0	7.732	6.802	10.05	2.704	7.698	2.973
30.0	8.537	7.569	11.11	3.065	8.547	3.359
35.0	9.348	8.371	12.25	3.448	9.468	3.763
40.0	10.15	9.238	13.44	3.841	10.47	4.172
45.0	11.03	10.01	14.71	4.254	11.58	4.600
pH = 4.0 (m ^h) = 0.315 mol kg ⁻¹)						
15.0	12.57	5.029	13.91	1.909	11.21	2.236
20.0	14.16	5.754	15.64	2.235	12.58	2.591
25.0	15.81	6.412	17.39	2.577	13.95	2.965
30.0	17.52	7.043	19.29	2.916	15.46	3.352
35.0	19.26	7.890	21.27	3.285	17.02	3.759
40.0	21.06	8.455	23.30	3.667	18.85	4.166
45.0	22.90	9.340	25.50	4.051	20.64	4.598

Table 3.3 continued

$t/^{\circ}\text{C}$	$m \leq \text{cmc1}$		$\text{cmc1} < m \leq \text{cmc2}$		$m > \text{cmc2}$	
	$a \times 10^2$	b	$a \times 10^2$	b	$a \times 10^2$	b
(a in S m^{-1} and b in $\text{S m}^{-1} \text{ mol}^{-1} \text{ kg}$)						

$\text{pH} = 4.4 \text{ (m}^{\text{h}}) = 0.373 \text{ mol kg}^{-1}$						

15.0	24.75	5.470	25.75	1.711	22.15	2.112
20.0	27.88	6.224	28.98	1.983	24.88	2.449
25.0	31.15	6.747	32.26	2.357	27.76	2.800
30.0	34.50	7.582	35.74	2.672	30.75	3.167
35.0	37.99	7.896	39.35	3.004	33.90	3.545
40.0	41.54	8.683	43.04	3.374	37.18	3.933
45.0	45.15	8.588	46.67	3.834	40.69	4.332

$\text{pH} = 4.8 \text{ (m}^{\text{h}}) = 0.564 \text{ mol kg}^{-1}$						

15.0	36.71	5.111	37.35	1.768	35.13	2.008
20.0	41.32	5.937	42.05	2.058	39.67	2.321
25.0	46.17	6.437	46.92	2.359	44.32	2.652
30.0	51.13	7.022	51.98	2.675	49.28	2.989
35.0	56.27	7.413	57.17	3.005	54.39	3.341
40.0	61.54	7.775	62.51	3.341	59.68	3.702
45.0	66.69	9.504	68.03	3.701	65.17	4.073

Table 3.3 continued

t/°C	m ≤ cmc1		cmc1 < m ≤ cmc2		m > cmc2	
	a × 10 ²	b	a × 10 ²	b	a × 10 ²	b
	(a in S m ⁻¹ and b in S m ⁻¹ mol ⁻¹ kg)					
	pH = 5.2 (m ^h) = 0.418 mol kg ⁻¹)					
15.0	47.14	4.200	47.56	1.747	44.95	1.960
20.0	53.08	4.751	53.53	2.021	51.16	2.244
25.0	59.24	5.171	59.69	2.333	56.38	2.602
30.0	65.58	5.717	66.05	2.675	62.52	2.938
35.0	72.08	5.838	72.53	3.017	68.80	3.291
40.0	78.81	6.448	79.33	3.334	75.38	3.647
45.0	85.15	10.37	86.33	3.680	82.69	4.004
	pH = 5.6 (m ^h) = 0.569 mol kg ⁻¹)					
15.0	53.17	2.985	53.45	1.714	51.87	1.890
20.0	59.79	3.861	60.11	2.001	58.47	2.189
25.0	66.61	4.761	67.02	2.293	65.31	2.501
30.0	73.68	5.733	74.20	2.543	72.36	2.827
35.0	80.95	6.015	81.47	2.927	79.70	3.157
40.0	88.32	7.803	89.07	3.173	85.71	3.591
45.0	95.96	8.538	96.80	3.609	93.26	3.947

Table 3.3 continued

t/°C	m ≤ cmc1		cmc1 < m ≤ cmc2		m > cmc2	
	a x 10 ²	b	a x 10 ²	b	a x 10 ²	b

(a in S m⁻¹ and b in S m⁻¹ mol⁻¹kg)

$$\text{pH} = 6.0 \text{ (m}^{\text{h}}\text{)} = 0.582 \text{ mol kg}^{-1}$$

15.0	58.09	2.452	58.26	1.745	57.37	1.859
20.0	65.30	2.915	65.54	1.988	64.50	2.157
25.0	72.76	3.371	73.01	2.312	72.02	2.463
30.0	80.36	4.183	80.78	2.617	79.88	2.778
35.0	88.28	4.795	88.68	2.936	87.73	3.109
40.0	96.36	5.058	96.85	3.256	96.20	3.435
45.0	104.5	6.091	105.3	3.589	104.6	3.779

h) highest concentration of the solution studied.

Table 3.4 Values of First and Second CMC of SDS in Sodium Acetate - Acetic Acid Buffer

t/°C	pH						
	3.6	4.0	4.4	4.8	5.2	5.6	6.0
	cmcl x 10 ³ and cmc2 x 10 ² (within parentheses)/mol kg ⁻¹						
15.0	5.80 (8.20)	4.29 (8.26)	2.66 (8.98)	1.91 (9.25)	1.71 (12.25)	2.20 (8.98)	2.40 (7.81)
20.0	5.73 (8.28)	4.20 (8.60)	2.59 (8.80)	1.88 (9.05)	1.65 (10.63)	1.72 (8.72)	2.59 (6.15)
25.0	5.66 (8.74)	4.12 (8.87)	2.53 (10.16)	1.84 (8.87)	1.59 (12.30)	1.66 (8.22)	2.36 (6.56)
30.0	5.71 (8.72)	4.29 (8.78)	2.53 (10.08)	1.95 (8.60)	1.55 (13.42)	1.63 (6.48)	2.68 (5.59)
35.0	5.89 (8.83)	4.36 (8.97)	2.78 (10.07)	2.04 (8.27)	1.60 (13.61)	1.68 (7.70)	2.15 (5.49)
40.0	6.10 (8.97)	4.68 (8.92)	2.83 (10.48)	2.19 (7.84)	1.67 (12.62)	1.62 (8.04)	2.72 (3.63)
45.0	6.39 (9.05)	4.92 (8.88)	3.20 (12.00)	2.31 (7.69)	1.76 (11.23)	1.70 (10.47)	3.20 (3.68)

Table 3.5 Specific Conductance (k) of SDS in Acetic Acid of
 pH = 1.79 at 25°C

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/mS m ⁻¹
0.0333	1.7487	0.0704	1.7719
0.1215	1.8102	0.2522	1.8864
0.5480	2.0097	0.8053	2.1457
1.0618	2.2517	1.3915	2.4120
2.4870	2.8454	5.4595	3.7828
11.8710	5.5126	25.1756	8.6885
36.6198	11.2391	51.1762	13.9387
72.1654	17.2135		

Table 3.6 Values of Enthalpy and Standard Free Energy Changes Due to Micellization of SDS in Sodium Acetate - Acetic Acid Buffer

pH	$\Delta H_m^0 / \text{kJ.mol}^{-1}$ at		$\Delta G^0 / RT$ at 25°C
	15 - 25°C	35 - 45°C	
3.6 (0.0074M ^{a)} ; 0.0926M ^{b)}	1.76	-6.61	-15.20 (-15.9 ^{c)})
4.0 (0.018M; 0.082M)	2.89	-9.87	-15.14
4.4 (0.039M; 0.061M)	3.59	-12.88	-15.17
4.8 (0.06M; 0.04M)	2.68	-10.13	-15.20
5.2 (0.079M; 0.021M)	5.23	-7.82	-15.18
5.6 (0.0904M; 0.0096M)	*	*	-15.02
6.0 (0.096M; 0.004M)	*	*	-14.59

a) Concentration of NaAc in the buffer solution.

b) Concentration of AcH in the buffer solution.

c) Average value of $\Delta G^0 / RT$ reported for SDS in NaCl solutions (ref. 14).

* No regular trend of cmcl with temperature.

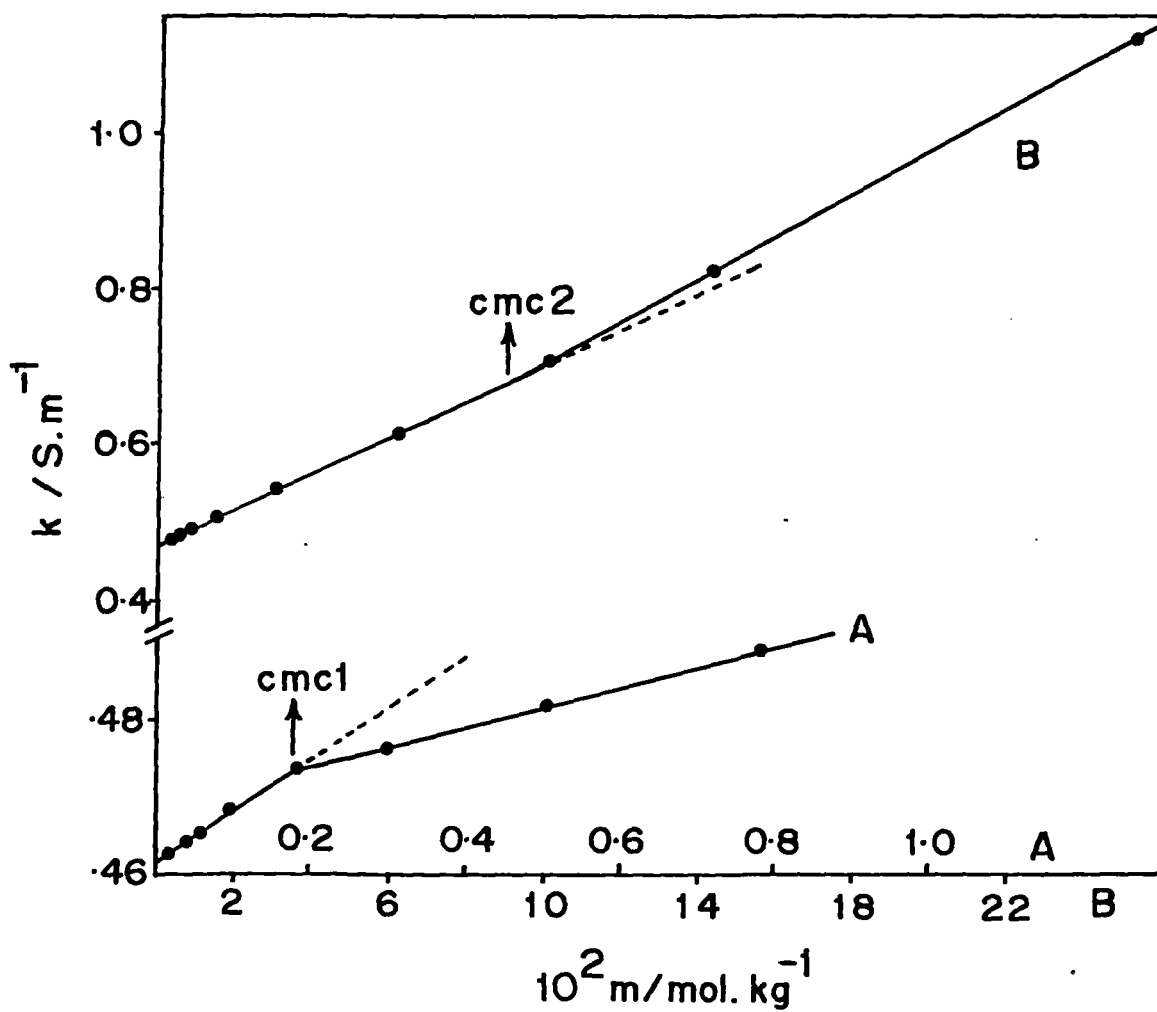


Fig 3.1 Plot of specific conductivity of SDS in NaAc + AcH buffer of pH = 4.8 at 25°C versus concentration.

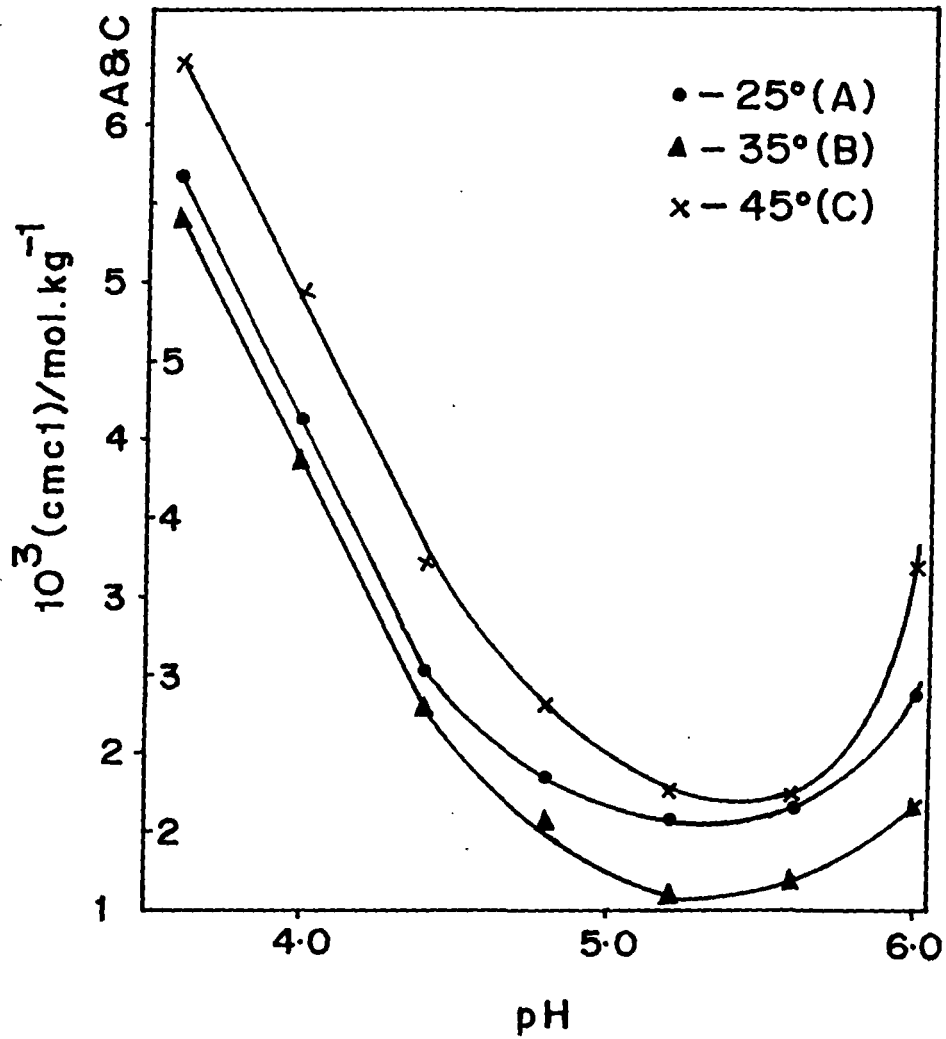


Fig 3.2 Variation of cmc1 of SDS in NaAc + AcH buffer with pH at different temperatures.

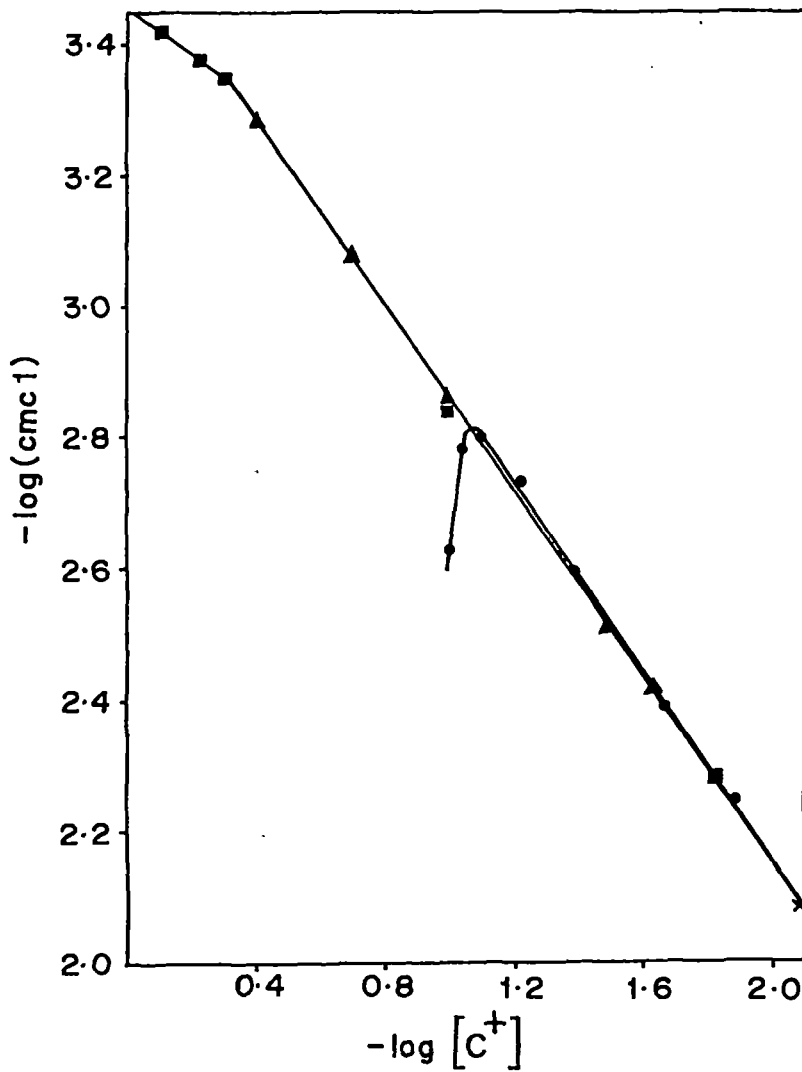


Fig 3.3 Plot of $\log(\text{cmc}1)$ of SDS in NaAc + AcH buffer (●), in H_2O (x), and in NaCl solutions (reported data; ▲ -ref.14 and ■ -ref.15) at 25°C versus $\log[c^+]$.

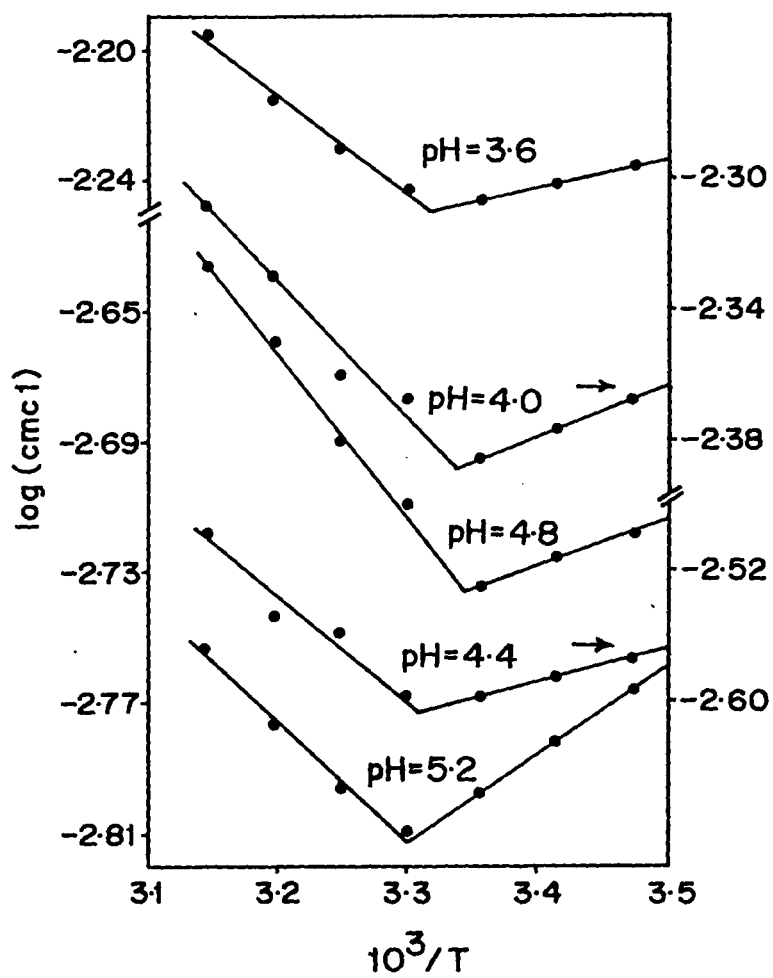


Fig 3.4 Plot of $\log(\text{cmcl})$ of SDS in NaAc + AcH buffer versus reciprocal of temperature.

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Chapter 4

Micellization of Sodium Dodecyl Sulfate in Aqueous Sodium Acetate and Sodium Propionate Solutions

4.1 INTRODUCTION

In the previous chapter¹ while studying the micellization behaviour of SDS in aqueous sodium acetate and acetic acid buffer, we surprisingly observed the dependence of cmc on the acetate ion (the coion) concentration above ca. 0.08 mol dm^{-3} . Effect of coion on the micellization parameters has been noticed by several workers.²⁻⁴ By measuring cmc of fluorine- labeled surfactants in NaCl and NaOH solutions Muller and Birkhahn² remarked that at higher electrolyte concentrations the nature of the coion (also called as similion) does have a measurable effect on the cmc. Reported³ values of cmc for 1-hexadecylpyridinium bromide (HDPB) in aqueous electrolytic solutions also indicate the influence of coion on cmc. Ikeda⁴ et al., on the other hand, reported that the coions affect the molecular weight of the micelle. It is therefore worthwhile to undertake the study of the role of coion on the micellization parameters. Since the acetate ion appears to affect the cmc of SDS, in this chapter we have made an attempt to study the micellization of SDS in aqueous sodium

acetate and sodium propionate solutions using conductance method with a view to ascertain the role of acetate and propionate ions on the micellization parameters.

4.2 EXPERIMENTAL SECTION

SDS (Fluka, > 99%), anhydrous sodium acetate (Glaxo and SD, analytical reagent grade), sodium propionate (Sigma, ~ 99%) and sodium chloride (Qualigen, analytical reagent grade) were used without further purification. First aqueous molal solution of the electrolyte was prepared and then its conductance was measured as described in the previous chapter after each addition of weighed amount of SDS. Temperature of the solution was maintained throughout at 25^oC.

4.3 RESULTS AND DISCUSSION

The specific conductivity data of SDS at 25^oC in sodium acetate solutions of different concentrations are given in Table 4.1. For the purpose of cmc determination conductivity data are plotted against concentration of SDS. These plots are shown in Fig.4.1. The cmc values were

determined by fitting the conductivity data to linear equations above and below the cmc as described in chapter 3 and these values are given in Table 4.2. From the plot of cmc versus sodium acetate concentration (Fig.4.2) it is apparent that cmc decreases with increase in sodium acetate concentration upto $\sim 0.1833 \text{ mol kg}^{-1}$ and above this concentration cmc has a tendency to increase with further increase in sodium acetate concentration. It is therefore evident that the micellization behaviour of SDS in sodium acetate solutions of concentration $> 0.1833 \text{ mol kg}^{-1}$ is not similar to that in sodium chloride solution. Repetition of conductance measurement three times using 2 different samples of sodium acetate (Glaxo and SD, AR grade) has also confirmed the unusual micellization behaviour of SDS in sodium acetate solutions of concentration $> 0.1833 \text{ mol kg}^{-1}$.

With a view to establish further the effect of acetate coion on the cmc of SDS we also measured the specific conductance of SDS at 25°C in sodium propionate solution expecting a similar behaviour of SDS micelles with respect to propionate coion. The conductance data of SDS in sodium propionate solutions are given in Table 4.3. The

values of cmc of SDS in sodium propionate solutions derived from the conductance data (Fig.4.3) are given in Table 4.4. In Fig.4.2 we have also illustrated the dependence of cmc of SDS on sodium propionate concentration. The cmc of SDS in sodium propionate solution of concentration $> 0.03 \text{ mol kg}^{-1}$ is higher than in sodium acetate solutions as apparent from Fig.4.2. This again indicates the fact that the coion has an effect on the cmc of surfactants. In sodium propionate solution also the cmc of SDS decreases initially with increase in propionate concentration upto $\sim 0.175 \text{ mol kg}^{-1}$ and thereafter cmc increases with further increase in electrolyte concentration as in the case of sodium acetate solution.

It is commented⁵ that at high electrolyte concentrations the conductance method of cmc determination becomes less sensitive. This is because of the fact that the background conductance of the surfactant solution itself becomes very high due to the high conductivity of the supporting electrolyte. However, this kind of inaccuracy in the conductance method arises only if the conductivity meter does not respond to small variations in conductance caused

by the addition of surfactant. This particular problem and the uncertainty in the cmc determination by the conductance method are ruled out in the present work since the LCR meter employed for the conductance measurement is precise and has a resolution of 0.01 ns. In order to ascertain further that the conductance method gives reliable cmc values even at high electrolyte concentration, we repeated the conductance measurement of SDS in NaCl solution also since precise cmc values of SDS in NaCl solutions of concentration upto 0.8 mol dm⁻³ are available in literature.⁶⁻⁸ The conductance data of SDS in different NaCl solutions are given in Table 4.5. The cmc values of SDS in NaCl solution determined from these conductance data (Fig. 4.4) are given in Table 4.6. The variation of cmc with concentration of NaCl solution is shown in Fig.4.2. There is a good agreement between our values and the reported⁶⁻⁸ values of cmc of SDS in NaCl solution. Therefore the unusual dependence of cmc of SDS on electrolyte concentration observed in this study above ~ 0.1833 mol kg⁻¹ sodium acetate concentration and above ~ 0.175 mol kg⁻¹ sodium propionate concentration is not certainly due to experimental artifact or error. In sodium

acetate - acetic acid buffer the increase in cmc of SDS starts around 0.08 mol dm^{-3} of sodium acetate solution as mentioned in chapter 3 unlike the case in pure sodium acetate solution. It therefore appears that acetic acid present in the buffer solution also causes increase of cmc of SDS.

The cmc data of SDS in sodium acetate, sodium propionate and sodium chloride solutions in the concentration region where cmc decreases with electrolyte concentration were fitted to the equation,^{6,9,10}

$$\ln x_{\text{cmc}} = A - \beta \ln x_{\text{c}+} \quad (4.1)$$

x_{cmc} is the cmc in mole fraction unit, $x_{\text{c}+}$ is the total concentration of counterion in mole fraction unit, β is the counter-ion binding constant and A is a constant related to free energy of micellization. Eq 4.1 is the same as eq.3.2 but for the concentration units. The advantage of using mole fraction units was highlighted by Tanford.¹¹ The least-squares fitted values of A and β are given in Table 4.7. The linearity of the plot of $\ln x_{\text{cmc}}$ vs. $\ln x_{\text{c}+}$ (Fig 4.5) indicates that eq 4.1 fully describes the variation of cmc of SDS with the concentration of 3 different electrolytes

under study in the concentration regions specified in Table 4.7. It may however be noticed from Fig.4.5 that in the case of sodium propionate solution eventhough cmc decreases with propionate concentration upto $0.1749 \text{ mol kg}^{-1}$, the cmc values of SDS in 0.1511 and $0.1749 \text{ mol kg}^{-1}$ sodium propionate solutions deviate from the linear plot of $\ln x_{\text{cmc}}$ vs. $\ln x_c$. Therefore eq 4.1 is applicable in sodium propionate solution only upto $\sim 0.0923 \text{ mol kg}^{-1}$. From Table 4.7 it is apparent that both acetate and propionate coions affect the value of counter ion binding constant. The effect of coion on A is however not very significant. Therefore, in the electrolytic concentration range listed in Table 4.7 the cmc of SDS and hence the free energy of micellization per mole of monomer, ΔG^0 ($\approx RT \ln A$ where R is the gas constant and T is the temperature) are controlled by the counterion. ΔG^0 values of SDS in sodium acetate solutions of concentration $> 0.1833 \text{ mol. kg}^{-1}$ and in sodium propionate solutions of concentration $> 0.0923 \text{ mol g}^{-1}$ were calculated using the relation,¹

$$\Delta G^0/RT = \ln x_{\text{cmc}} + \beta \ln x_c + \quad (4.2)$$

The values of β required in eq 4.2 for calculating $\Delta G^0/RT$

were assumed to be same as obtained from eq 4.1 (Table 4.7). The values of $\Delta G^0/RT$ of SDS in the different electrolytes calculated using eqs 4.1 and 4.2 are given in Tables 4.2, 4.4 and 4.6.

The free energy change of ionic micelle formation, per mole of monomer has been considered to compose of two factors¹²⁻¹⁵ and is written as

$$\Delta G^0 = (\mu_{mic}^0 - \mu_w^0) = \Delta G_{HC}^0 + \Delta G_{el}^0 \quad (4.3)$$

ΔG_{HC}^0 is the hydrophobic free energy and is closely related to the free energy of transfer of a hydrocarbon chain from water to a liquid hydrocarbon (or to the inside of a micelle). It represents the contribution of attractive force and therefore is a negative term. ΔG_{el}^0 is an electrostatic free energy and is positive as it represents the repulsive force. The normal decrease of cmc with increasing electrolytic concentration is due to the decrease in ΔG_{el}^0 . ΔG_{el}^0 is directly proportional to the surface potential of the micelle which decreases on addition of electrolyte due to the decrease in the effective charge on the micelle. The increase of cmc caused by the acetate or propionate coion may be attributed, on the other hand, to the influence of

coion on the hydrophobic interactions causing ΔG_{HC}° to increase on addition of electrolyte.

In order to verify the above plausible interpretation of the effect of coion on cmc we estimated the value of $\Delta G_{el}^{\circ}/RT$ from the relation¹³⁻¹⁵

$$\Delta G_{el}^{\circ}/RT = e\psi_0/k_B T \quad (4.4)$$

e is the electronic charge, k_B is the Boltzmann constant and ψ_0 is the electrostatic potential at the micellar surface which can be calculated by solving the Poisson-Boltzmann equation. For calculating $\Delta G_{el}^{\circ}/RT$ we used the surface potentials reported recently by Healy et al.⁸ for SDS/NaCl system. These surface potentials were determined experimentally using acid-base indicators¹⁶⁻¹⁸ and Healy et al.⁸ proved that the experimentally determined surface potentials are equal to ψ_0 . The calculated values of $\Delta G_{el}^{\circ}/RT$ are listed in Tables 4.2, 4.4 and 4.6. These values of $\Delta G_{el}^{\circ}/RT$ are relatively less than the values reported by others¹³⁻¹⁵ which is due to the differences in the values of ψ_0 used for calculating $\Delta G_{el}^{\circ}/RT$. Knowing the values of $\Delta G_{el}^{\circ}/RT$ and $\Delta G^{\circ}/RT$, the values of $\Delta G_{HC}^{\circ}/RT$ for SDS micelles in different electrolytes were calculated using eq 4.3 and

are also listed in Tables 4.2, 4.4 and 4.6. From the values of $\Delta G^{\circ}/RT$, $\Delta G_{el}^{\circ}/RT$ and $\Delta G_{HC}^{\circ}/RT$ given in Tables 4.2, 4.4 and 4.6 it is evident that the decrease in cmc is due to the decrease in $\Delta G_{el}^{\circ}/RT$ caused by the addition of electrolyte. ΔG_{HC}° increases by the addition of electrolyte in the entire concentration range of study. From the values of $\Delta G_{HC}^{\circ}/RT$ given in Tables 4.2, 4.4 and 4.6 it seems that the increase in cmc of SDS above $0.1833 \text{ mol kg}^{-1}$ sodium acetate and $0.0923 \text{ mol kg}^{-1}$ sodium propionate is not due to increase in $\Delta G_{HC}^{\circ}/RT$. Therefore the increase of cmc of SDS with increase in acetate and propionate concentrations does not seem to be controlled by the influence of coion on the hydrophobic interactions although hydrophobic hydration of acetate and propionate ions is reported.¹⁹

Acetate and propionate ions can be considered to have a hydrophobic surface equal to that of methanol and ethanol, respectively. Methanol is known to cause increase of cmc on its addition to an ionic surfactant solution whereas addition of ethanol causes the cmc to decrease initially and then to increase.²⁰⁻²⁶ The variation in cmc due to the addition of alcohols could not be explained in

terms of hydrophobic and dielectric constant changes produced in the solvent media.²⁰ The effect of alcohols on cmc was explained, on the other hand, as due to the penetration of the micelle interior by the hydrocarbon chain of alcohols.²⁰ Similarly, in the case of acetate and propionate ions also the increase of cmc is probably attributable to the penetration of micelle by these ions from their hydrocarbon chain end with the ionic group (COO^-) projecting out of the micellar surface. It may therefore be concluded that acetate and propionate ions behave differently from other inorganic ions and they can penetrate the micelle from their hydrocarbon chain end causing demicellization as the case with methanol and ethanol.

Table 4.1 Specific Conductance (k) of SDS in Sodium Acetate Solutions of Different Concentrations (C_e) at 25°C

Conc. of SDS x 10^2 / mol kg ⁻¹	$10^{-2}k$ / mS m ⁻¹	Conc. of SDS x 10^2 / mol kg ⁻¹	$10^{-2}k$ / mS m ⁻¹

$C_e = 0.0071 \text{ mol kg}^{-1}$			

0.0017	0.6553	0.0043	0.6587
0.0078	0.6625	0.0195	0.6709
0.0274	0.6779	0.0400	0.6876
0.0591	0.7022	0.0869	0.7211
0.1182	0.7430	0.1590	0.7719
0.1851	0.7904	0.2789	0.8542
0.3541	0.9056	0.4358	0.9593
0.5449	1.0262	0.6830	1.0812
0.8099	1.1180	0.9768	1.1618
1.2101	1.2220	1.3822	1.2662
1.5690	1.3147	1.8114	1.3759
2.2255	1.4809	2.6248	1.5832
3.1497	1.7196		

Table 4.1 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹

$C_e = 0.0135 \text{ mol kg}^{-1}$			
0.0039	1.1857	0.0069	1.1890
0.0152	1.1959	0.0278	1.2037
0.0369	1.2107	0.0499	1.2188
0.0729	1.2351	0.1020	1.2530
0.1407	1.2789	0.2084	1.3224
0.2814	1.3689	0.3899	1.4367
0.4915	1.4877	0.6266	1.5305
0.8211	1.5812	0.9787	1.6221
1.1494	1.6638	1.3439	1.7119
1.6179	1.7795	1.9280	1.8557
2.3162	1.9548	2.6206	2.0310
2.9927	2.1239		

Table 4.1 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
$C_e = 0.0275 \text{ mol kg}^{-1}$			
0.0056	2.3096	0.0078	2.3133
0.0130	2.3174	0.0212	2.3225
0.0269	2.3263	0.0351	2.3322
0.0451	2.3396	0.0594	2.3475
0.0889	2.3660	0.1049	2.3759
0.1482	2.4023	0.1812	2.4227
0.2206	2.4466	0.2662	2.4739
0.3533	2.5117	0.4222	2.5327
0.5150	2.5568	0.6758	2.5951
0.8297	2.6324	0.9884	2.6711
1.2576	2.7355	1.4548	2.7820
1.7999	2.8672	2.2937	2.9879
2.7021	3.0889		

Table 4.1 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
$C_e = 0.0548 \text{ mol kg}^{-1}$			
0.0034	4.3184	0.0052	4.3215
0.0061	4.3232	0.0082	4.3256
0.0108	4.3273	0.0130	4.3283
0.0169	4.3306	0.0221	4.3362
0.0290	4.3408	0.0390	4.3458
0.0585	4.3563	0.0746	4.3663
0.1088	4.3863	0.1465	4.4063
0.1916	4.4297	0.2480	4.4470
0.3191	4.4683	0.3959	4.4855
0.4757	4.5064	0.5915	4.5361
0.7376	4.5679	0.8837	4.6037
1.1183	4.6604	1.3486	4.7128
1.6257	4.7802	2.0715	4.8837

Table 4.1 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
C _e = 0.1014 mol kg ⁻¹			
0.0030	7.4806	0.0039	7.4829
0.0047	7.4841	0.0073	7.4852
0.0112	7.4887	0.0152	7.4922
0.0191	7.4934	0.0277	7.4992
0.0403	7.5074	0.0524	7.5144
0.0659	7.5214	0.0828	7.5330
0.1209	7.5494	0.1517	7.5622
0.2349	7.5832	0.3112	7.6030
0.4347	7.6333	0.5669	7.6660
0.7169	7.7022	0.8673	7.7348
1.1039	7.7920	1.2999	7.8386
1.5578	7.9004	1.8434	7.9681
2.1251	8.0334	2.4870	8.1197

Table 4.1 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
$C_e = 0.1522 \text{ mol kg}^{-1}$			
0.0017	10.6447	0.0026	10.6482
0.0034	10.6494	0.0069	10.6505
0.0087	10.6540	0.0156	10.6575
0.0221	10.6610	0.0351	10.6692
0.0481	10.6785	0.0620	10.6855
0.0828	10.6960	0.1184	10.7077
0.1609	10.7170	0.2073	10.7287
0.2758	10.7473	0.3582	10.7660
0.5052	10.8021	0.6574	10.8395
0.8565	10.8873	1.0929	10.9421
1.3726	11.0074	1.7204	11.0867
1.9980	11.1497	2.3332	11.2278

Table 4.1 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
$C_e = 0.1833 \text{ mol kg}^{-1}$			
0.0008	12.4863	0.0026	12.4886
0.0065	12.4944	0.0100	12.4956
0.0156	12.4979	0.0238	12.5038
0.0303	12.5073	0.0403	12.5119
0.0555	12.5224	0.0703	12.5283
0.0859	12.5387	0.1167	12.5457
0.1561	12.5562	0.2039	12.5644
0.3019	12.5889	0.4103	12.6122
0.5466	12.6437	0.7140	12.6810
0.8845	12.7195	1.0606	12.7650
1.2866	12.8163	1.5378	12.8723
2.0392	12.9866	2.6847	13.1336

Table 4.1 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
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$$C_e = 0.1934 \text{ mol kg}^{-1}$$

0.0029	13.0636	0.0071	13.0682
0.0100	13.0706	0.0183	13.0741
0.0250	13.0776	0.0362	13.0822
0.0512	13.0892	0.0737	13.0997
0.0991	13.1114	0.1337	13.1184
0.1866	13.1312	0.2420	13.1476
0.3133	13.1627	0.4145	13.1860
0.5111	13.2082	0.6590	13.2444
0.8611	13.2922	1.0590	13.3365
1.3310	13.3983	1.7659	13.4986

Table 4.1 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
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$$c_e = 0.2005 \text{ mol kg}^{-1}$$

0.0019	13.3038	0.0042	13.3097
0.0061	13.3155	0.0099	13.3190
0.0130	13.3237	0.0211	13.3283
0.0276	13.3318	0.0360	13.3388
0.0506	13.3470	0.0663	13.3587
0.0847	13.3715	0.1130	13.3855
0.1483	13.3983	0.1782	13.4088
0.2257	13.4251	0.2844	13.4415
0.3560	13.4555	0.4538	13.4788
0.5890	13.5103	0.7611	13.5511
0.9830	13.6059		

Table 4.1 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
$C_e = 0.2154 \text{ mol kg}^{-1}$			
0.0017	14.3022	0.0056	14.3057
0.0082	14.3068	0.0146	14.3092
0.0215	14.3115	0.0388	14.3173
0.0569	14.3243	0.0850	14.3348
0.1255	14.3500	0.1773	14.3617
0.2385	14.3780	0.3369	14.3978
0.4749	14.4328	0.6061	14.4620
0.7790	14.5004	1.0508	14.5576
1.4585	14.6497	1.9451	14.7570
$C_e = 0.2271 \text{ mol kg}^{-1}$			
0.0017	14.9238	0.0052	14.9273
0.0087	14.9331	0.0238	14.9390
0.0407	14.9436	0.0685	14.9553
0.0941	14.9646	0.1426	14.9786
0.1964	14.9950	0.2606	15.0124
0.3660	15.0369	0.5199	15.0708
0.6821	15.1081	0.9479	15.1676
1.4518	15.2807	2.0455	15.4113

Table 4.1 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
----- C _e = 0.2364 mol kg ⁻¹ -----			
0.0042	15.4510		
0.0050	15.4533	0.0096	15.4545
0.0134	15.4568	0.0231	15.4591
0.0332	15.4638	0.0550	15.4720
0.0878	15.4825	0.1260	15.4953
0.1865	15.5093	0.2604	15.5303
0.3373	15.5478	0.4255	15.5688
0.5502	15.6014	0.7187	15.6376
0.9640	15.6936	1.3428	15.7764
1.7566	15.8697		
----- C _e = 0.2539 mol kg ⁻¹ -----			
0.0021	16.4062	0.0063	16.4085
0.0109	16.4132	0.0155	16.4108
0.0272	16.4167	0.0431	16.4225
0.0612	16.4248	0.1140	16.4458
0.1554	16.4586	0.2384	16.4773
0.2966	16.4913	0.3670	16.5065
0.4747	16.5286	0.5841	16.5508
0.7375	16.5881	0.9369	16.6313

Table 4.1 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
----- C _e = 0.2918 mol kg ⁻¹ -----			
0.0025	18.3702	0.0046	18.3714
0.0080	18.3725	0.0139	18.3737
0.0232	18.3772	0.0342	18.3830
0.0482	18.3865	0.0655	18.3959
0.0896	18.3994	0.1188	18.4110
0.1700	18.4238	0.2059	18.4367
0.2617	18.4518	0.3412	18.4705
0.4220	18.4880	0.5061	18.5066
0.6499	18.5370	0.8215	18.5766
1.1167	18.6373		
----- C _e = 0.3858 mol kg ⁻¹ -----			
0.0063	22.9619	0.0109	22.9665
0.0181	22.9712	0.0345	22.9724
0.0476	22.9759	0.0682	22.9829
0.1103	22.9922	0.1533	23.0050
0.2021	23.0179	0.2779	23.0400
0.3369	23.0493	0.4194	23.0703
0.5247	23.0913	0.6755	23.1228
0.8141	23.1508	1.0364	23.1963

Table 4.2 Critical Micelle Concentration and Free Energy of
Micellization of SDS in Sodium Acetate Solutions
at 25°C

Conc. of Sod.Ac./ mol kg ⁻¹	10 ³ xcmc/ mol kg ⁻¹	$\Delta G^{\circ}/RT$	$\psi_o^a)/mV$	$\Delta G_{el}^{\circ}/RT$ (= $e\psi_o/k_B T$)	$\Delta G_{HC}^{\circ}/RT$
0.00	8.20	-14.97 ^{b)}	-141	5.48	-20.45
0.0071	5.81	-14.97	-133	5.17	-20.12
0.0135	4.68	-14.97	-128	4.98	-19.93
0.0275	3.14	-14.97	-120	4.67	-19.62
0.0548	2.11	-14.97	-110	4.28	-19.23
0.1014	1.56	-14.97	-95	3.70	-18.65
0.1522	0.98	-14.97	-90	3.50	-18.45
0.1833	0.93	-14.97	-87	3.38	-18.33
0.1934	1.04	-14.79	-86	3.35	-18.14
0.2005	1.22	-14.61	-85	3.31	-17.92
0.2154	1.43	-14.40	-83	3.23	-17.63
0.2271	1.55	-14.28	-81	3.15	-17.43
0.2364	1.63	-14.20	-80	3.11	-17.31
0.2539	1.70	-14.11	-78	3.03	-17.14
0.2918	2.07	-13.82	-55	2.92	-16.74
0.3858	3.03	-13.25	-70	2.72	-15.97

a) Values obtained after interpolation of reported (ref.8) ψ_o values for SDS/NaCl system.

b) Obtained from eq 4.1 (see Table 4.7, $\Delta G_o/RT=A$) Details about ψ_o , ΔG_{el}° and ΔG_{HC}° are given in the text.



Table 4.3 Specific Conductance (k) of SDS in Sodium Propionate Solutions of Different Concentrations (C_e) at 25°C

Conc. of SDS x 10^2 / mol kg ⁻¹	10^{-2} k / mS m ⁻¹	Conc. of SDS x 10^2 / mol kg ⁻¹	10^{-2} k / mS m ⁻¹
$C_e = 0.0049 \text{ mol kg}^{-1}$			
0.0113	0.4295	0.0240	0.4371
0.0408	0.4464	0.0635	0.4597
0.0832	0.4729	0.1182	0.4958
0.1556	0.5194	0.2119	0.5564
0.2738	0.5979	0.3427	0.6417
0.4231	0.6951	0.5286	0.7632
0.6506	0.8351	0.7671	0.8804
0.8911	0.9158	1.0127	0.9490
1.1514	0.9840	1.3171	1.0252
1.5573	1.0839		
$C_e = 0.0175 \text{ mol kg}^{-1}$			
0.0077	1.4123	0.0223	1.4228
0.0393	1.4333	0.0592	1.4440
0.0888	1.4632	0.1277	1.4863
0.1582	1.5052	0.2040	1.5334
0.2620	1.5681	0.3151	1.6007
0.3861	1.6402	0.4644	1.6738

Table 4.3 continued

Conc. of	$10^{-2}k/$	Conc. of	$10^{-2}k/$
SDS x $10^2/$	mS m^{-1}	SDS x $10^2/$	mS m^{-1}
mol kg^{-1}		mol kg^{-1}	

$$C_e = 0.0175 \text{ mol } kg^{-1}$$

0.5577	1.7035	0.6826	1.7373
0.8079	1.7672	0.9580	1.8034
1.1721	1.8572	1.3778	1.9067

$$C_e = 0.0356 \text{ mol } kg^{-1}$$

0.0064	2.7225	0.0187	2.7311
0.0347	2.7416	0.0498	2.7498
0.0678	2.7614	0.0897	2.7707
0.1152	2.7846	0.1495	2.8058
0.1934	2.8304	0.2432	2.8578
0.2911	2.8827	0.3625	2.9073
0.4438	2.9266	0.5243	2.9498
0.6165	2.9687	0.7799	3.0082
0.9410	3.0468	1.1544	3.0964

Table 4.3 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
$C_e = 0.0612 \text{ mol kg}^{-1}$			
0.0067	4.4442	0.0170	4.4536
0.0282	4.4563	0.0456	4.4695
0.0611	4.4773	0.0861	4.4909
0.1079	4.5049	0.1318	4.5154
0.1778	4.5402	0.2183	4.5587
0.2778	4.5729	0.3282	4.5875
0.4291	4.6123	0.5299	4.6350
0.6307	4.6608	0.7637	4.6918
0.9363	4.7306	1.1086	4.7712

Table 4.3 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
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$$C_e = 0.0923 \text{ mol kg}^{-1}$$

0.0115	6.4007	0.0200	6.4080
0.0330	6.4175	0.0465	6.4206
0.0737	6.4332	0.0979	6.4458
0.1240	6.4637	0.1575	6.4837
0.1874	6.4900	0.2158	6.5005
0.2681	6.5141	0.3288	6.5309
0.3887	6.5404	0.4843	6.5666
0.5984	6.5898	0.8442	6.6517
1.0201	6.6948	1.1964	6.7337

$$C_e = 0.1512 \text{ mol kg}^{-1}$$

0.0072	9.8200	0.0221	9.8295
0.0351	9.8358	0.0572	9.8453
0.0843	9.8558	0.1133	9.8705
0.1419	9.8799	0.1777	9.8873
0.2193	9.9030	0.2875	9.9209

Table 4.3 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
----- C _e = 0.1512 mol kg ⁻¹ -----			
0.3634	9.9398	0.4405	9.9608
0.5259	9.9808	0.6499	10.0102
0.7853	10.0427	0.9573	10.0806
1.1239	10.1236		
----- C _e = 0.1749 mol kg ⁻¹ -----			
0.0111	11.1101	0.0212	11.1143
0.0353	11.1237	0.0506	11.1321
0.0651	11.1405	0.0878	11.1531
0.1157	11.1699	0.1633	11.1962
0.2139	11.2004	0.2813	11.2246
0.3461	11.2403	0.4313	11.2561
0.5243	11.2802	0.6769	11.3149
0.8145	11.3517	0.9418	11.3769
1.0959	11.4147		

Table 4.3 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
----- C _e = 0.2029 mol kg ⁻¹ -----			
0.0100	12.5681	0.0445	12.5818
0.0656	12.5965	0.1094	12.6154
0.1378	12.6270	0.1693	12.6364
0.2107	12.6469	0.2768	12.6637
0.3555	12.6921	0.4418	12.7026
0.5662	12.7352	0.6894	12.7625
0.8196	12.7930	0.9551	12.8150
1.0964	12.8602		
----- C _e = 0.2139 mol kg ⁻¹ -----			
0.0091	13.1312	0.0178	13.1375
0.0301	13.1449	0.0450	13.1543
0.0617	13.1627	0.0788	13.1785

Table 4.3 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
----- C _e = 0.2139 mol kg ⁻¹ -----			
0.1010	13.1890	0.1271	13.2005
0.1533	13.2174	0.1944	13.2268
0.2481	13.2520	0.3193	13.2730
0.4025	13.2877	0.4850	13.3056
0.5918	13.3308	0.7452	13.3665
0.8941	13.4012	1.1183	13.4474
C _e = 0.2486 mol kg ⁻¹ -----			
0.0347	14.8351	0.0525	14.8498
0.0762	14.8582	0.1020	14.8656
0.1438	14.8824	0.1904	14.9139
0.2307	14.9150	0.2962	14.9360
0.3705	14.9570	1.4962	14.9948
0.6082	15.0211	0.7806	15.0683

Table 4.4 Critical Micelle Concentration and Free Energies
of Micellization of SDS in Sodium Propionate
Solutions at 25°C

Conc. of Sod.Pr./ mol kg ⁻¹	10 ³ xcmc/ mol kg ⁻¹	$\Delta G^{\circ}/RT$	$\psi_o^{a)}/mV$	$\Delta G_{el}^{\circ}/RT$ (= $e\psi_o/k_B T$)	$\Delta G_{HC}^{\circ}/RT$
0.0049	6.90	-14.65 ^{b)}	-135	5.25	-20.01
0.0175	4.33	-14.65	-124	4.82	-19.58
0.0356	3.12	-14.65	-117	4.55	-19.31
0.0612	2.11	-14.65	-108	4.20	-18.96
0.0923	1.68	-14.65	-98	3.81	-18.57
0.1511	1.60	-14.47	-90	3.50	-17.97
0.1749	1.55	-14.40	-87	3.38	-17.78
0.2028	1.88	-14.11	-85	3.31	-17.42
0.2138	1.94	-14.04	-83	3.23	-17.27
0.2485	2.07	-13.88	-78	3.03	-16.91

a) Values obtained after interpolation of reported (ref.8)
 ψ_o values for SDS/NaCl system.

b) Obtained from eq. 4.1 (see Table 4.7, $\Delta G^{\circ}/RT=A$)
Details about ψ_o , ΔG° , ΔG_{el}° and ΔG_{HC}° are given in the text.

Table 4.5 Specific Conductance (k) of SDS in Sodium Chloride Solutions of Different Concentrations (C_e) at 25°C

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
$C_e = 0.055 \text{ mol dm}^{-3}$			
0.0121	5.9162	0.0162	5.9272
0.0243	5.9361	0.0452	5.9494
0.0632	5.9671	0.0898	5.9848
0.1150	6.0080	0.1487	6.0301
0.1945	6.0567	0.2574	6.0755
0.3711	6.1098	0.4499	6.1364
0.5818	6.1729	0.7293	6.2172
0.9090	6.2703	1.1046	6.3267
1.3169	6.3887	1.6999	6.5005
1.9954	6.5857		

Table 4.5 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
C _e = 0.10 mol dm ⁻³			
0.0068	10.8917	0.0128	10.8983
0.0219	10.9116	0.0303	10.9193
0.0400	10.9326	0.0550	10.9470
0.0647	10.9570	0.0762	10.9658
0.0963	10.9713	0.1210	10.9902
0.1777	11.0112	0.2623	11.0300
0.4114	11.0743	0.5726	11.1196
0.6896	11.1551	0.8760	11.2071
1.0980	11.2613	1.3035	11.3177
1.6418	11.4074		
C _e = 0.18 mol dm ⁻³			
0.0079	19.0068	0.0194	19.0178
0.0282	19.0289	0.0392	19.0400
0.0674	19.0577	0.1104	19.0721
0.1489	19.0920	0.1958	19.1019
0.2544	19.1174	0.3775	19.1495
0.4874	19.1705	0.6301	19.2015
0.8299	19.2480	1.1974	19.3177
1.5223	19.3897		

Table 4.5 continued

Conc. of	$10^{-2}k/$	Conc. of	$10^{-2}k/$
SDS x $10^2/$	$mS m^{-1}$	SDS x $10^2/$	$mS m^{-1}$
$mol kg^{-1}$		$mol kg^{-1}$	

$$C_e = 0.30 \text{ mol dm}^{-3}$$

0.0051	24.7746	0.0083	24.7990
0.0190	24.8034	0.0284	24.8090
0.0378	24.8178	0.0555	24.8355
0.0832	24.8388	0.1395	24.8477
0.2357	24.8599	0.3681	24.8709
0.5327	24.8831	0.8978	24.9218
1.1663	24.9639		

$$C_e = 0.40 \text{ mol dm}^{-3}$$

0.0065	28.2827	0.0106	28.3038
0.0162	28.3137	0.0255	28.3325
0.0386	28.3569	0.0513	28.3801
0.0883	28.3934	0.1862	28.4045
0.3137	28.4111	0.5509	28.4255
0.8471	28.4465	1.1450	28.4675

Table 4.5 continued

Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹	Conc. of SDS x 10 ² / mol kg ⁻¹	10 ⁻² k/ mS m ⁻¹
C _e = 0.50 mol dm ⁻³			
0.0051	30.6001	0.0118	30.6156
0.0195	30.6609	0.0299	30.6941
0.0549	30.7307	0.1021	30.7517
0.1945	30.7594	0.3438	30.7672
0.6318	30.7561	1.0329	30.7650

Table 4.6 Critical Micelle Concentration and Free Energies of Micellization of SDS in Sodium Chloride Solutions at 25°C

Conc. of NaCl/ mol kg ⁻¹	10 ³ xcmc/ mol kg ⁻¹	$\Delta G^{\circ}/RT$	$\psi_0^{a)}/mV$	$\Delta G_{el}^{\circ}/RT$ (= $e\psi_0/k_B T$)	$\Delta G_{HC}^{\circ}/RT$
0.055	2.06	-15.07 ^{b)}	-109	4.24	-19.31
0.10	1.40	-15.07	-95	3.70	-18.77
0.18	0.91	-15.07	-87	3.38	-18.45
0.30	0.62	-15.07	-73	2.84	-17.91
0.40	0.55	-15.07	-68	2.64	-17.71
0.50	0.45	-15.07	-66	2.57	-17.64

Reported cmc values (ref.6-8)

0.01	5.20
0.02	3.82
0.03	3.09
0.05	2.14
0.1	1.39
0.2	0.83
0.4	0.52
0.5	0.45
0.6	0.42
0.8	0.38

a) Values obtained after interpolation of reported (ref.8) values.

b) Obtained from eq.4.1 (see Table 4.7, $\Delta G^{\circ}/RT=A$) Details about ψ_0 , ΔG° , ΔG_{el}° , and ΔG_{HC}° , are given in the text.

Table 4.7 Least-Square fitted values of the Parameters of Eq
4.1 for SDS in Different Eletrolytic Solutions

Electrolyte	Conc.Range of Electrolyte	A	β	Corr. Coeff.
CH ₃ COONa	0-0.1833 mol kg ⁻¹	-14.973	0.696	-0.9979
C ₂ H ₅ COONa	0.0923 mol kg ⁻¹	-14.655	0.665	-0.9987
NaCl	0-0.5 mol kg ⁻¹	-15.068	0.708	-0.9997

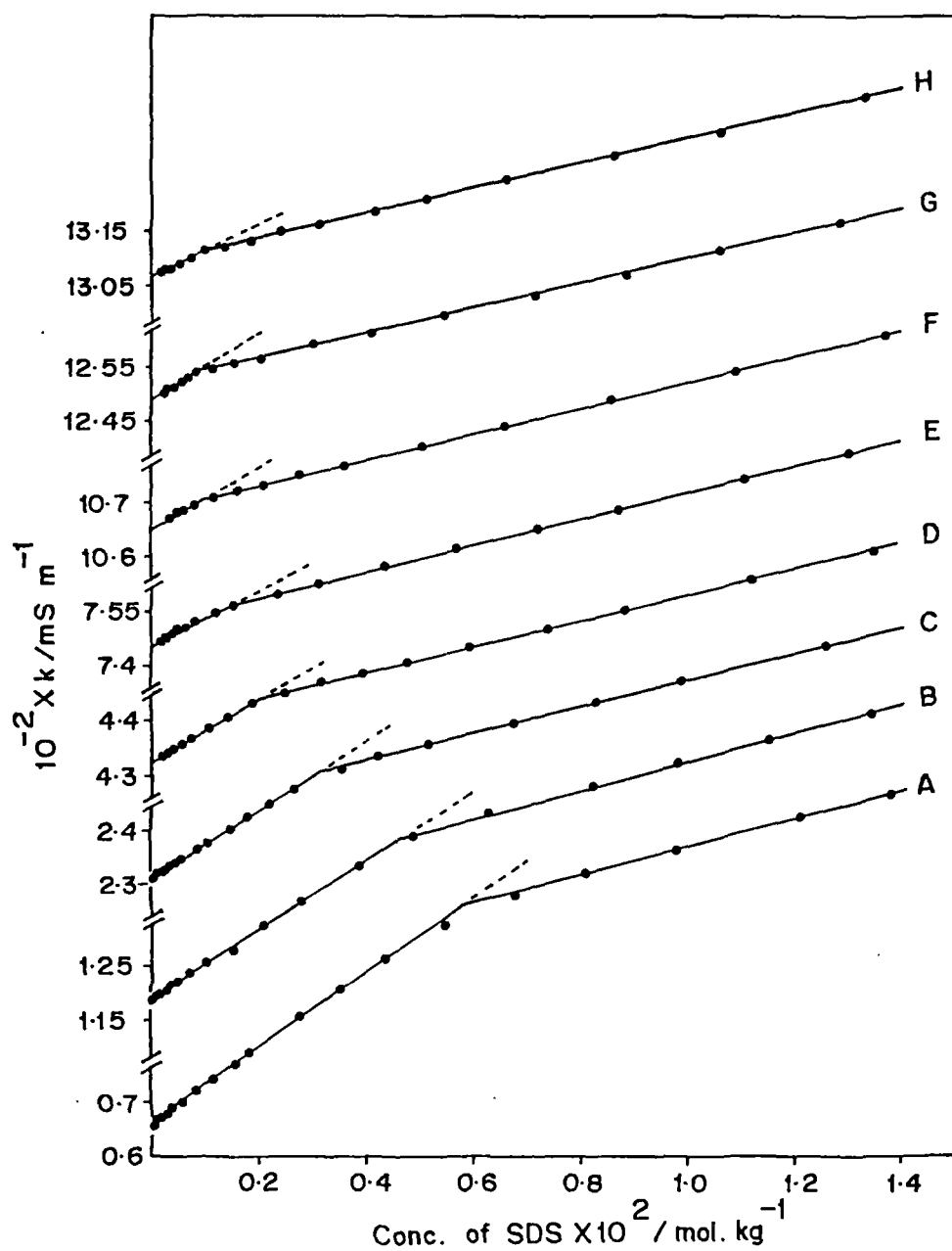


Fig 4.1a Plots of specific conductivity of SDS in sodium acetate solutions of different concentrations at 25°C versus concentration. Concentrations (mol kg^{-1}) of sodium acetate solution: A = 0.0071, B = 0.0135, C = 0.0275, D = 0.0548, E = 0.1014, F = 0.1522, G = 0.1833, H = 0.1934.

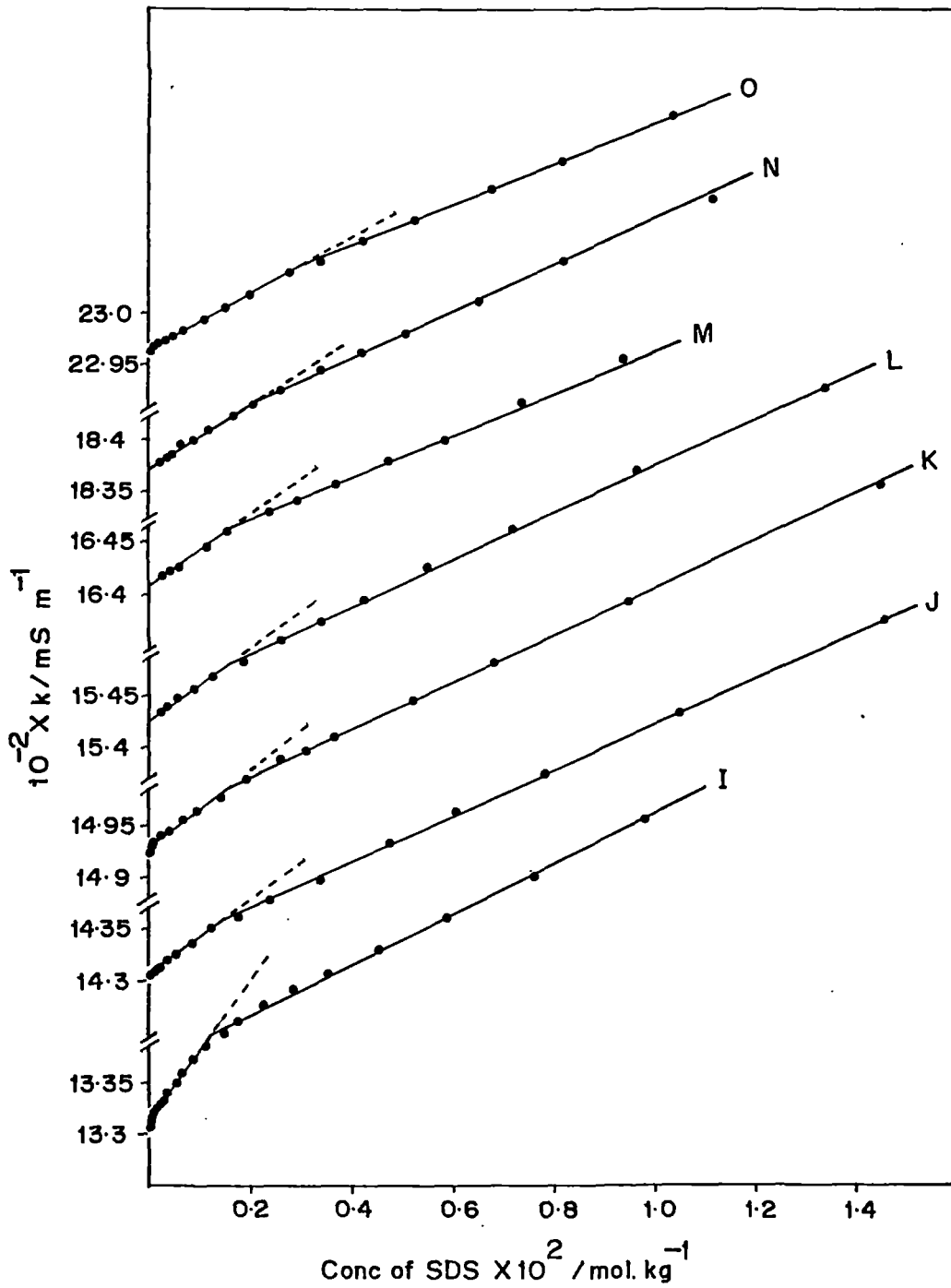


Fig 4.1b Plots of specific conductivity of SDS in sodium acetate solution of different concentrations at 25°C versus concentration. Concentrations (mol kg^{-1}) of sodium acetate solution: I = 0.2005, J = 0.2154, K = 0.2271, L = 0.2364, M = 0.2539, N = 0.2918, O = 0.3858.

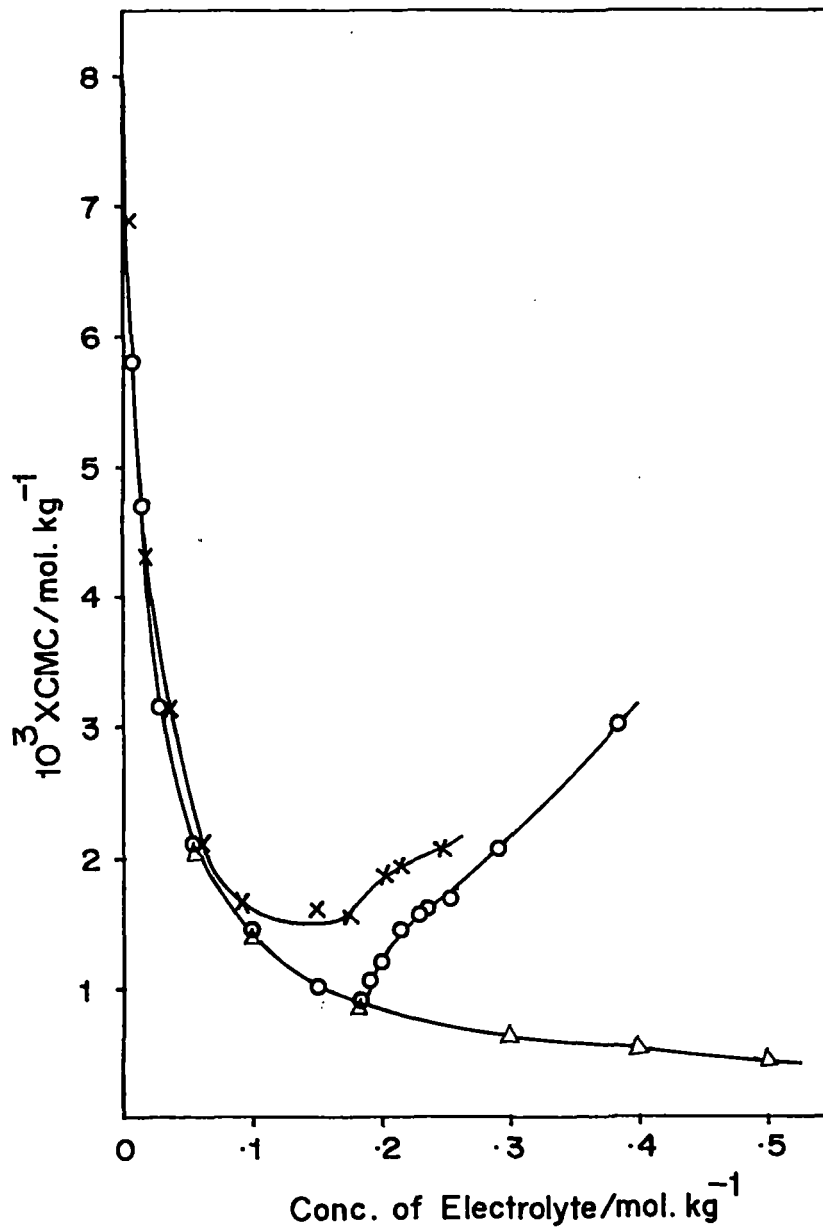


Fig 4.2 Variation of cmc of SDS with concentration in sodium acetate (o), sodium propionate (x), and sodium chloride (Δ) solutions at 25°C.

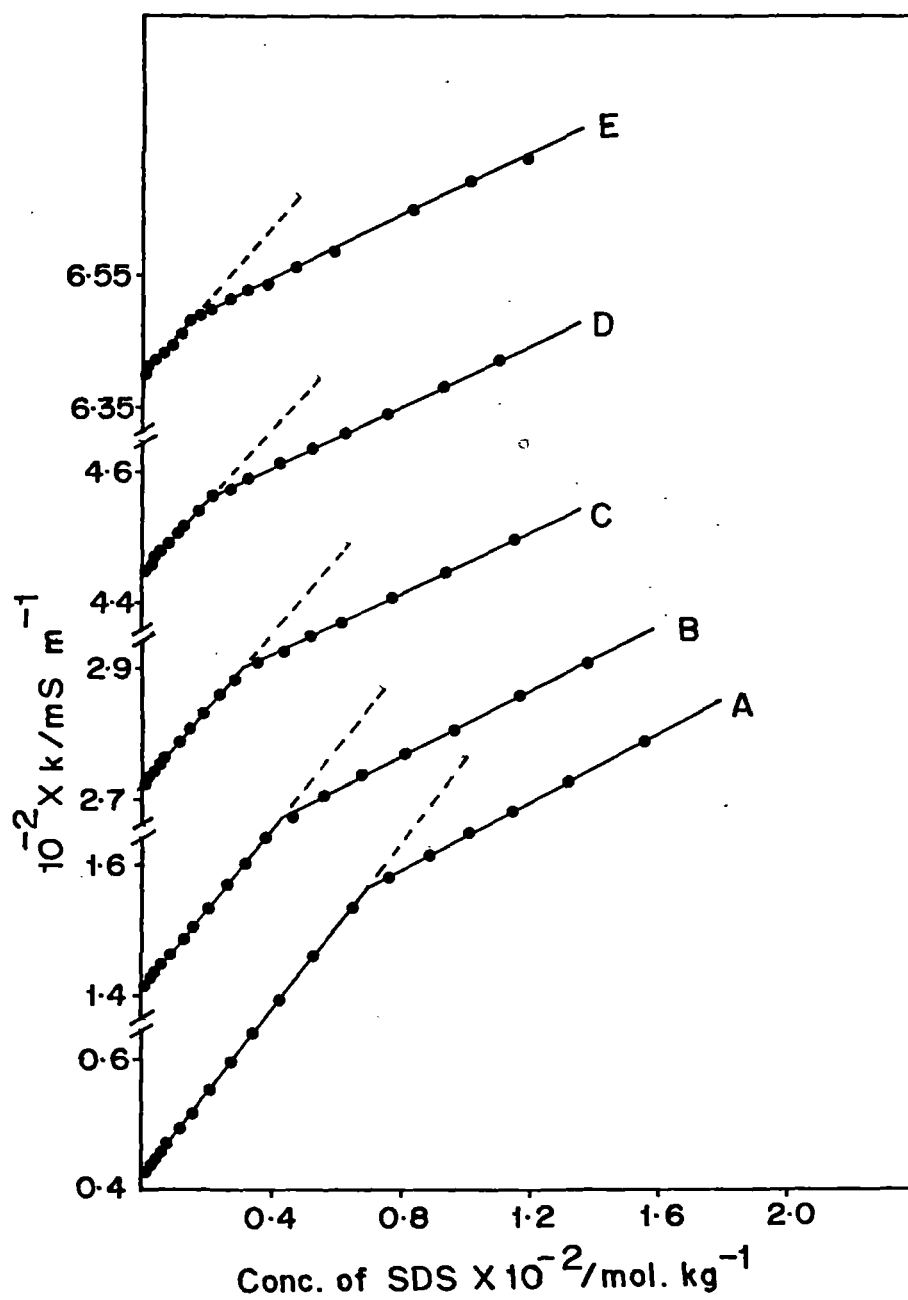


Fig 4.3a Plots of specific conductivity of SDS in sodium propionate solutions of different concentrations at 25°C versus concentration. Concentrations (mol kg^{-1}) of sodium propionate solution: A = 0.0049, B = 0.0175, C = 0.0356, D = 0.0612, E = 0.0923.

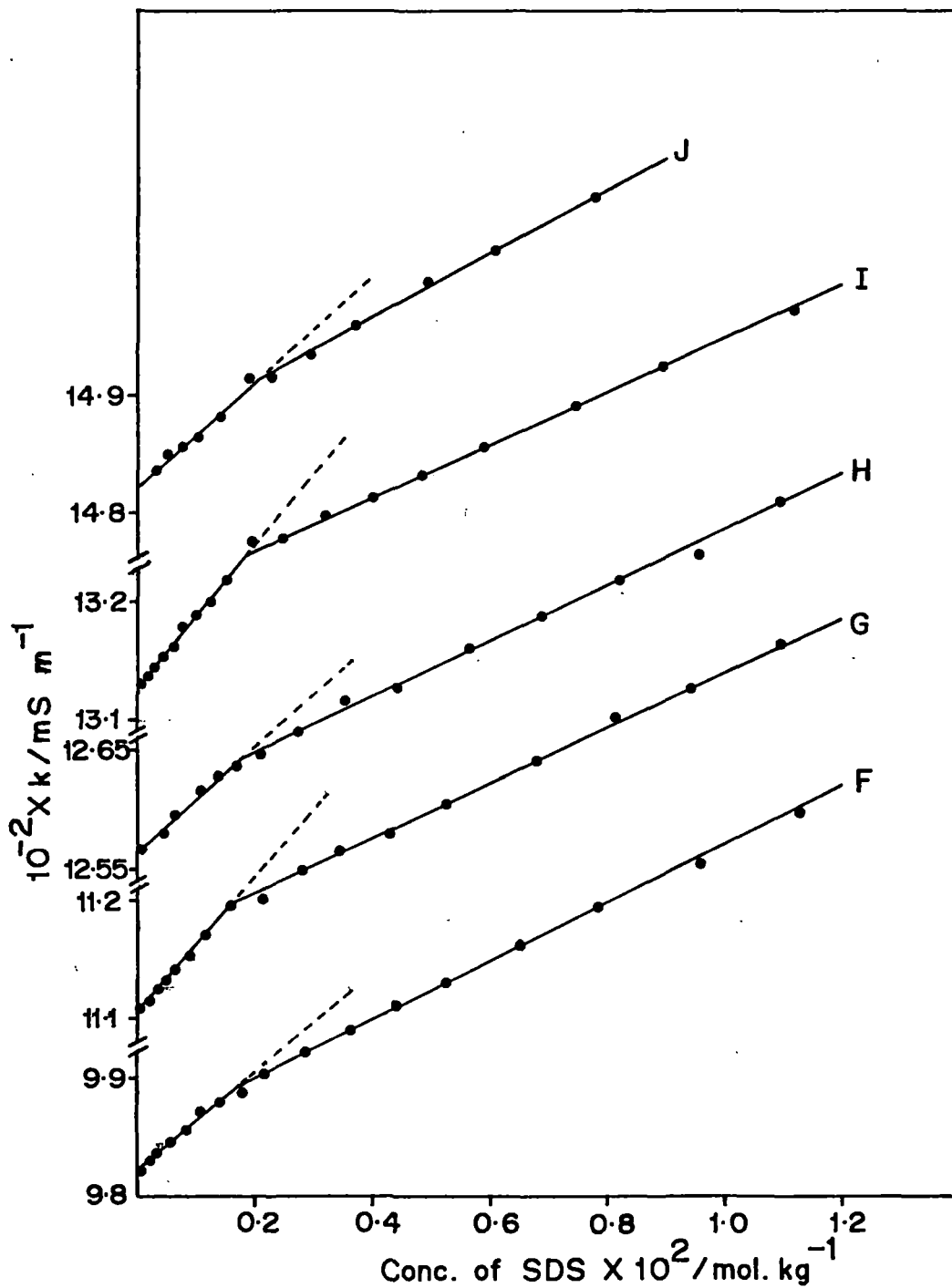


Fig 4.3b Plots of specific conductivity of SDS in sodium propionate solutions of different concentrations at 25°C versus concentration. Concentrations (mol kg^{-1}) of sodium propionate solution: F = 0.1511, G = 0.1749, H = 0.2028, I = 0.2138, J = 0.2485.

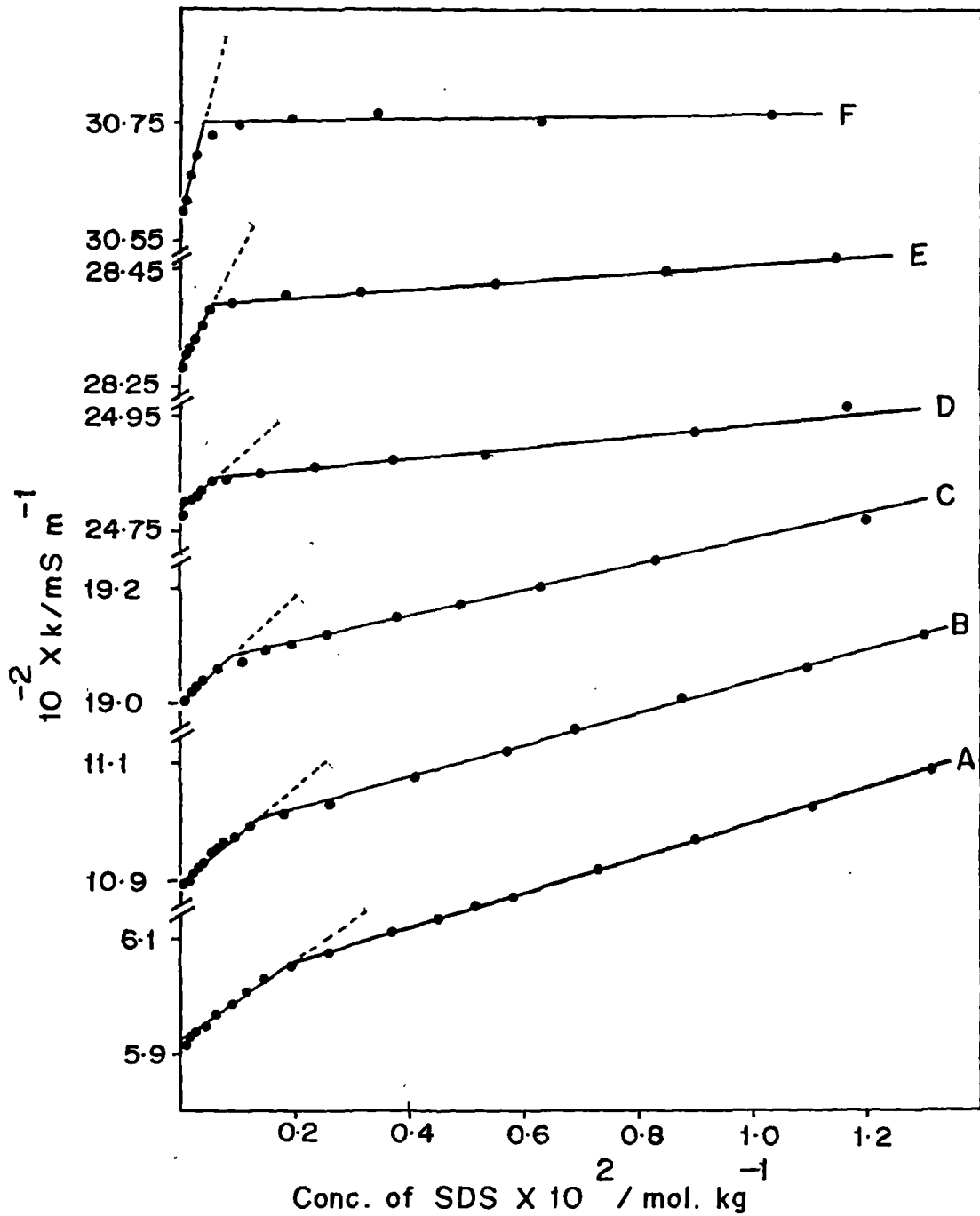


Fig 4.4 Plots of specific conductivity of SDS in sodium chloride solutions of different concentrations at 25°C versus concentration. Concentrations (mol kg⁻¹) of sodium chloride solution: A = 0.055, B = 0.10, C = 0.18, D = 0.30, E = 0.40, F = 0.50.

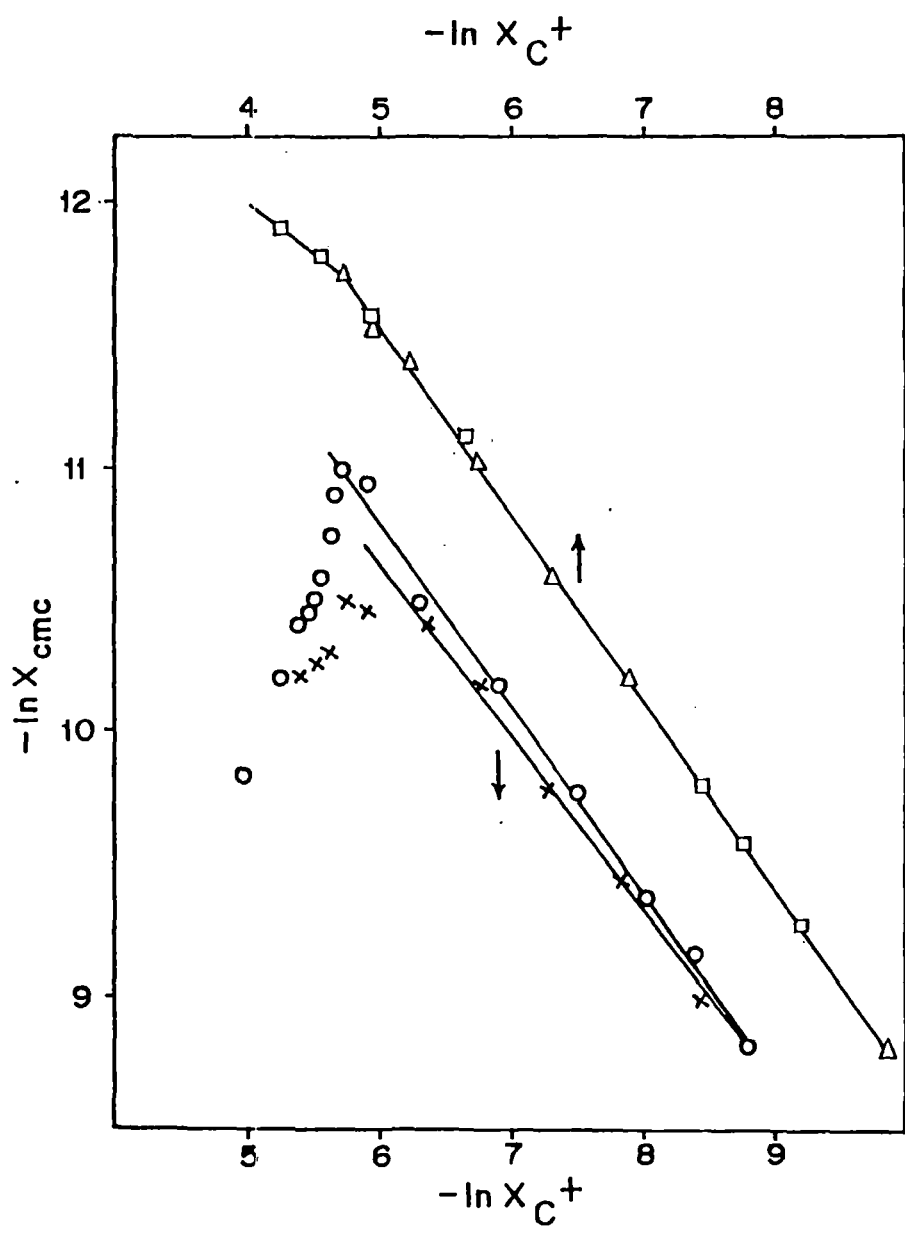


Fig 4.5 Plot of $\ln x_{cmc}$ of SDS in sodium acetate(o), sodium propionate (x) and sodium chloride (Δ : present, \square : ref. 6-8) of different concentrations at 25°C versus $\ln x_{c+}$

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Chapter 5

Estimation of Micellization Parameters of Surfactants in Aqueous Medium from Conductivity Data Considering Ion-Ion Interactions

5.1 INTRODUCTION

One of the widely used experimental methods to determine the cmc of ionic surfactant solutions is the conductivity method. Nearly all aqueous ionic surfactants have been observed to undergo a change in slope in the conductivity versus concentration plot at the cmc. Besides cmc the other two important parameters which characterize a micellization process are the counterion binding constant (β) and the aggregation number (n). Attempts have been made by several workers¹⁻⁴ to estimate all the three micellization parameters from the conductivity data. Evans¹ proposed a simple method for calculating the micellization parameters from conductivity data presuming equivalent conductances of monomers, counterions and micelles to be independent of concentration. Using Stokes law for deducing the equivalent conductance of charged micelle, Evans¹ suggested the expression

$$s_2 = [n^{-1/3} (1-\beta)^2 (10^3 s_1 - \Lambda_x) + (1-\beta) \Lambda_x] 10^{-3} \quad (5.1)$$

where s_1 and s_2 are the slopes of the specific conductance versus concentration plot below and above the

cmc, respectively. Λ_x is the equivalent conductance of the counterion. β and n are defined above. In Evans approach using eq 5.1 n or β can be calculated if the value of one of them is known from another source. Considering micelle to be spherical n was estimated by Evans from the expression

$$n = (4/3M_w) \pi l^3 N_A d \quad (5.2)$$

where l is the length of the hydrocarbon chain of the surfactant molecule, d is the density of a hydrocarbon of molecular weight M_w which is structurally similar to the hydrocarbon chain of the surfactant (dodecane in the case of SDS) and N_A is the Avogadro number. Thus β can be calculated from eq 5.1 after obtaining n from eq 5.2. Another frequently used method for calculating β is by determining cmc of a surfactant as a function of concentration of added electrolyte and then by applying Corrin-Harkins equation as described in previous chapters. However, from this method an average value of β is obtained and β for different concentrations of counterion cannot be estimated. Kimizuka and Satake² in their conductivity method to estimate the micellar charge made an attempt to account for the ion-ion

interaction by using the limiting-law of conductance. However, the inadequacy of simple limiting-law was noticed at concentrations above the cmc. After calculating micellar charge Kimizuka and Satake² obtained the value of β by knowing aggregation number from light scattering experiments. Nishikido³ by using essentially the same approach as that of Evans calculated n and β by combining conductivity and counterion activity data. An improved method for the estimation of all the three micellization parameters from the conductivity data without ignoring the ion-ion interactions has been proposed recently by Shanks and Frances.⁴ Attempt has been made here to estimate the micellization parameters of surfactants from the available conductance data using an approach similar to that of Shanks and Frances.⁴

5.2 THEORY

Mass-action model (cf. chapter 1) has been used to explain the conductivity behaviour of ionic surfactants. According to this model the electrical conductivity of a surfactant solution with no added electrolyte must be due to the result of ionic conductances of three species, viz., monomer ion, counterion and charged

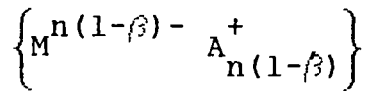
micelle. Although this model ignores polydispersity in n and β (due to polydisperse micelle sizes) and the dependence of average aggregation number on concentration, it can still describe some of the salient aspects of conductivity of surfactant solutions. For deriving a conductivity equation the micellar systems consisting of aqueous monomers and micelles are treated as a solution of mixed electrolytes. The two electrolytes are (1) aqueous solution containing monomers and an equivalent number of counterions to make the solution electrically neutral (aqueous phase) and (2) micellar solution containing micelles and counterions (micellar phase). The micellar solution is also treated as electrically neutral. It is considered that neutral micelles are formed which then dissociate into charged micelles and corresponding number of counterions.

For a surfactant of the type $A_{r+}^{z+} B_{r-}^{z-}$, the correlation between equivalent conductance, Λ_{leq} , and molar conductance, Λ_{lm} , of the surfactant in aqueous solution is given by⁵

$$\Lambda_{lm} = \Lambda_{leq} r_+ z_+ = k/C \quad (5.3)$$

where k is the specific conductance and C is the

concentration of the surfactant solution. For SDS r_+ , z_+ , r_- and z_- are equal to unity. Molar conductance Λ_{lm} is the conductance due to 1 mole of surfactant in the aqueous solution. We represent a neutral micelle as



where M is an anionic micelle with $n(1-\beta)$ negative charges. M consists of n monomers and $n\beta$ counterions (A^+). This neutral micelle dissociates to give one mole of ionic micelle $M^{n(1-\beta)-}$ and $n(1-\beta)$ moles of counterions in the micellar solution. The molar conductance, Λ_{nm} , of the above represented micelle is related to its equivalent conductance, Λ_{neq} , by the relation

$$\Lambda_{nm} = \Lambda_{neq} n(1-\beta) \quad (5.4)$$

It may be noted that Λ_{nm} is the conductance due to 1 mole of micelle in the micellar solution.

Therefore, by treating a surfactant solution as a solution of mixed electrolytes the molar conductance of a surfactant in solution, Λ_m , can be written as

$$\Lambda_m = \Lambda_{lm} P_{aq} + \Lambda_{lmic} P_{mic} \quad (5.5)$$

Λ_{lmic} is the molar conductance of surfactant when it is in the micellar solution. P_{aq} is the probability that the

surfactant molecule is in the aqueous solution whereas P_{mic} is the probability that the surfactant molecule is in the micellar phase. Λ_{lmic} is related to Λ_{nm} by the relation

$$\Lambda_{lmic} = \Lambda_{nm}/n \quad (5.6)$$

The probability terms can be calculated from the relations

$$P_{aq} = C_o/C_t \quad (5.7)$$

and
$$P_{mic} = (C - C_o)/C_t = nC_n/C_t \quad (5.8)$$

C_o is the cmc, C_t is the total concentration of the surfactant and C_n is the molar concentration of micelle which is equal to $(C-C_o)/n$. Thus

$$\begin{aligned} \Lambda_m &= \Lambda_{lm} (C_o/C_t) + \Lambda_{nm} (C_n/C_t) \\ &= \Lambda_{leq} (C_o/C_t) + \Lambda_{neq} n(1-\beta) (C_n/C_t) \end{aligned} \quad (5.9)$$

Interionic interactions reduce the equivalent conductances of electrolytic solutions. The amount of decrease in equivalent conductance is dependent on size, charge and limiting conductances of the individual ions and also on the effective ionic strength. These interactions are due to hydrodynamic and electrostatic effects. We make use of the Debye-Huckel-Onsager (DHO) approach⁶ to account for the effect of interionic interactions on electrical conductance. Application of DHO approach is more

appropriate in dilute solutions. Mukerjee et al.⁷, in fact, used DHO conductance equation to describe the conductance behaviour of surfactant solution below cmc and to derive information about the pre-micellar association. However, as an approximation DHO approach has been adopted here to obtain an improved conductance equation for interpreting the conductance behaviour of surfactant solutions above cmc as was done by Shanks and Franses.⁴ According to this approach eq.5.9 for Λ_m which is the molar conductance of a solution containing monomers and micelles becomes

$$\Lambda_m = \left[\Lambda_1^o - \frac{A_1 I^{1/2}}{1 + B_o a_1} \right] \frac{C_o}{C_t} + \left[\Lambda_n^o - \frac{A_n I^{1/2}}{1 + B_o a_n} \right] \frac{n C_n (1-\beta)}{C_t}$$

.....(5.10)

where B_o^{-1} is referred to as the Debye-Hückel reciprocal length. B_o is given by

$$B_o = [8\pi N_A e_o^2 / (10^3 \epsilon k_B T)]^{1/2} I^{1/2} \quad (5.11)$$

In eq 5.11 k_B is the Boltzmann constant, T is the absolute temperature, ϵ is the dielectric constant of water and e_o is the electronic charge. In eq 5.10 a_1 and a_n are the effective ionic radii in the aqueous and micellar solutions, respectively. The constants A_1 and A_n actually

control the effect of interionic interactions on molar conductance. The constant A_1 for monomers and A_n for micelles are determined independently from the expression⁸

$$A_i = \frac{2.801 \times 10^6 |z_+ z_-| q \Lambda_i^0}{(\epsilon T)^{1.5} (1+q)^{0.5}} + \frac{41.25 (|z_+| + |z_-|)}{\eta (\epsilon T)^{0.5}} \quad (5.12)$$

The term q in eq 5.12 is given by

$$q = \frac{|z_+ z_-|}{|z_+| + |z_-|} \times \frac{\lambda_+^0 + \lambda_-^0}{|z_+| \lambda_-^0 + |z_-| \lambda_+^0} \quad (5.13)$$

Eq 5.12 for A_i is in cgs units and $i=1$ for monomers or n for micelles. η is the solvent viscosity. In eqs 5.10 and 5.11 I refers to the effective ionic strength. In order to apply eqs 5.10, 5.12 and 5.13 for data fitting we require the limiting equivalent conductances Λ_1^0 and Λ_n^0 as well as limiting ionic conductances λ_+^0 and λ_-^0 . For monomers Λ_1^0 , λ_+^0 and λ_-^0 are experimentally determinable quantities. In the case of micelles the value of limiting ionic conductance of the counterion is available whereas that of ionic micelle is not directly accessible experimentally. Therefore, for the purpose of evaluating λ_-^0 of a micelle (the case of an anionic micelle is

considered here) we make use of the Stokes-Einstein relation.⁵ Stokes-Einstein expression is written for λ_{-}° of a micelle as

$$\lambda_{-}^{\circ}(\text{micelle}) \equiv \lambda_{n}^{\circ} = z_{n}^2 e_{o} F / 6\pi\eta r_{n} \quad (5.14)$$

where F is the Faraday constant, z_{n} is the charge on the micellar ion and r_{n} is the radius of micelle. The shape of micelle is presumed to be spherical here. The radius of the micellar ion is evaluated approximately by using the relation

$$r_{n} = n^{1/3} r_{1} \quad (5.15)$$

where r_{1} is the radius of the monomeric ion.

5.3 COMPUTATION PROCEDURE

In order to compute the values of $C_{o,n}$ and β from eq 5.10 the values of r_{n} , a_{1} , a_{n} , A_{1} , A_{n} , Λ_{1}° , Λ_{n}° , B_{o} and I need to be determined. r_{n} is evaluated using eq 5.15 in which r_{1} is obtained from the relation⁹

$$r_{1} = [(3/4\pi)(27.4 + 29.6n_{c})]^{1/3} \quad (5.16)$$

where n_{c} is the number of carbon atoms in the hydrocarbon chain of the surfactant used. r_{1} obtained from eq 5.16 will be in \AA . Once r_{n} is determined λ_{n}° can be evaluated using eq 5.14. Subsequently, Λ_{n}° and A_{n} can also

be evaluated. A_1 can easily be determined directly from eqns 5.12 and 5.13. a_1 and a_n are evaluated by adding Stokes ionic radius of counterion to r_1 and to r_n , respectively.

The important issue which comes next is that of the evaluation of ionic strength, I , which is required for data fitting. Different earlier studies have indicated that the highly charged micelles do not contribute to the ionic strength as the smaller unaggregated ions do.^{4,10-12} Accordingly, Shanks and Franses⁴ while analyzing the conductance data of SDS in water in the light of eq 5.10 examined four possible expressions for the effective ionic strength of a micellar solution, each accounting for different individual ionic contributions. These four models for the evaluation of ionic strength have been used in the present study and the models are listed in Table 5.1. It has been established experimentally that the activity/concentration of amphiphilic ion decreases and that of counterion increases with the increase of amphiphilic concentration above the cmc.¹³⁻¹⁸ However, in the models listed in Table 5.1 the concentration of surfactant monomers has been treated as

approximately constant. Model 3 is intermediate between models 1 and 2 as it includes only a fraction of the micellar counterions and this fraction was arbitrarily assigned by Shanks and Franses⁴ to be $(1-\beta)$ times the concentration of free micellar counterions.

For fitting the conductance data to eq 5.10 an iterative least-squares method was used. This program was developed essentially on the basis of the Newton-Raphson method.¹⁹ In this program the calculation is started by selecting and feeding into the computer the initial approximate values of C_0 , n and β . In fact, initial value of C_0 is taken to be the value obtained from the plot of specific conductance versus concentration of surfactant. The computer then improves the values of the parameters in every cycle by minimizing the square of the deviation and using Newton-Raphson method. Refined values of the parameters become their initial values for the next cycle. The cycle was continued till the best-fit was obtained. Similar computation procedure was used by Kay in electrolytic solutions.²⁰ The listing of the program developed by us is given in Appendix 5.1.

5.4 EXPERIMENTAL SECTION

The conductances of hexadecyl pyridinium chloride (Aldrich) at 25⁰C were measured by using the same experimental procedure described in the preceding chapters.

5.5 RESULTS AND DISCUSSION

All the conductance data given in chapter 4, the reported²¹ conductance data of aqueous solutions of sodium decyl sulfonate, sodium dodecyl sulfonate and sodium tetradecyl sulfonate as well as the measured conductance data (Table 5.2) of hexadecyl pyridinium chloride (CPC) were fitted to eq 5.10.

The results of the fits of the data of SDS + H₂O are given in Table 5.3. For the data fitting Λ_1^0 of SDS was taken to be 73.0 S cm²eq⁻¹ which was determined by extrapolation of conductance data to zero concentration. Data in two different concentration regions (A : 2.4x10⁻³ to 246.2x10⁻³ mol kg⁻¹ and B : 2.4x10⁻³ to 97.25x10⁻³ mol kg⁻¹) were fitted to eq5.10. From Table 5.3 it is evident that model 1 fits the data better than other models when the concentration range of SDS covered in the data fitting is larger. This is in accordance with the finding made by

Shanks and Franses.⁴ The best-fit values of cmc , β and n are $0.00846 \text{ mol kg}^{-1}$, 0.7 and 44 , respectively which are in good agreement with the values reported by Shanks and Franses.⁴ In some cases the best-fit value of cmc (cmc_{bf}) is in agreement with its value obtained from conductance versus concentration plot (cmc_{ex}). In those cases where cmc_{bf} differed from cmc_{ex} , we did another data fitting keeping cmc_{ex} constant and the parameters obtained from this fit are also included in Table 5.3. When a narrow range of concentration (range B) was used for the data fitting it was found that models 1, 2 and 3 fit the data almost equally well although for model 1 the standard deviation is minimum. Similar observation was made by Shanks and Franses.⁴ By varying the concentration range of data fitting values of cmc , B and n also seem to vary. Model 4 gives abnormally low values of n and therefore this model is not applicable indicating that micelles contribute to the conductance but not to the effective ionic strength as reported by others.^{4,10-12}

The above conclusions about the suitability of different models for ionic strength for describing the conductance data of surfactant solutions are supported

further by the results obtained from the fits of the conductance data of sodium alkyl sulfonates²¹ and CPC (Table 5.4). In the case of sodium decyl sulfonate the concentration range used is from 1 to 200 mol dm⁻³ and the conductance data is best represented by model 1. For sodium dodecyl sulfonate, since the concentration range of the data fitting is 1 to 100 mol dm⁻³, in addition to model 1 which represents the data best models 2 and 3 also appear to fit the data reasonably well as it is observed above for SDS solution. In the case of sodium tetradecyl sulfonate the concentration range of data fitting is still less (2 to 20 mol dm⁻³) and it is apparent from Table 5.4 that good fits of the data to eq 5.10 are obtainable using all the four models. However, the value of n computed using model 4 is relatively low. The concentration range of data fitting for CPC is the lowest, i.e., from 0.1048 to 16.5 mol kg⁻¹, and in this case all the 4 models describe the conductance data equally well. It may be noted that in this particular case even model 4 provides acceptable value of n. The best-fit cmc values of sodium alkyl sulfonates and CPC are in reasonably good agreement with the experimental cmc values (Table 5.4). The aggregation numbers of these surfactants

given in Table 5.4 are also comparable with the reported²² values.

The results of the fits of conductance data of SDS + CH₃COONa, SDS + C₂H₅COONa and SDS + NaCl (Chapter 4) to eq 5.10 are shown in Tables 5.5 - 5.7. The added electrolyte increases the effective ionic strength of the solution. Moreover, the specific conductance of the electrolyte solution without surfactant is considered to contribute a constant background conductivity to the system. The concentration ranges of SDS used for the data fitting are the same as that shown in Tables 4.1, 4.3 and 4.5 of chapter 4. In all the three electrolytes the concentration ranges of SDS used for data fitting are narrow and consequently models 1 to 3 and sometimes all the 4 models fit the data equally well. The best-fit cmc values differed from cmc_{ex} and in such cases fits were also done keeping cmc_{ex} constant as was done for SDS + H₂O system. No regular trend in the variation of n with electrolyte concentration has been observed although n is known to increase with increase in electrolyte concentration.²³⁻²⁷ The values of n estimated from the conductance data seem to be invariably less than the values obtained from light scattering and other methods.²³⁻²⁷ An

overall decrease in the value of counterion binding constant has been observed. Shanks and Franses⁴ also observed decrease of β with increase in salinity. In the case of SDS + CH₃COONa system upto $\sim 0.2 \text{ mol kg}^{-1}$ CH₃COONa the best-fit values of cmc are in agreement within $\pm 0.2 \times 10^{-3} \text{ mol kg}^{-1}$ with the experimental cmc values. Above this concentration of CH₃COONa good agreement between cmc_{bf} and cmc_{ex} has not been achieved. In the case of SDS + C₂H₅COONa, for the entire concentration range of C₂H₅COONa studied here, i.e., upto $0.2139 \text{ mol kg}^{-1}$, cmc_{bf} is in agreement within $\pm 0.2 \times 10^{-3} \text{ mol kg}^{-1}$ with the cmc_{ex} . Fits obtained in the case of SDS + NaCl are relatively poor especially above 0.18 mol kg^{-1} which may likely be due to limited data points.

It may be concluded that model 1 for ionic strength is superior when the concentration range of surfactant covered in the data fitting is large. Models 2 and 3 also describe the conductance data equally well if a narrow concentration range of surfactant is covered in the data fitting. Model 4 is not suitable for estimating micellization parameters from the conductance data. Thus micelles do not contribute to ionic strength of a surfactant solution which substantiates the conclusion drawn by earlier

workers.^{4,10-12} The aggregation numbers obtained by fitting conductance data in the different concentration regions of surfactant are different envisaging thereby the dependence of aggregation number on concentration. This comply with the recent reports^{28,29} that aggregation number varies as a function of $C^{1/\gamma}$, where C is the surfactant concentration and $\gamma \approx 0.25$ for sodium alkyl sulphate micelles. In general, aggregation numbers estimated from conductance data are lower than those obtained from light scattering method. Finally, this work has established the applicability of the new conductance equaltion (eq 5.10) which was first proposed by Shanks and Franses⁴ for the estimation of micellization parameters.

Table 5.1 The Models used for the evaluation of Ionic Strength

Model	Expression for $I^{a)}$
1	$I = c_t, c_t < c_o$ $= c_o, c_t > c_o$
2	$I = c_t, c_t < c_o$ $= c_o + 0.5n(1-\beta)c_n, c_t > c_o$
3	$I = c_t, c_t < c_o$ $= c_o + 0.5n(1-\beta)^2c_n, c_t > c_o$
4	$I = c_t, c_t < c_o$ $= c_o + 0.5n(1-\beta)c_n [1+n(1-\beta)],$ $c_t > c_o$

a) The above expressions are used for the different models in the absence of added electrolyte. In the presence of added electrolyte, the fixed concentration of the 1:1 electrolyte has been added to the different expressions to get the value of I .

Table 5.2 Specific Conductance (k) of CPC in Aqueous Solution
at 25°C

10^4 x conc. of CPC/mol kg ⁻¹	10^4 x k/ S m ⁻¹	10^4 x conc. of CPC/mol kg ⁻¹	10^4 x k/ S m ⁻¹
1.048	14.49	1.449	19.89
1.845	24.85	2.236	30.04
2.622	32.99	3.566	43.22
4.481	52.57	5.368	62.13
6.228	70.83	7.874	86.98
9.426	101.23	10.893	109.98
12.281	116.75	14.845	128.51
17.161	139.44	22.934	165.80

Table 5.3 Values of Micellization Parameters of SDS in H₂O
at 25°C

Conc.range	cmc ^{a)} ± 0.01 ^{b)}	β ± 0.002 ^{b)}	n ± 2 ^{b)}	10 ³ x Std.dev.

Model 1				
A ^{c)}	8.46	0.700	44	0.0378
A	8.10	0.700	44	0.0396
B ^{d)}	9.10	0.699	36	0.0207
Model 2				
A	8.10	0.630	34	0.1194
B	9.01	0.683	45	0.0275
Model 3				
A	8.10	0.700	74	0.0832
B	9.02	0.709	56	0.0229
Model 4				
A	8.00	0.0470	7	0.1036
A	8.10	0.470	7	0.1040
B	8.90	0.480	1	0.0261

(a) in 10⁻³ mol kg⁻¹ (b) These upper and lower limits of the values of cmc, β and n indicate variations possible in their respective values without causing significant changes in the listed standard deviations (c) refers to the range from 2.4 x 10⁻³ mol kg⁻¹ to 246.2 x 10⁻³ mol kg⁻¹ (d) refers to the range from 2.4 x 10⁻³ mol kg⁻¹ to 97.25 x 10⁻³ mol kg⁻¹.

Table 5.4 Values of Micellization Parameters of Sodium Decyl Sulfonate, Sodium Dodecyl Sulfonate and Sodium Tetradecyl Sulfonate at 40°C and of CPC at 25°C in H₂O

$10^3 \times \text{Conc. range / Model}$ mol dm ⁻³	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}}$ mol dm ⁻³	$\beta \pm 0.002^{\text{a)}}$	$n \pm 2^{\text{a)}}$	$10^3 \times \text{Std. dev.}$
<u>Sodium Decyl Sulfonate^{b)}</u>				
1 to 200	1 38.2 (40.0) ^{c)}	0.516	53	0.0428
	2 37.0	0.410	21	0.1405
	3 36.1	0.421	18	0.0843
	4 33.9	0.130	6	0.1473
<u>Sodium Dodecyl Sulfonate^{b)}</u>				
1 to 100	1 10.5 (11.0)	0.657	68	0.0135
	2 9.8	0.537	21	0.0373
	3 10.0	0.543	17	0.0263
	4 10.1	0.360	3	0.0333

Table 5.4 continued

$10^3 \times \text{Conc. range} /$ mol dm^{-3}	Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}}$ mol dm^{-3}	$\beta \pm 0.002^{\text{a)}}$	$n \pm 2^{\text{a)}}$	$10^3 \times \text{Std. dev.}$
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Sodium Tetradecyl Sulfonate^{b)}

	1	2.72	0.681	45	0.0061
	2	2.75	0.681	56	0.0022
	3	2.78	0.680	47	0.0031
	4	2.77	0.541	15	0.0061

CPC^{c)}

0.1048 to 16.5	1	0.825 (0.920) ^{d)}	0.800	84	0.0125
	2	0.825	0.800	69	0.0125
	3	0.825	0.807	84	0.0125
	4	0.825	0.790	86	0.0126

(a) Details given in the footnote in Table 5.3

(b) Conductance and Λ^0 data from ref.21

(c) Concentration range and cmc are in mol kg^{-1} for CPC

(d) Experimental cmc.

Table 5.5 Values of Micellization Parameters of SDS in Aqueous Sodium acetate solutions at 25^oC

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}}$ mol dm ⁻³	$\beta \pm 0.002^{\text{a)}}$	$n \pm 2^{\text{a)}}$	$10^3 \times$ std.dev.
<u>$m^{\text{b)}} = 0.0071$</u>				
1	6.02	0.709	60	0.0096
	5.81	0.704	60	0.0110
2	5.98	0.702	60	0.0095
	5.81	0.697	60	0.0105
3	6.36	0.711	54	0.0084
	5.81	0.702	60	0.0108
4	5.97	0.589	10	0.0092
	5.81	0.574	48	0.0097
<u>$m = 0.0135$</u>				
1	4.70	0.724	83	0.0027
	4.68	0.723	82	0.0028
2	4.68	0.717	83	0.0024

Table 5.5 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}} / \text{mol dm}^{-3}$	$\beta \pm 0.002^{\text{a)}} /$	$n \pm 2^{\text{a)}} /$	$10^3 \times \text{Std.dev.}$
<u>$m = 0.0135$</u>				
3	4.68	0.722	84	0.0025
4	4.75	0.625	18	0.0057
	4.68	0.630	22	0.0074
<u>$m = 0.0275$</u>				
1	3.19	0.701	65	0.0032
	3.14	0.699	63	0.0034
2	3.20	0.697	66	0.0033
	3.14	0.694	63	0.0034
3	3.20	0.700	66	0.0032
	3.14	0.699	67	0.0034
4	3.14	0.610	10	0.0036

Table 5.5 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}} / \text{mol dm}^{-3}$	$\beta \pm 0.002^{\text{a)}} / \text{mol dm}^{-3}$	$n \pm 2^{\text{a)}} / \text{mol dm}^{-3}$	$10^3 \times \text{Std.dev.}$
<u>m = 0.0548</u>				
1	2.07	0.674	56	0.0027
	2.11	0.674	53	0.0029
2	2.02	0.670	58	0.0025
	2.11	0.672	55	0.0030
3	2.01	0.671	58	0.0025
	2.11	0.673	53	0.0029
4	2.00	0.616	12	0.0026
	2.11	0.616	11	0.0033
<u>m = 0.1014</u>				
1	1.54	0.628	61	0.0033
	1.56	0.628	61	0.0034
2	1.49	0.622	61	0.0032
	1.56	0.623	64	0.0034

Table 5.5 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}} / \beta \pm 0.002^{\text{a)}} \quad n \pm 2^{\text{a)}} \quad 10^3 \times$			
	mol dm^{-3}			Std.dev.
<u>$m = 0.1014$</u>				
3	1.49	0.624	62	0.0032
	1.56	0.623	68	0.0034
4	1.47	0.590	10	0.0032
	1.56	0.590	9	0.0035
<u>$m = 0.1522$</u>				
1	1.20	0.554	66	0.0072
	0.98	0.555	61	0.0089
2	1.20	0.545	66	0.0070
	0.98	0.546	62	0.0086
3	1.30	0.553	67	0.0068
	0.98	0.553	61	0.0087
4	1.30	0.578	10	0.0067
	0.98	0.567	10	0.0084

Table 5.5 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a})}$ mol dm ⁻³	$\beta \pm 0.002^{\text{a})}$	$n \pm 2^{\text{a})}$	$10^3 \times$ Std.dev.
<u>m = 0.1833</u>				
1	1.01	0.548	60	0.0035
	0.93	0.544	60	0.0039
2	1.01	0.546	59	0.0035
	0.93	0.543	59	0.0038
3	1.01	0.546	60	0.0035
	0.93	0.543	59	0.0037
4	1.00	0.582	12	0.0035
	0.93	0.582	12	0.0039
<u>m = 0.1934</u>				
1	0.95	0.587	37	0.0021
	1.04	0.590	40	0.0030
2	0.95	0.587	36	0.0021
	1.04	0.590	38	0.0031

Table 5.5 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}} / \beta \pm 0.002^{\text{a)}} \quad n \pm 2^{\text{a)}} \quad 10^3 \times$			
	mol dm^{-3}			Std.dev.
<u>m = 0.1934</u>				
3	0.95	0.587	36	0.0022
	1.04	0.590	39	0.0031
4	0.95	0.578	10	0.0022
	1.04	0.578	10	0.0035
<u>m = 0.2005</u>				
1	1.42	0.300	27	0.0617
	1.22	0.290	25	0.0624
2	1.42	0.290	27	0.0617
	1.22	0.290	25	0.0624
3	1.42	0.230	30	0.0617
	1.22	0.290	25	0.0624
4	1.42	0.190	30	0.0615
	1.22	0.250	25	0.0616

Table 5.5 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}} / \text{mol dm}^{-3}$	$\beta \pm 0.002^{\text{a)}} / \text{mol dm}^{-3}$	$n \pm 2^{\text{a)}} / \text{mol dm}^{-3}$	$10^3 \times \text{Std.dev.}$
<u>$m = 0.2154$</u>				
1	0.89	0.608	27	0.0055
	1.43	0.590	63	0.0127
2	0.89	0.607	25	0.0055
	1.43	0.590	63	0.0129
3	0.89	0.607	28	0.0055
	1.43	0.590	28	0.0128
4	0.89	0.601	15	0.0057
	1.43	0.618	10	0.0129
<u>$m = 0.2271$</u>				
1	1.24	0.569	51	0.0064
	1.55	0.576	56	0.0107
2	1.24	0.569	50	0.0065
	1.55	0.570	55	0.0108
3	1.24	0.565	51	0.0064

Table 5.5 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}} / \beta \pm 0.002^{\text{a)}} \quad n \pm 2^{\text{a)}} \quad 10^3 \times$			
	mol dm^{-3}			Std.dev.
<u>m = 0.2271</u>				
	1.55	0.576	56	0.0107
4	1.24	0.577	35	0.0074
	1.55	0.592	37	0.0117
<u>m = 0.2364</u>				
1	0.74	0.572	38	0.0041
	1.63	0.529	67	0.0154
2	0.74	0.572	38	0.0041
	1.63	0.528	66	0.0155
3	0.74	0.572	38	0.0041
	1.63	0.528	67	0.0154
4	0.74	0.576	10	0.0041
	1.63	0.620	10	0.0155

Table 5.5 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}} /$ mol dm^{-3}	$\beta \pm 0.002^{\text{a)}} /$	$n \pm 2^{\text{a)}} /$	$10^3 \times$ Std.dev.
<u>$m = 0.2539$</u>				
1	0.80	0.600	30	0.0039
	1.70	0.675	73	0.0146
2	0.80	0.600	30	0.0039
	1.70	0.675	73	0.0146
3	0.80	0.600	29	0.0039
	1.70	0.675	73	0.0146
4	0.80	0.600	30	0.0041
	1.70	0.693	10	0.0146
<u>$m = 0.2918$</u>				
1	1.55	0.645	35	0.0132
	2.07	0.683	66	0.0196
2	1.55	0.647	37	0.0132
	2.07	0.680	67	0.0196
3	1.55	0.648	36	0.0132
	2.07	0.680	66	0.0196
4	1.55	0.645	30	0.0133
	2.07	0.683	60	0.0198

Table 5.5 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}$ mol dm ⁻³	$\beta \pm 0.002^{\text{a)}$	$n \pm 2^{\text{a)}$	$10^3 \times$ Std.dev.
		<u>$m = 0.3858$</u>		
1	0.08	0.580	26	0.0077
	3.03	0.850	21	0.0445
2	0.08	0.571	23	0.0072
	3.03	0.850	28	0.0445
3	0.08	0.571	23	0.0072
	3.03	0.850	32	0.0445
4	0.08	0.568	22	0.0072
	3.03	0.850	32	0.0445

(a) Details given in the footnote in Table 5.3

(b) Concentration of sodium acetate solution in mol kg⁻¹

Table 5.6 Values of Micellization Parameters of SDS in Aqueous Sodium Propionate Solution at 25°C

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}} / \text{mol dm}^{-3}$	$\beta \pm 0.002^{\text{a)}} / \text{mol dm}^{-3}$	$n \pm 2^{\text{a)}} / \text{mol dm}^{-3}$	$10^3 \times \text{Std.dev.}$
<u>$m^{\text{b)}} = 0.0049$</u>				
1	6.79	0.740	54	0.0093
	6.90	0.740	54	0.0096
2	6.79	0.731	55	0.0091
	6.90	0.737	54	0.0097
3	6.79	0.733	54	0.0091
	6.90	0.738	54	0.0097
4	6.79	0.633	10	0.0093
	6.90	0.649	10	0.0098
<u>$m = 0.0175$</u>				
1	4.23	0.700	30	0.0070
	4.33	0.700	30	0.0077
2	4.23	0.696	33	0.0068

Table 5.6 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}$ mol dm ⁻³	$\beta \pm 0.002^{\text{a)}$	$n \pm 2^{\text{a)}$	$10^3 \times$ std.dev.
<u>m = 0.0175</u>				
	4.33	0.701	32	0.0077
3	4.23	0.697	32	0.0068
	4.33	0.701	31	0.0077
4	4.23	0.666	26	0.0072
	4.33	0.663	18	0.0080
<u>m = 0.0356</u>				
1	2.99	0.699	31	0.0064
	3.12	0.699	31	0.0071
2	2.99	0.689	31	0.0060
	3.12	0.700	31	0.0072
3	2.99	0.689	31	0.0060
	3.12	0.700	31	0.0071

Table 5.6 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}$ mol dm ⁻³	$\beta \pm 0.002^{\text{a)}$	$n \pm 2^{\text{a)}$	$10^3 \times$ std.dev.
<u>m = 0.0356</u>				
4	2.99	0.680	34	0.0064
	3.12	0.688	30	0.0075
<u>m = 0.0612</u>				
1	2.04	0.673	58	0.0029
	2.11	0.677	54	0.0037
2	2.04	0.672	60	0.0029
	2.11	0.674	55	0.0038
3	2.04	0.673	59	0.0029
	2.11	0.676	52	0.0037

Table 5.6 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}} / \beta \pm 0.002^{\text{a)}} n \pm 2^{\text{a)}}$	$10^3 \times$	std.dev.	
	mol dm^{-3}			
<u>m = 0.0612</u>				
4	2.04	0.624	12	0.0030
	2.11	0.625	10	0.0038
<u>m = 0.0923</u>				
1	1.85	0.620	59	0.0104
	1.68	0.607	56	0.0115
2	1.85	0.616	58	0.0104
	1.68	0.606	55	0.0115
3	1.85	0.616	59	0.0104
	1.68	0.606	56	0.0115
4	1.85	0.600	32	0.0102
	1.68	0.557	10	0.0118

Table 5.6 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}} /$ mol dm^{-3}	$\beta \pm 0.002^{\text{a)}} /$	$n \pm 2^{\text{a)}} /$	$10^3 \times$ std.dev.
<u>m = 0.1512</u>				
1	1.54	0.570	60	0.0063
	1.60	0.570	63	0.0065
2	1.54	0.570	59	0.0063
	1.60	0.570	62	0.0065
3	1.54	0.570	60	0.0063
	1.60	0.570	63	0.0065
4	1.54	0.590	21	0.0063
	1.60	0.581	10	0.0066
<u>m = 0.1749</u>				
1	1.64	0.516	56	0.0070
	1.55	0.523	51	0.0078
2	1.64	0.516	55	0.0070
	1.55	0.522	52	0.0077

Table 5.6 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}$ mol dm ⁻³	$\beta \pm 0.002^{\text{a)}$	$n \pm 2^{\text{a)}$	$10^3 \times$ std.dev.
<u>m = 0.1749</u>				
3	1.64	0.516	56	0.0070
	1.55	0.522	51	0.0077
4	1.64	0.559	27	0.0068
	1.55	0.551	11	0.0078
<u>m = 0.2029</u>				
1	1.86	0.550	53	0.0087
	1.88	0.553	53	0.0087
2	1.86	0.550	52	0.0087
	1.88	0.553	52	0.0087
3	1.86	0.550	53	0.0087
	1.88	0.553	53	0.0087
4	1.86	0.586	19	0.0087
	1.88	0.586	17	0.0087

Table 5.6 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}$	$\beta \pm 0.002^{\text{a)}$	$n \pm 2^{\text{a)}$	$10^3 \times$ std.dev.
	mol dm^{-3}			
<u>$m = 0.2139$</u>				
1	2.14	0.418	51	0.0110
	1.94	0.418	51	0.0116
2	2.14	0.418	51	0.0110
	1.94	0.418	51	0.0116
3	2.14	0.418	51	0.0111
	1.94	0.418	51	0.0117
4	2.14	0.418	51	0.0126
	1.94	0.372	42	0.0106

(a) Details given in the footnote in Table 5.3.

(b) Concentration of Sodium propionate solution in mol kg^{-1} .

Table 5.7 Values of Micellization Parameters of SDS in Aqueous Sodium Chloride Solution at 25° C

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}$ mol dm ⁻³	$\beta \pm 0.002^{\text{a)}$	$n \pm 2^{\text{a)}$	$10^3 \times$ std.dev.
<u>$m^b = 0.055$</u>				
1	3.11	0.579	39	0.0273
	2.06	0.565	59	0.0326
2	3.11	0.579	39	0.0272
	2.06	0.565	59	0.0323
3	3.11	0.579	39	0.0272
	2.06	0.565	59	0.0324
4	3.10	0.520	34	0.0266
	2.06	0.488	30	0.0292
<u>$m = 0.1$</u>				
1	1.77	0.365	67	0.0481
	1.41	0.362	66	0.0499

Table 5.7 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}$	$\beta \pm 0.002^{\text{a)}$	$n \pm 2^{\text{a)}$	$10^3 \times$ std.dev.
	mol dm^{-3}			
<u>m = 0.1</u>				
2	1.77	0.365	67	0.0476
	1.41	0.362	66	0.0496
3	1.77	0.365	67	0.0478
	1.41	0.362	66	0.0497
4	2.70	0.482	25	0.0451
	1.41	0.395	33	0.0469
<u>m = 0.18</u>				
1	4.00	0.539	50	0.0719
	0.91	0.348	36	0.0853
2	4.00	0.561	55	0.0716
	0.91	0.348	36	0.0851
3	4.0	0.561	55	0.0717
	0.91	0.348	36	0.0852

Table 5.7 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}$ mol dm ⁻³	$\beta \pm 0.002^{\text{a)}$	$n \pm 2^{\text{a)}$	$10^3 \times$ std.dev.
<u>m = 0.18</u>				
4	4.0	0.561	40	0.0716
	0.91	0.349	26	0.0826
<u>m = 0.30</u>				
1	2.20	0.296	42	0.1126
	0.62	0.290	31	0.1196
2	2.20	0.296	43	0.1125
	0.62	0.296	31	0.1195
3	2.20	0.296	43	0.1125
	0.62	0.295	31	0.1195
4	2.20	0.295	38	0.1121
	0.62	0.295	31	0.1189

Table 5.7 continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}} /$ mol dm^{-3}	$\beta \pm 0.002^{\text{a)}} /$	$n \pm 2^{\text{a)}} /$	$10^3 \times$ std.dev.
<u>m = 0.4</u>				
1	1.99	0.292	35	0.1205
	0.55	0.289	25	0.1272
2	1.99	0.292	35	0.1205
	0.55	0.289	24	0.1272
3	1.99	0.292	35	0.1205
	0.55	0.289	24	0.1272
4	1.99	0.290	32	0.1201
	0.55	0.280	23	0.1206
<u>m = 0.5</u>				
1	2.05	0.110	22	0.1715
	0.45	0.110	15	0.1772
2	2.05	0.110	23	0.1714
	0.45	0.109	14	0.1771

Table 5.7. continued.

Model	$10^3 \times \text{cmc} \pm 0.01^{\text{a)}$ mol dm ⁻³	$\beta \pm 0.002^{\text{a)}$	$n \pm 2^{\text{a)}$	$10^3 \times$ std.dev.
		<u>m = 0.5</u>		
3	2.05	0.110	23	0.1714
	0.45	0.109	14	0.1771
4	2.05	0.110	23	0.1713
	0.45	0.109	14	0.1765

(a) Details given in the footnote in Table 5.3.

(b) Concentration of NaCl in mol dm⁻³.

APPENDIX 5.1

```

10  REM*ANALYSIS OF COND DATA OF SDS IN WATER BY DHO EQN*
20  DIM X(100),Y(100),AK1(100),YC(100),FC(100),SDEV(100),CN(100),SI(100)
30  DIM AK11(100),AKN1(100),YC11(100),YC12(100),YCI(100),EC1(100),SDEV1(100)
40  DIM P1(100),P2(100),P3(100),P4(100),DLDC0(100),DLDN1(100),DLDN2(100)
50  DIM DLDN3(100),DLDN(100),DLDB1(100),DLDB2(100),DLDB3(100),DLDB(100)
55  DIM DLDC01(100),DLDC02(100),DLDN4(100),DLDB4(100)
60  DELC0=0!
70  DELN=0!
80  DELB=0!
90  AGN=80!
100 CMC=.0081
110 B=.65
120 FOR NI=1 TO 5
130 VIS=.008904
140 DC=78.3
150 T=298!
160 DCT=DC*T
163 ADC=0!
165 BUFFER=0!
167 ELEC=0!
170 AL0=73!
180 AL1=50.1
190 ALS=AL0-AL1
200 R1=1.84E-08
210 R2=4.37E-08
220 ND=28
230 AL2=1.6E-19*96485!*1E+07/(6!*3.1416*VIS*R2)
240 AGN=AGN+DELN
250 CMC=CMC+DELC0
260 B=B+DELB
270 RN=AGN^(1!/3!)*R2
280 SIZE1=R1+R2
290 SIZEN=R1+RN
300 A1=2801000!* .5*AL0/(DCT^1.5*(1!+SQR(.5)))+(41.25*2!/(VIS*DCT^.5))
310 ZM=AGN*(1!-B)
320 ALN=AL2*AGN^(2!/3!)*(1!-B)
330 ALN0=ALN+AL1
340 U=ZM*ALN0
350 V=(ZM+1!)*(ZM*AL1+ALN)
360 Q=U/V
370 AN=2801000!*ZM*Q*ALN0/(DCT^1.5*(1!+SQR(Q)))+(41.25*(ZM+1!)/(VIS*DCT^.5))
380 DUDN=(1!-B)*(ALN0+(2!/3!)*ALN)
390 DVDN=(1!-B)*(2!*ZM*AL1+ALN0+2!*AL2/(3!*AGN^(1!/3!)))
400 DQDN=(V*DUDN-U*DVDN)/V^2!

```

```

410 DANDN1=2801000!*(1!-B)^2!*AL2*AGN^(2!/3!)/DCT^1.5
420 DANDN2=(5!/3!)*Q/(1!+SQR(Q))+AGN*DQDN*(1!+.5*SQR(Q))/(1!+SQR(Q))^2!
430 DANDN3=41.25*(1!-B)/(VIS*DCT^.5)
440 DANDN=DANDN1*DANDN2+DANDN3
450 DUDB=-ZM*AL2*AGN^(2!/3!)-AGN*ALN0
460 DVDB=-(ZM+1!)*(AGN*AL1+AGN^(2!/3!)*AL2)-AGN*(ZM*AL1+ALN)
470 DQDB=(V*DUDB-U*DVDB)/V^2!
480 DANDB1=2801000!*AGN^(5!/3!)*(1!-B)/DCT^1.5
490 DANDB2=(1!-B)*(1!+.5*SQR(Q))*DQDB/(1!+SQR(Q))^2!-2!*Q/(1!+SQR(Q))
500 DANDB3=41.25*AGN/(VIS*DCT^.5)
510 DANDB=DANDB1*DANDB2-DANDB3
520 SUM=0!
525 SUM0=0!
530 SUMC0=0!
540 SUMCN=0!
550 SUMCB=0!
560 SUMN=0!
570 SUMNB=0!
580 SUMB=0!
590 SUMYC=0!
600 SUMYN=0!
610 SUMYB=0!
620 FOR I=1 TO ND
630 READ X(I),Y(I)
640 IF X(I)>CMC THEN 720
650 AK1(I)=1!+3.286E+07*SQR(X(I)+ELEC)*SIZE1
660 YC(I)=AL0-A1*SQR(X(I)+ELEC)/AK1(I)
670 EC(I)=YC(I)*(X(I))/1000!+ADC
680 SDEV(I)=(Y(I)-EC(I))^2!
690 SUM=SUM+SDEV(I)
700 SUM1=SUM
705 SUM0=SUM0+Y(I)
710 GOTO 1400
720 CN(I)=(X(I)-CMC)/AGN
730 REM*MODEL 1,I=CMC*
740 SI(I)=CMC+ELEC
750 DSIDC0=1!
760 DSIDN=0!
770 DSIDB=0!
790 GOTO 1010
800 REM*MODEL 2,I=CMC+0.5N(1-B)(CN)*
810 SI(I)=CMC+.5*AGN*(1-B)*CN(I)+ELEC
820 DSIDC0=1!-.5*(1!-B)
830 DSIDN=0!
840 DSIDB=-.5*AGN*CN(I)

```

```

860 GOTO 1010
870 REM*MODEL 3, I=CMC+0.5N(1-B)(1-B)(CN)*
880 SI(I)=CMC+.5*CN(I)*AGN*(1-B)^2!+ELEC
890 DSIDC0=1!-.5*(1!-B)^2!
900 DSIDN=0!
910 DSIDB=-AGN*CN(I)*(1!-B)
930 GOTO 1010
940 REM*MODEL 4, I=CMC+0.5N(CN)(1-B)(1+N(1-B))*
950 SI(I)=CMC+.5*CN(I)*AGN*(1!-B)*(1!+AGN*(1!-B))+ELEC
960 DSIDC0=1!-.5*(1!-B)*(1!+AGN*(1!-B))
970 DSIDN=.5*AGN*CN(I)*(1!-B)^2!
980 DSIDB=-.5*AGN*CN(I)-AGN^2!*CN(I)*(1!-B)
1010 AK11(I)=1!+3.286E+07*SQR(SI(I))*SIZE1
1020 AKN1(I)=1!+3.286E+07*SQR(SI(I))*SIZEN
1030 YC11(I)=(AL0-A1*SQR(SI(I))/AK11(I))*CMC/X(I)
1040 YC12(I)=(ALN0-AN*SQR(SI(I))/AKN1(I))*ZM*CN(I)/X(I)
1050 YC1(I)=YC11(I)+YC12(I)
1060 EC1(I)=YC1(I)*(X(I))/1000!+ADC
1070 SDEV1(I)=(Y(I)-EC1(I))^2!
1080 SUM1=SUM1+SDEV1(I)
1085 SUM0=SUM0+Y(I)
1090 P1(I)=(3.286E+07*SIZE1*SQR(SI(I))/AK11(I))-1!
1100 P2(I)=(3.286E+07*SIZEN*SQR(SI(I))/AKN1(I))-1!
1110 P3(I)=CMC*A1/(X(I)*AK11(I)*2!*SQR(SI(I)))
1120 P4(I)=ZM*CN(I)*AN/(X(I)*AKN1(I)*2!*SQR(SI(I)))
1130 DLDC01(I)=(YC11(I)/CMC)+DSIDC0*P3(I)*P1(I)-(YC12(I)/(AGN+CN(I)))
1135 DLDC02(I)=P4(I)*DSIDC0*P2(I)
1140 DLDC0(I)=DLDC01(I)+DLDC02(I)
1145 DLDN1(I)=P3(I)*DSIDN*P1(I)
1150 DLDN2(I)=(ZM*CN(I)/X(I))*(2!*ALN/(3!*AGN)-SQR(SI(I))*DANDN/AKN1(I))
1160 DLDN3(I)=ZM*CN(I)*AN*3.286E+07*SI(I)*R2/(X(I)*3!*AGN^(2!/3!)*AKN1(I)^2)
1165 DLDN4(I)=P4(I)*DSIDN*P2(I)
1170 DLDN(I)=DLDN1(I)+DLDN2(I)+DLDN3(I)+DLDN4(I)
1180 DLDB1(I)=P3(I)*DSIDB*P1(I)-(YC12(I)/(1!-B))
1190 DLDB2(I)=P4(I)*DSIDB*P2(I)-ZM*CN(I)*AL2*AGN^(2!/3!)/X(I)
1200 DLDB3(I)=ZM*CN(I)*AN*3.286E+07*SI(I)*R2/(X(I)*3!*AGN^(2!/3!)*AKN1(I)^2)
1205 DLDB4(I)=ZM*CN(I)*SQR(SI(I))*DANDB/(X(I)*AKN1(I))
1210 DLDB(I)=DLDB1(I)+DLDB2(I)+DLDB3(I)-DLDB4(I)
1220 SUMC0=SUMC0+DLDC0(I)^2!
1230 SUMCN=SUMCN+DLDC0(I)*DLDN(I)
1240 SUMCB=SUMCB+DLDC0(I)*DLDB(I)
1250 SUMN=SUMN+DLDN(I)^2!
1260 SUMNB=SUMNB+DLDN(I)*DLDB(I)
1270 SUMB=SUMB+DLDB(I)^2!
1280 SUMYC=SUMYC+SQR(SDEV1(I))*DLDC0(I)
1290 SUMYN=SUMYN+SQR(SDEV1(I))*DLDN(I)
1300 SUMYB=SUMYB+SQR(SDEV1(I))*DLDB(I)

```

```

1400 NEXT I
1410 DIN1=SUMC0*(SUMN*SUMB-SUMNB*SUNB)-SUMCN*(SUMCN*SUMB-SUMCB*SUNB)
1415 DIN2=SUMCB*(SUMCN*SUNB-SUMCB*SUN)
1420 DIN=DIN1+DIN2
1425 ANUMC1=SUMYC*(SUMN*SUMB-SUMNB*SUNB)-SUMCN*(SUMYN*SUMB-SUMYB*SUNB)
1430 ANUMC2=SUMCB*(SUMYN*SUNB-SUMYB*SUN)
1435 ANUMC=ANUMC1+ANUMC2
1440 ANUMN1=SUMC0*(SUMYN*SUMB-SUMYB*SUNB)-SUMYC*(SUMCN*SUMB-SUMCB*SUNB)
1445 ANUMN2=SUMCB*(SUMCN*SUNB-SUMCB*SUN)
1450 ANUMN=ANUMN1+ANUMN2
1455 ANUMB1=SUMC0*(SUMN*SUNB-SUMNB*SUN)
1460 ANUMB2=SUMYC*(SUMCN*SUNB-SUMCB*SUN)
1465 ANUMB=ANUMB1+ANUMB2
1470 DELC0=ANUMC/DIN
1480 DELN=ANUMN/DIN
1490 DELB=ANUMB/DIN
1500 SD1=SQR(SUM1/ND)
1502 AY=SUM0/ND
1505 AVD=SD1/AY
1510 PRINT
1520 PRINT "CMC="CMC,"N="AGN,"B="B,"STD.DEV="SD1,"NITER="NI,"AVD="AVD
1530 PRINT
1540 PRINT "DELC0="DELC0,"DELN="DELN,"DELB="DELB,"L0SDS,EXP.="ALS,"L0,CAL="AL2
1550 PRINT
1560 RESTORE
1570 NEXT NI
1572 DATA 0.2400e-02,17.3580e-05,0.3500e-02,25.3370e-05
1574 DATA 0.4100e-02,29.6240e-05,0.5300e-02,38.3180e-05
1576 DATA 0.5940e-02,42.9260e-05,0.6251e-02,45.1020e-05
1580 DATA 0.6552E-02,47.1750E-05,0.6859E-02,49.3100E-05
1590 DATA 0.7155E-02,51.3450E-05,0.7465E-02,53.5280E-05
1600 DATA 0.7578E-02,54.2100E-05,0.7755E-02,55.4890E-05
1610 DATA 0.8041E-02,57.1970E-05,0.8309E-02,58.5500E-05
1620 DATA 0.8589E-02,59.7400E-05,0.8853E-02,60.6610E-05
1630 DATA 0.9126e-02,61.5710e-05,0.9296e-02,61.9100e-05
1640 DATA 0.9385e-02,62.3410e-05,0.9654e-02,63.1570e-05
1650 DATA 0.9895e-02,63.8450e-05,1.0200e-02,64.7080e-05
1660 DATA 1.8420e-02,85.6500e-05,2.2950e-02,97.1500e-05
1670 DATA 4.4140e-02,15.2990e-04,7.1660e-02,22.6990e-04
1680 DATA 9.7250e-02,29.6490e-04,2.4624e-01,73.2330e-04
1790 END

```

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Chapter 6

Computation of Surface Potentials of Ionic Micelles

6.1 INTRODUCTION

In a surfactant solution wherein the surfactant concentration is more than its cmc different regions coexist, viz., a micellar region and a bulk (solution) region separated by an interfacial region. Such systems are therefore also termed as compartmentalized liquids. The micellar phase behaves differently from the solution phase because of interfacial solvent and electrostatic characteristics of micelle.¹ Interfacial solvent characteristic is reflected on the dielectric constant value at the micelle-solution interfacial region. Electrostatic characteristic of a micelle is due to its surface charge. Therefore in order to predict or estimate any change in a particular chemical phenomenon on the micellar surface one needs to know the surface potential of an ionic micelle as well as the dielectric constant of the interfacial region. In this work we focus our interest only on the estimation of surface potential of ionic micelles.

Experimentally surface potential of a micelle is estimated by measuring the pK of a probe, normally an indicator dye, in the micellar solution.¹ Well known spectroscopic methods are available for this purpose.¹⁻³ In the absence of specific molecular interactions and interfacial salt effects, the equilibrium of an indicator at the surface of a charged micelle is affected by the microenvironment it experiences at the micelle surface and by surface potential of the micelle. Therefore, the apparent pK of an indicator residing in the vicinity of a charged interface, pK_{app} , is composed of an electrostatic component due to the surface potential and an inherent interfacial nonelectrostatic component. It is represented by the relation,¹⁻³ (cf. chapter 1)

$$pK_{app} = pK^i - F\psi / (2.303RT) \quad (6.1)$$

where pK^i is the apparent pK of the indicator in the absence of any potential, ψ is the mean surface potential of the micelle, F is the Faraday constant, R the gas constant and T the absolute temperature. pK^i is related either to the pK of the same indicator in a nonionic micellar solution or sometimes to the pK in aqueous medium. Knowing pK_{app} and pK^i , ψ can be estimated

experimentally from eq 6.1.

The other approach to estimate ψ is based on theoretical calculations. In this chapter we have made an attempt to compute by numerical analysis the surface potentials of ionic micelles.

6.2 THEORY

The starting point for the theoretical calculation of micellar surface potentials is the Poisson's equation. Poisson's equation is derived from the Gauss's law.

A sphere of radius r is considered. The electric field, X_r , due to charge in the sphere will be normal to the surface of the sphere and equal everywhere on the surface. The total field over the surface of the sphere will be equal to X_r times the area of the surface, i.e., $X_r 4\pi r^2$. According to Gauss's law, this total field is equal to $4\pi/\epsilon$ times the total charge contained in the sphere, ϵ is the dielectric constant. If ρ_r is the charge density at a distance r from the centre of the sphere, the Gauss's law can be written as

$$X_r 4\pi r^2 = (4\pi/\epsilon) \int_0^r 4\pi r^2 \rho_r dr \quad (6.2)$$

or

$$r^2 X_r = (4\pi/\epsilon) \int_0^r r^2 \rho_r dr \quad (6.3)$$

The integral in eq 6.2 refers to the total charge contained in the sphere. According to the definition of electrostatic potential ψ_r at a point r , we get

$$\psi_r = - \int_{\infty}^r X_r dr \quad \text{or} \quad X_r = -d\psi_r/dr \quad (6.4)$$

Substituting eq.6.3 in eq.6.4, one gets

$$r^2 (d\psi_r/dr) = -(4\pi/\epsilon) \int_0^r r^2 \rho_r dr \quad (6.5)$$

On differentiating both sides with respect to r , eq 6.5 becomes

$$(d/dr) (r^2 d\psi_r/dr) = -(4\pi r^2/\epsilon) \rho_r \quad (6.6)$$

or

$$\nabla^2 \psi_r \equiv d^2 \psi_r / dr^2 + (2/r) d\psi_r / dr = -(4\pi/\epsilon) \rho_r \quad (6.7)$$

Eq 6.7 is known as Poisson's equation for a spherically symmetrical charge distribution.⁴

In order to apply the Poisson's equation to a micellar solution, we consider an ionic micelle of spherical shape. Then ρ_r is the charge density inside an infinitesimally small volume element dv situated at a distance r from the reference micelle. ψ_r is the electrostatic potential due to the micelle in the volume element dv . The excess charge density ρ_r in the volume

element dv is equal to the total ion density times the charge on these ions. If there are per unit volume n_1, n_2, \dots, n_i ions of charge $z_1 e_o, z_2 e_o, \dots, z_i e_o$ respectively, then

$$\rho_r = \sum_i n_i z_i e_o \quad (6.8)$$

z_i is the valency of the ions and e_o is the electronic charge. From Boltzmann distribution law

$$n_i = n_i^o \exp(-z_i e_o \psi_r / k_B T) \quad (6.9)$$

where k_B is the Boltzmann constant.

When there are only two types of ions in the solution, cations and anions of univalence, eq 6.8 becomes

$$\rho_r = n_+^o e_o \exp(-e_o \psi_r / k_B T) - n_-^o e_o \exp(e_o \psi_r / k_B T) \quad (6.10)$$

By substituting eq 6.10 in eq 6.7, we get

$$\nabla^2 \psi_r = (8\pi n_o e_o / \epsilon) \sinh(e_o \psi_r / k_B T) \quad (6.11)$$

where $n_o = n_+^o = n_-^o$

Eq 6.11 is known as the non-linear Poisson-Boltzmann equation in spherical geometry.⁴

It may be noted that in a simple electrolytic solution $z_i e_o \psi_r / k_B T$ is considered to be $\ll 1$ and eq.6.11 takes the form

$$\nabla^2 \psi_r = 8\pi n_o e_o^2 \psi_r / \epsilon k_B T \quad (6.12)$$

which is known as the linearized Poisson-Boltzmann equation

and is employed in Debye-Hückel theory.

6.3 COMPUTATION PROCEDURE

For the computation of surface potentials of micelles the following assumptions were made: (1) The micelles are monodisperse impenetrable spheres of radius a with uniformly distributed surface charge and an average aggregation number denoted by n . (2) The micelle concentration is considered to be infinitely dilute, i.e., for computation purpose the surfactant solution is assumed to consist one micellar species only.^{5,6}

The unmodified non-linearized Poisson-Boltzmann eq 6.11 was used to calculate the surface potentials with boundary conditions

$$\psi_r \longrightarrow 0 \text{ as } r \longrightarrow \infty \quad (6.13)$$

$$\text{and } d\psi_r/dr = -4\pi\rho_r/\epsilon \text{ at } r = a \quad (6.14)$$

We introduced the new variables x and y which are defined as

$$x = (B_0 r)^{-1} \quad (6.15)$$

$$\text{and } y = e\psi_r/k_B T \quad (6.16)$$

where B_0 is given by

$$B_0 = (8\pi n_0 e^2 / \epsilon k_B T)^{1/2} \quad (6.17)$$

Using the new variables x and y , eq.6.11 becomes

$$d^2y / dx^2 = (1/2x^4) (e^y - e^{-y}) \quad (6.18)$$

and the boundary conditions become

$$y = 0 \text{ as } x \longrightarrow 0 \quad (6.19)$$

$$dy/dx = 4\pi\rho_a e_o / \epsilon B_o k_B T x_a^2 \quad (6.20)$$

where $x_a = 1/B_o a$

We wrote a computer program to solve eq 6.18 numerically using the fourth order Runge-Kutta method⁷ for 300 intervals. The computer program developed by us is listed in Appendix 6.1

In the calculation of B_o it was assumed that

$$n_o = n_{cmc} + n_s \quad (6.21)$$

where n_{cmc} is the critical micelle number concentration and n_s is the number concentration of added electrolyte.

The surface charge density of the micelle, ρ_a was calculated using the expression

$$\rho_a = e_o n / 4\pi a^2 \quad (6.22)$$

The radius a of the micelle was determined using the relation

$$a = (3nV/4\pi)^{1/3} \quad (6.23)$$

where V is the volume of the hydrocarbon chain of the surfactant molecule and was determined from⁸

$$V = (27.4 + 29.6 n_c) 10^{-24} \text{ cm}^3 \quad (6.24)$$

where n_c is the number of carbon atoms per hydrocarbon chain.

6.4 RESULTS AND DISCUSSION

Using the computer program which we developed as described above, surface potentials in aqueous medium of (1) dodecyltrimethylammonium bromide (DTAB) in the absence and presence of NaBr, (2) dodecyltrimethylammonium chloride (DTAC) in the absence and presence of NaCl, (3) SDS in the absence and presence of NaCl and (4) of SDS in the presence of pentanol were calculated using reported data on n and cmc of these systems.^{5,9}

To start the calculation it is necessary to supply the initial values of x, y and dy/dx . Although at $r = \infty$, $x = 0$ and $y = 0$, it is observed that starting values of x and y cannot be given as zero because this leads to zero increment in y after every interval. Therefore, it is required to give suitable nonzero starting values for x and y . To select the initial value of x we first made an attempt to use the cell model.^{10,11} According to the cell model of polyelectrolyte solutions, the whole system is treated as an ensemble of equal and independent cells. Each cell consists of a polyion

(micelle) and equivalent amount of coions and counterions so that every cell is electrically neutral. The radius b of each cell is then calculated as

$$b = [3000 n / 4\pi N_A (C_t - cmc)]^{1/3} \quad (6.25)$$

where N_A is the Avogadro number and C_t is the total concentration of the surfactant. x_{cell} is equated to $1/B_o b$. The computer program was then run by choosing the initial values of x, y and dy/dx as

$$\begin{aligned} x_{start} &= x_{cell} \\ y_{start} &= x_{cell} \\ (dy/dx)_{start} &= 1 \end{aligned} \quad (6.26)$$

We however found that x_{cell} value does not provide a suitable x_{start} value since the boundary condition given by eq 6.20 was not fulfilled. Therefore we altered the program so that for an arbitrarily chosen initial x value the first cycle of calculation was done. For every arbitrarily chosen initial x value the initial y value was taken as equal to x ($-x$ in the case of anionic micelles) and $(dy/dx)_{start}$ was taken to be 1.

If the boundary condition was not satisfied in the first cycle, the second cycle of calculation begins with a modified initial x value depending upon the given increment.

It may be noted that in every cycle the numerical solution of eq 6.18 was obtained using fourth-order Runge-Kutta procedure for 300 intervals. The cycle continues till the boundary condition given by eq 6.20 was fulfilled upto <0.001%.

In this fashion we calculated surface potentials of the systems mentioned above. The results of the computation are listed in Tables 6.1-6.4. The x_{start} values listed in Tables 6.1-6.4 correspond to initial values of x which when used in the program give the solution of eq 6.18 in one cycle itself.

From Tables 6.1-6.4 it is apparent that the calculated surface potentials are much higher than the experimental values. This is expected because we have not taken into consideration the counterion binding in the calculation of ψ_r . Due to counterion binding the surface charge on the micelle will become less than $e_0 n$. Therefore eq 6.22 for the surface density needs to be modified. It was modified as suggested by Drummond et al.⁵ to

$$\rho_a = e_0 n (1-\beta) / (4\pi a^2) \quad (6.27)$$

where β is the counterion binding constant. The program was run again by adjusting the value of β such that the

calculated value of ψ_r becomes equal to its experimental value. During this, the values of x_{start} were also found to change. The values of β and the new values of x_{start} are listed in Tables 6.1-6.4. A typical plot of ψ_r versus r is shown in Fig 6.1 for SDS micelle in water. Our results are in complete agreement with the reported results^{5,9} (Tables 6.1-6.4) which therefore shows that the computer program developed by us satisfactorily computes the surface potentials of ionic micelles.

Having tested our computer program we computed the surface potentials for SDS micelles in water as well as in sodium acetate, sodium propionate and sodium chloride solutions using the cmc, n and β data given in chapter 5. The computed surface potentials and x_{start} values are given in Table 6.5. The ψ values listed in Table 6.5 do not appear to show a regular trend with respect to electrolyte concentration. This is due to the fact that the values of n obtained from the conductance data (chapter 5) failed to show a regular variation with electrolyte concentration. However, in the case of SDS + NaCl system excepting $0.055 \text{ mol dm}^{-3}$ NaCl solution the negative potential of SDS micelle decreases with increase in NaCl concentration and

the values of $-\psi$ are about 10 mV less than the reported values.^{9,12,13} ψ of SDS micelle in 0.1 mol dm^{-3} NaCl (-101.25mV) is in very good agreement with the reported value (-101mV).¹³ The negative potential of SDS micelle in CH_3COONa and $\text{C}_2\text{H}_5\text{COONa}$ solutions appear to be less than that in NaCl solution.

The computations of ψ using our program has revealed the following points:(i) x_{cell} value is not a suitable x_{start} value. For SDS in H_2O x_{start} is about 0.06 to 0.08 units less than x_{cell} . In the presence of electrolyte x_{start} is, on the other hand, larger than x_{cell} . The difference in x_{start} and x_{cell} is also a function of β (Tables 6.1-6.4). (ii) The fulfilment of the boundary condition can be monitored fully by varying the initial value of x alone. (iii) $y = x_{\text{start}}$ and $(dy/dx) = 1$ are good starting values for y and (dy/dx) .

Table 6.1 Surface Potentials of Dodecyltrimethylammonium Bromide
Micelles in Aqueous Medium Containing NaBr

cmc+NaBr ^{b)} / mol dm ⁻³	n ^{b)}	a/A ^o	ψ_{cal} /mV	$\psi_{rep}^{b)}$ /mV	$\psi_{exp}^{b)}$ /mV	β	$10^3 x_{start}$	$10^3 x_{cell}$
0.0148 (no NaBr)	53	16.4	172.79	173	118	0.56	403.78 (445.09) ^{a)}	297.077
0.0218	55	16.6	164.24	164	109	0.57	358.18 (392.96)	241.73
0.0401	58	16.9	150.31	150	96	0.58	298.19 (325.15)	175.77
0.718	61	17.2	136.96	137	85	0.59	250.25 (271.99)	128.70
0.1047	63	17.4	128.30	128	83	0.55	222.98 (238.61)	105.44
0.3333	69	17.9	102.34	102	58	0.58	154.40 (165.28)	57.33
0.6667	73	18.3	86.82	87	48	0.57	121.36 (128.23)	39.78
1.0000	76	18.5	78.58	78	44	0.54	104.75 (110.23)	32.04
4.0020	86	19.3	51.57	52	18	0.69	60.44 (64.24)	15.37

a) The values in the parentheses are x_{start} values corresponding to $\beta \neq 0$

b) From ref.5.

Table 6.2 Surface Potentials of Dodecyltrimethylammonium Chloride Micelles
in Aqueous Medium Containing NaCl

$\text{cmc+NaCl}^{b)}/n^{b)}$ mol dm^{-3}	$a/\text{\AA}^{\circ}$	$\psi_{\text{cal}}/\text{mV}$	$\psi_{\text{rep}}^{b)}/\text{mV}$	$\psi_{\text{exp}}^{b)}/\text{mV}$	β	$10^3 x_{\text{start}}$	$10^3 x_{\text{cell}}$	
0.0193	46	15.7	162.47	163	129	0.39	368.07 (406.21) ^{a)}	272.72
0.0269	47	15.8	154.89	155	125	0.37	349.53 (365.16)	229.35
0.0456	50	16.1	143.57	143	118	0.34	297.37 (307.85)	172.56
0.0751	53	16.4	132.78	133	109	0.33	255.20 (263.19)	131.88
0.1076	55	16.6	124.84	124	105	0.29	228.45 (234.13)	108.82
0.3333	61	17.2	99.7	100	85	0.24	159.01 (161.82)	59.73
0.6660	66	17.7	84.93	85	75	0.18	124.57 (126.82)	41.16
1.0000	69	17.9	76.92	77	69	0.15	107.51 (108.48)	33.09
4.0000	80	18.8	50.72	51	47	0.09	61.84 (62.09)	15.75

a) The values in the parentheses are x_{start} values corresponding to $\beta \neq 0$.

b) From ref.5.

Table 6.3 Surface Potentials of Sodium Dodecylsulphate Micelles in Aqueous Medium Containing NaCl

$\text{cmc} + \text{NaCl}^{\text{b)}}$ mol dm^{-3}	$n^{\text{b)}}$	a/A°	$\psi_{\text{cal}}/\text{mV}$	$\psi_{\text{exp}}^{\text{b)}}$ mV	β	$10^3 x_{\text{start}}$	$10^3 x_{\text{cell}}$
0.008 (no NaCl)	64	17.6	-192.03	-141±5	0.54	315.3197 (326.398) ^{a)}	379.7449
0.020	65	17.7	-169.37	-125±5	0.53	274.6576 (285.4101)	238.747
0.025	66	17.8	-164.08	-122±5	0.52	263.9305 (274.2081)	212.45
0.065	70	18.1	-141.08	-110±5	0.45	217.938 (224.887)	122.022
0.102	75	18.6	-131.78	-95±5	0.44	194.455 (200.533)	100.7949
0.202	87	19.5	-118.28	-85±5	0.42	159.4395 (163.933)	68.1675
0.302	101	20.5	-111.39	-73±5	0.48	138.128 (142.812)	53.0455
0.481	129	22.2	-104.96	-67±5	0.49	113.658 (117.21)	38.739

a) The values in the parentheses are x_{start} values corresponding to $\beta \neq 0$

b) From ref.9.

Table 6.4 Surface Potentials of Sodium Dodecylsulphate in Presence of Added Pentanol

Pentanol/ mol dm ⁻³	cmc ^{b)}	n ^{b)}	a/A ⁰	ψ_{cal} /mV	$\psi_{exp}^{b)}$ /mV	β	$10^3 x_{start}$	$10^3 x_{cell}$
0.05	0.005	52	17.8	-189.46	-102±5	0.70	390.4691 (447.408) ^{a)}	514.365
0.10	0.003	32	16.1	-180.25	-83±5	0.72	451.4101 (572.47)	780.694
0.20	0.003	27	16.3	-165.89	-52±5	0.78	456.8601 (653.65)	826.1828
0.27	0.002	26	16.4	-170.90	-37±5	0.86	353.8628 (846.061)	1024.672

a) The values in the parentheses are x_{start} values corresponding to $\beta \neq 0$

b) From ref.9.

Table 6.5 Surface Potentials of SDS Micelles in Aqueous Media Containing Sodium Acetate, Sodium Propionate and Sodium Chloride

$(cmc^{a}) + Elec) /$ $mol\ kg^{-1}$	$n^{a)}$	$\beta^{a)}$	a/A^0	$-\psi_{cal}/mV$	$10^3 x_{start}$	$10^3 x_{cell}$
<u>SDS + H₂O</u>						
0.0081	44	0.700	15.90	93.81	358.4646	427.2661
<u>SDS + CH₃COONa + H₂O</u>						
0.0129	60	0.704	17.63	95.29	321.4515	305.1959
0.0182	82	0.723	19.56	93.96	291.4820	231.7526
0.0306	63	0.694	17.92	82.67	277.9215	194.9103
0.0569	53	0.674	16.91	70.60	255.5429	151.6310
0.1029	61	0.628	17.73	69.68	215.4876	107.4768
0.1532	62	0.546	17.82	72.45	191.6102	87.6383
0.1842	59	0.543	17.53	68.14	185.0942	81.2446
0.1944	40	0.590	15.40	54.66	203.0562	90.0215
0.2017	25	0.290	13.17	70.83	210.5111	103.3722
0.2168	63	0.590	17.92	61.12	176.7971	73.2687
0.2286	56	0.576	17.23	59.51	178.8263	74.2068
0.2380	67	0.529	18.29	67.07	167.6566	68.5097
0.2556	73	0.675	18.82	50.65	167.2981	64.2498
0.2939	66	0.683	18.20	45.84	165.7552	61.9678
0.3888	21	0.850	12.42	15.04	239.6112	78.9112

Table 6.5 Continued

$(\text{cmc}^{\text{a)}} + \text{Elec}) / \text{mol kg}^{-1}$	$n^{\text{a)}$	$\beta^{\text{a)}$	a/A°	$-\psi_{\text{cal}}/\text{mV}$	$10^3 x_{\text{start}}$	$10^3 x_{\text{cell}}$
<u>SDS + C₂H₅COONa + H₂O</u>						
0.0118	54	0.740	17.02	85.04	337.1186	330.6379
0.0218	30	0.700	13.99	67.00	339.8018	295.7036
0.0387	31	0.699	14.15	60.05	310.4008	219.6189
0.0633	54	0.677	17.02	68.63	249.5247	142.7440
0.0940	56	0.607	17.23	72.38	222.6120	115.7475
0.1528	63	0.570	17.92	70.08	192.0731	87.2805
0.2048	53	0.553	16.91	62.96	185.3225	79.8649
0.2158	51	0.418	16.70	74.18	179.7641	78.7957
<u>SDS + NaCl + H₂O^{b)}</u>						
0.0570	59	0.565	17.53	89.19	241.4484	145.9854
0.1014	66	0.362	18.20	101.25	202.4623	105.4882
0.1809	36	0.348	14.87	76.37	200.7628	96.6628
0.3006	25	0.290	13.17	63.31	191.5904	84.6777
0.4005	25	0.289	13.17	58.16	178.1690	73.3584
0.5004	15	0.110	11.10	55.07	186.1085	77.8119

a) The values cmc, n and β taken from chapter 5

b) For this system the values of (cmc + Elec) are in mol dm⁻³

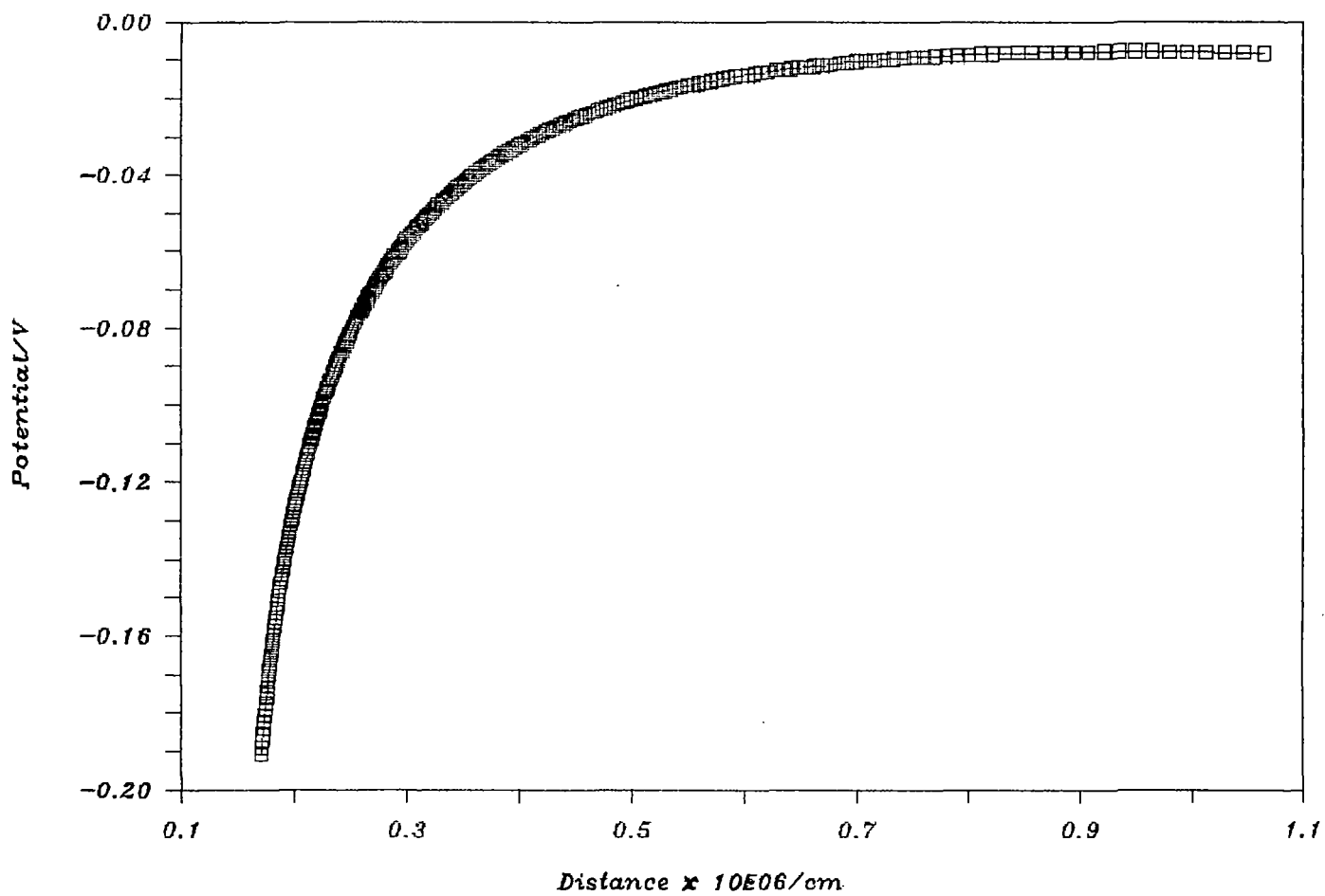


Fig 6.1 Plot of potential due to SDS micelle versus distance from the centre of micelle for $n = 64$, $\text{cmc} = 0.008 \text{ mol dm}^{-3}$, $b = 0$ and $a = 17.6 \text{ \AA}$

APPENDIX 6.1

```

10 REM*calculation of surface potential and plotting*
20 DIM VRT$(16)
30 OPEN "o",#2,"FIL:$1"
40 NS=60
45 VOL=(27.4+29.6*12!)*10^(-24)
50 A=((3!*NS*VOL)/(4!*3.1416))^(1!/3!)
60 C=.0081/1000
70 F=0
80 KAPPA=((8*3.14159*C*6.022E+23*4.8E-10^2)/(78.54*1.38E-16*298))^.5
90 X0=1/(KAPPA*A)
100 Y0= -(NS*(4.8E-10)^2*(1-F))/(78.54*A^2*1.38E-16*298*KAPPA*X0^2)
110 XCELL=1/(KAPPA*(3000*NS/(3.1416*4*(.05-.0148)*6.022E+23))^.33333)
120 X=.3152281493#
130 REM*FOR K = 1 TO 2*
140 X = X + .0000001
150 GOTO 170
160 X=X+.01
170 Y1 = -X
180 H=(X0-X)/300
190 YP = 1
200 J =0
210 DY=0
220 DYP=0
230 FOR I= 1 TO 301
240 J=J+1
250 X1 = X+(J-1)*H
260 Y1 = Y1+DY
270 YP =YP+DYP
280 YG=-YP
290 R1=1/(X1*KAPPA)
300 IF YG>1000 GOTO 160 ELSE 310
310 Y = (Y1*1.38E-16*298/4.8E-10)*300
320 F1=(1/(2*X1^4))*(EXP(Y1)-EXP(-Y1))*H
330 X2=X1+H/2
340 Y2=Y1+YP*H/2+F1*H/8
350 F2=(1/(2*X2^4))*(EXP(Y2)-EXP(-Y2))*H
360 X3=X1+H
370 Y3=Y1+YP*H+F2*H/2
380 F3=(1/(2*X3^4))*(EXP(Y3)-EXP(-Y3))*H
390 DY=H*(YP+(F1+2*F2)/6)
395 DYP =(F1 + 4*F2 +F3)/6
400 PRINT

```

```

410 PRINT R1;Y;YP;KAPPA;XCELL;X0;Y0;A;X
420 IF K=2 THEN PRINT #2,R1,Y
430 NEXT I
440 PRINT I
445 REM*PRINT R1;Y;YP;KAPPA;XCELL;X0;Y0;A;X *
450 REM*NEXT K *
460 CLOSE #2
465 GOTO 810
470 REM*plotting*
480 KEY OFF
490 FOR I= 1 TO 9:READ VRT$(I):NEXT I
500 DATA p,o,t,e,n,t,i,a,l,
510 SCREEN 2
520 INPUT " hor scale";HV:INPUT"vert scale";VV
530 VV = -VV
540 CLS
550 LINE (20,7)-(20,175)
560 LINE -(640,175)
570 FOR I =.007 TO .217 STEP .03
580 LINE (15,808*I)-(20,808*I)
590 NEXT I
600 LOCATE 4,4:PRINT -100
610 LOCATE 7,4:PRINT -120
620 LOCATE 10,4:PRINT -140
630 LOCATE 13,4:PRINT -160
640 LOCATE 16,4:PRINT -180
650 LOCATE 19,4:PRINT -200
660 FOR I=.0000001 TO .0000013 STEP .0000002
670 LINE (I*460000000#,170)-(I*460000000#,175)
680 NEXT I
690 LOCATE 22,11:PRINT TAB(4)10;TAB(16)30;TAB(28)50;TAB(39)70;TAB(50)90;TAB(61)
110;TAB(73)130
700 LOCATE 24,28:PRINT"d i s t a n c e (in Ao)"
710 FOR I= 1 TO 9:LOCATE 5+I,1:PRINT VRT$(I):NEXT I
720 OPEN"i",#2,"fil$1"
730 INPUT #2,R1,Y1
740 INPUT #2,R2,Y2
750 LINE (R1*HV,Y1*VV)-(R2*HV,Y2*VV)
760 INPUT #2,R,Y
770 IF EOF(2) THEN 800
780 LINE -(R*HV,Y*VV)
790 GOTO 760
800 LOCATE 22,1:CLOSE
810 END

```

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PART 2

A Study on the Indicator Equilibria in Microemulsion Media

Chapter 7

A Study on the Acid-Base Behaviour of Methyl Red and Neutral Red in Microemulsions

Publication based on a part of the work of this chapter :

T. K. Barman, B. C. Paul and K. Ismail, Bull. Chem. Soc. Jpn.,
67, 3349 (1994).

7.1 INTRODUCTION

The main objective of this study as already mentioned in chapter 1 (sections 1.13 and 1.14) is to investigate the acid-base behaviour of indicators in microemulsion media. Acid-base behaviour of a chemical system is an important and useful property having relevance in in-vitro and in-vivo processes. Its quantification is necessary as it finds application in chemical, biochemical and industrial works. Microemulsions which behave like compartmentalized liquids have attracted in recent years more attention not only because of their useful industrial applications but also due to the fact that they serve as suitable model systems for biological membranes. Variety of microemulsions can be prepared by the different combinations of surfactant, cosurfactant and oil. In this study benzene-water microemulsions have been used. Surfactants used for stabilizing the microemulsions are SDS and hexadecyl pyridinium chloride (CPC). Butanol and propanol are used as cosurfactants. Methyl red (MR) is the indicator chosen for investigation in this work.

MR exhibits interesting acid-base equilibria due to the presence of two different types of protonation sites, viz., carboxylic acid group and azo group. The acid-base equilibria may be represented as



MR^- , HMR and H_2MR^+ represent deprotonated, singly protonated and doubly protonated species of MR, respectively. Normally azo group gets protonated first followed by the protonation of carboxylic acid group. Reverse order of protonation has also been reported depending upon the medium.¹ The different species involved in the acid-base equilibria of methyl red in pure water are given in Figs. 7.1 and 7.2. The pK values of HMR , $\text{pK}(1)$, and H_2MR^+ , $\text{pK}(2)$, in water are reported to be 5.0 ± 0.1 ^{1,3-7} and 2.25 ± 0.15 ,^{1,4,6} respectively. It is rather difficult to find exactly the two pH values at which 100% HMR with zero percent MR^- and H_2MR^+ and 100% H_2MR^+ with zero per cent MR^- and HMR exist. Estimation of these two

limiting pH values is necessary for the precise evaluation of pK(1) and pK(2). Fortunately, slight variations in the values of these two limiting pH's do not seriously affect the values of pK's of MR.

The spectrophotometric technique has been adopted to study the acid-base equilibria of MR. Spectral behaviour of MR has been studied earlier in water,^{1,3-7} alcohol + water,⁸ dioxane + water,¹ pure nonaqueous media,⁷ and in aqueous micellar solution solutions,^{1,7} The solvent medium affects the acid-base equilibria of MR and also the energy associated with the $\Pi-\Pi^*$ electronic transitions of each of the acid-base forms of MR. Relatively very few studies have been made on the dissociation equilibria of indicators in microemulsion media. Although there is a report on the study of pK of MR in heptane/SDS/butanol/water microemulsion,⁹ a detailed investigation of the acid-base behaviour of MR in microemulsion media has not been done upto now. Therefore, acid - base equilibria of MR has been studied here spectrophotometrically in benzene / SDS /butanol /water, benzene / SDS / propanol / water, and benzene/ CPC /

propanol / water microemulsions of varying compositions. For the purpose of comparison, acid - base equilibrium of neutral red (NR) indicator (Fig.7.3) has also been studied briefly in benzene / SDS / butanol / water and benzene / SDS / propanol / water microemulsions of fixed composition.

7.2 EXPERIMENTAL SECTION

Methyl red (SD fine chemicals) was purified by slow crystallization from distilled toluene solution. Neutral red (CDH, AR grade) was used as supplied.

Acid - base equilibrium of methyl red was investigated using buffer solutions made from sodium acetate (SD fine chemicals, AR grade) and glacial acetic acid (Merck). Buffer solutions of different pH in the range from 3.6 to 6.8 were prepared by mixing appropriate amounts of 0.2 mol dm^{-3} sodium acetate, 0.2 mol dm^{-3} acetic acid and double distilled water according to the standard buffer table,¹⁰ Solutions of pH = 0.9, 2.7, 9.0 and 12.3 were prepared from 0.2 mol dm^{-3} hydrochloric acid (Merck), 0.2 mol dm^{-3} acetic acid, 0.2 mol dm^{-3} sodium acetate and 0.2 mol dm^{-3} sodium hydroxide (Merck) solutions, respectively. Phosphate buffer was used for studying the acid - base equilibrium of neutral red. In this case buffer solutions in the pH range from 6.0 to 8.0 were prepared by mixing 0.1 mol dm^{-3} potassium dihydrogen orthophosphate (Glaxo, AR grade), 0.1 mol dm^{-3} sodium hydroxide and water according to the

ratios given in standard buffer tables.¹¹ Buffer solutions of pH= 9.5 and 10.7 were also prepared from 0.1 mol dm^{-3} KH_2PO_4 and 0.1 mol dm^{-3} NaOH solutions by mixing appropriately adjusted relative volumes of these two solutions with water. Solutions of pH = 1.2, 4.5, and 11.2 were made from 0.1 mol dm^{-3} HCl, 0.1 mol dm^{-3} KH_2PO_4 and 0.1 mol dm^{-3} NaOH solutions, respectively. pH of all the buffers and electrolyte solutions were checked and monitored by a Systronics Model 335 digital pH-meter using calomel and glass electrodes.

Before preparing the microemulsions stock solutions of the indicators of appropriate concentrations were prepared in the alcohol (butanol or propanol) used as cosurfactant. SDS (SISCO, extra pure grade) and CPC (Aldrich) were used directly. Their critical micelle concentrations were determined before use conductometrically as described in chapter 3 and were found to be $8.2 \times 10^{-3} \text{ mol kg}^{-1}$ and $9.2 \times 10^{-4} \text{ mol kg}^{-1}$ for SDS and CPC, respectively. These values of cmc's are in good agreement with the reported values.¹² Benzene (Merck, GR grade),

1-butanol (Merck, synthesis grade) and 1-propanol (Merck, synthesis grade) were also used directly. Microemulsions containing the indicator (MR and NR) were prepared by mixing thoroughly in stoppered sample tubes weighed amounts of benzene, SDS, aqueous buffer or electrolyte solution, cosurfactant and the indicator solution in the cosurfactant. In this manner microemulsions of different compositions were prepared by choosing different weight ratios of the components. The compositions of the microemulsions thus obtained are summarized in Table 7.1. Generally the composition and type of a microemulsion is identified from its R value which is defined as the molar ratio of water to surfactant. R values of the microemulsions prepared are given in Table 7.1. Microemulsions containing CPC were also prepared in a similar fashion. During the preparation of microemulsions it was found that in some cases microemulsions did not form. For example, benzene/ SDS/ butanol or propanol/ aqueous HCl (pH = 0.9) microemulsion of $R = 36$ could not be obtained. All the microemulsions prepared were found to be thermodynamically stable and

optically transparent. Phase diagrams of benzene/SDS/butanol/water and benzene/SDS/propanol/water microemulsions are already known¹³ and the compositions of the microemulsions prepared in the present study fell inside the single isotropic region in their reported¹³ phase diagrams.

The spectroscopic measurements were made using the Hitachi 330 spectrophotometer in the case of SDS stabilized microemulsions with an accuracy of ± 1 nm in wavelength and ± 0.001 unit in absorbance. In the case of CPC stabilized microemulsions the spectra were recorded in a Beckmann DU-650 spectrophotometer having accuracy of ± 0.1 nm in wavelength and ± 0.0001 unit in absorbance. All the spectra were recorded at 25.0°C in 1 cm quartz cells. Spectra were taken within 24 hours after the preparation of each sample. Stable absorbance values were obtained in all the cases except for NaOH containing microemulsions which has been discussed below under the result and discussion section.

Method Of pK Determination: The standard procedure used for the determination of pK of indicators is the spectrophotometric method. This is based on the fact that the acidic and basic forms of indicators mostly have well-separated absorption peaks enabling one to estimate the relative concentrations of the two forms from the absorbance values of the indicator. Writing the thermodynamic equilibrium constant for the acid - base equilibrium (7.1) and then rearranging the expression by using the assumption of ideal behaviour since indicator concentration is usually very low, we get

$$\text{pH} = \text{pK}(1) + \log D \quad (7.3)$$

where $D = [\text{MR}^-]/[\text{HMR}]$. $[\text{MR}^-]$ and $[\text{HMR}]$ correspond to the concentrations of MR^- and HMR , respectively. Eq (7.3) is known as the Henderson-Haselbach equation. Similar equation can also be written for the equilibrium (7.2) or for any other acid - base equilibrium. In terms of the degree of dissociation, α , of HMR , D can be written as

$$D = \alpha / (1 - \alpha) \quad (7.4)$$

Using the Beer-Lamberts' law, D can be related to the

absorbance of the experimental system as

$$D = (A_a - A) / (A - A_b) \quad (7.5)$$

where A_a , A_b and A are the absorbances of the system when it consists only acidic form, only basic form and mixture of the two forms of the indicator, respectively. Thus pK of indicators can be estimated by measuring the absorbances of indicator solutions as a function of pH .

In microemulsions, since pH of the medium cannot be determined precisely, for calculation of pK of indicators pH of the aqueous phase, pH_w , has been generally used. Accordingly pK of indicator in microemulsions obtained by substituting pH_w in eq (7.3) is termed as apparent pK and is denoted by pK_{app} . Eq (7.3) may therefore be written as

$$pH_w = pK_{app} + \log D \quad (7.6)$$

7.3 RESULTS AND DISCUSSION

Spectral behaviour of MR: The visible absorption spectra of MR in the various microemulsions as functions of pH are shown in Figs.7.4-7.17. The characteristics of these spectra are summarized in Tables 7.2-7.4.

From Table 7.2 and the spectra it is apparent that λ_{\max} of MR in microemulsions stabilized by SDS and containing HCl of pH = 0.9 is 519 ± 2 nm and is invariant with R value and is also independent of the 2 cosurfactants used. This value of λ_{\max} is assigned to the electronic transition in H_2MR^+ species and it is in good agreement with the value 517nm reported¹ in aqueous SDS solutions but more by 6 nm than the value in pure water. It may be noted that microemulsions could not be prepared using HCl of pH=0.9 for all the R values (Table 7.2). λ_{\max} of H_2MR^+ has been found to be 517nm even in o/w microemulsion stabilized by CPC (ME13 medium). However, in benzene/CPC/propanol/HCl (pH = 0.9) microemulsions of R = 6 (ME11, w/o region) and R = 36 (ME 12, bicontinuous region) the λ_{\max} values of methyl red are equal to 503nm and 511nm, respectively indicating

thereby either interaction between H_2MR^+ and CPC or absence of second protonation of MR in these two media. Furthermore, same value observed for λ_{max} of H_2MR^+ in media ME10 (benzene/SDS/propanol/HCl (pH = 0.9) of R = 66) and MEO (SDS/Propanol/HCl (pH = 0.9) of R = 66) suggests that presence of oil has no effect on the spectral behaviour of H_2MR^+ . This ascertains that H_2MR^+ species do not reside in the oil domain. From the reported¹ spectra of MR in dioxane-water mixtures it appears that the λ_{max} of H_2MR^+ exhibits slight blue shift due to the increase in the amount of dioxane. The dielectric constant of the medium therefore does not seem to have a strong effect on the λ_{max} of H_2MR^+ . The extinction coefficient, ϵ_e , of H_2MR^+ at the λ_{max} , on the other hand, increases with increase in R value of benzene/SDS/butanol/HCl microemulsion. Replacing butanol by propanol or SDS by CPC causes ϵ_e of H_2MR^+ to decrease. Presence or absence of benzene has no effect on ϵ_e of H_2MR^+ in o/w microemulsion of R = 66. From the above discussion it may be concluded that the H_2MR^+ species reside at the interfacial site between oil and aqueous domains. The

properties of the interfacial site occupied by H_2MR^+ seems to be independent of R. This may be anticipated since R is a parameter that primarily determines the size of the water cores of the droplets.¹³ Oldfield et al¹⁴ also suggested an interfacial location for p-nitrophenol based on its R-independent λ_{max} value in w/o microemulsions stabilized by AOT. The variation in extinction coefficient of H_2MR^+ without any spectral shift described above envisages that the microenvironment of the interface influences the spectral transition of H_2MR^+ .

In the case of HMR, its λ_{max} in the different microemulsions (Table 7.2) studied here is found to be dependent on R but independent of changing the cosurfactant from butanol to propanol. As R is decreased from 66 to 6 (media ME8 - ME1) λ_{max} of HMR undergoes hypsochromic shift from 510 to 495 nm. λ_{max} of HMR is 495 nm in w/o microemulsions, 501 ± 2 nm in the bicontinuous region and is 510 nm in o/w microemulsion. In dioxane-water mixture also similar trend in the λ_{max} of HMR with increase in dioxane amount can be noticed from the reported¹ spectra. As the

amount of dioxane is increased from 0 to 80 weight %, λ_{\max} of HMR shifts from 522 nm to ~492 nm.¹ In water as well as aqueous SDS solutions λ_{\max} of HMR is 522 nm, in aqueous non-ionic surfactant (Brij-35) solutions it is 508 nm and in aqueous n-dodecyltrimethylammonium bromide (DTAB) solutions it is equal to 513 ± 2 nm.¹ In acetonitrile (dielectric constant = 37) methyl red is reported⁷ to have λ_{\max} at 493 nm whereas in benzene (dielectric constant = 2.3) λ_{\max} of methyl red is found to be 484 nm (Fig.7.18). Hence it may be inferred that HMR does not reside completely in the oil domain eventhough methyl red is a hydrophobic indicator. This inference is further ascertained by the fact that in ME0 medium consisting of no oil the λ_{\max} of HMR is 510nm which is equal to that in microemulsions of R = 66. Another point to be noted is that in water and aqueous SDS solutions λ_{\max} of HMR is greater than that of H_2MR^+ .¹ On the other hand, in microemulsion media λ_{\max} of HMR is less than that of H_2MR^+ as is the case in dioxane - water mixtures containing more than 50 weight % dioxane and also in aqueous solutions of Brij-35. The extinction coefficient of HMR in

microemulsions may be presumed to be constant although a mild but irregular dependence on R is noticeable. Cosurfactants seems to affect the extinction coefficient since in microemulsions containing butanol the value of ϵ_e is higher than the value in microemulsions containing propanol. From the above observations it may be thought that HMR is partitioned between the oil domain and the interface. The solvent environment of HMR in the w/o microemulsion of R=6 is similar to that provided by acetonitrile or by about 70 weight % dioxane + water mixture. On the other hand, the solvent environment of HMR in the o/w microemulsion of R=66 is similar to that provided by ~50 weight % dioxane + water mixture or by aqueous Brij-35 solution or by SDS + propanol + acetic acid medium. Since propanol is soluble in water, in the ME0 medium most of the propanol may be present in the aqueous phase. Therefore in ME0 medium HMR may be considered to be partitioned between the micellar interface and the aqueous phase containing propanol. From the spectral behaviour of HMR in o/w and w/o microemulsions it appears that bulk oil phase (dispersing medium) and oil pools do not

provide similar environments as is the case with water pools and bulk aqueous phase.¹⁵ On the basis of the above discussion it may be concluded that in microemulsion medium HMR besides residing at the oil domain and interfacial region is also present in the aqueous domain. If the interfacial region is aqueous-like, then HMR may be confined only to oil domain and interface. In fact, Drummond et al.¹ suggested a aqueous-like interfacial microenvironment in SDS micelles. Thus it may be summarized that HMR is partitioned between the dispersing (oil or water depending on R) as well as the dispersed (consisting of interface and water or oil pool) media.

λ_{max} of MR^- is equal to 413 ± 2 nm as evident from Table 7.2 and Figs.7.4-7.17. The visible spectra of MR^- was obtained by using sodium acetate solution of pH = 9 as the aqueous phase in the microemulsions. We have also taken spectra of methyl red in microemulsions containing NaOH solution of pH = 12.3. In this case a slow increase in absorbance with time was observed. This may be due to the OH^- ion-catalyzed hydrolysis of SDS¹⁶ resulting in

progressive increase in the pH of the system. In the case of CPC, microemulsions do not form with NaOH solution. Accordingly, sodium acetate solution of pH = 9 was preferred for obtaining the spectra of MR^- . However, when microemulsions could not be prepared using sodium acetate solution, NaOH solution was used and the spectra recorded just after the freshly prepared microemulsion were considered. The value of λ_{max} of MR^- in microemulsions is 10 nm less than in water but comparable with the values reported in aqueous SDS and DTAB solutions.¹ In contrast to the case of HMR, the λ_{max} of MR^- is found to be independent of R, cosurfactant and surfactant as is the case with H_2MR^+ also. In dioxane-water mixture λ_{max} of MR^- exhibits blue shift with increase in dioxane content. In MEO medium with no oil and having an aqueous phase containing water and propanol λ_{max} of MR^- is 410nm which is equal to that reported¹ in aqueous solution of Brij-35 (409 nm). It may therefore be inferred that MR^- is partitioned between the aqueous phase and the interfacial region consisting of head groups of surfactant, counterion and interfacial water.

Drummond et al.¹ also concluded on the basis of their spectral investigation of methyl red in aqueous SDS solutions that MR^- solubilizes incompletely into the interfacial phase of the SDS micelles. From the spectral results¹ it is apparent that partitioning of MR^- from water into the micelle-water interfacial region decreases the λ_{max} of MR^- which is attributable to the relatively low dielectric constant at the interface. This blue shift in the λ_{max} of MR^- is comparatively more in the case of nonionic surfactant (423 nm to 409 nm) than in cationic or anionic surfactant (423 to 413 nm \pm 2 nm).¹ It may be commented that MR^- because of its negative charge is not expected to solubilize into the SDS micelle. However, this may not be the situation in reality and MR^- may solubilize into the SDS micelle from the side of the phenyl ring containing $-\text{N}(\text{CH}_3)_2$ group. The extinction coefficient of MR^- also seems to be almost independent of R. However, its value in microemulsion containing butanol (ME1 to ME8) is slightly higher than in microemulsion containing propanol.

A noteworthy feature of the spectra of methyl red in the microemulsion is the absence of a distinct isosbestic wavelength unlike the case in water, organic liquid+water mixture and in aqueous micellar solution. This may be attributed to two factors. (1) As discussed above, dissociation of methyl red involves three species and two acid-base equilibria due to the protonation of azo and carboxylic groups. In media other than microemulsion the two acid-base equilibria of methyl red exist at separated pH regions and hence exhibit two different isosbestic points. In microemulsion a drift in the pH range of acid-base equilibria of methyl red seems to take place. The actual pH at the site of protonation of methyl red may certainly be different from the pH of the aqueous buffer and estimation of the true pH has not been possible. (2) Secondly, the species involved in the acid-base equilibria of methyl red reside at different regions within the microemulsion as discussed above. The different sites of residence of the three species of methyl red may have different solvent properties causing the absence of precise isosbestic points

in microemulsions. Absence of distinct isosbestic points in the spectra of indicator dyes in microemulsions of constant pH but varying R values has been reported by Fletcher¹⁷ and Moulik et al.¹⁸

Acid-Base Behaviour of MR : In order to calculate the pK values of methyl red we have plotted pH_w versus $\log D$ in Figs. 7.19 and 7.20 using the data given in Table 7.3. For calculating D in a particular microemulsion A_a was taken as the absorbance at the minimum pH_w studied in that microemulsion. From the plots of pH_w versus $\log D$ shown in Figs. 7.19 and 7.20 it is obvious that the Henderson-Haselbach eq. 7.6 is not obeyed always. At lower pH_w there is increasing deviation from the linearity. This may be attributed to the fact that within the pH_w range covered in this study both the protonation equilibria (corresponding to the first and second protonation; cf. eqs. 7.1 and 7.2) coexist. However, in the case of media ME4, ME5 and ME7, the pH_w versus $\log D$ plots are linear since we did not cover the pH range from 4.8 to 3.6 and the $\text{pH} = 0.9$ during the spectral measurements of MR in these three media.

In the medium ME6 also the plot of pH versus logD is found to be linear since the spectral study could not be extended upto pH=0.9. In Fig. 7.21 we have shown similar plots in water, aqueous SDS and aqueous CPC solutions based on the reported spectral data for MR.⁷ In water as well as in aqueous CPC solution the plot of pH_w versus logD is linear over the pH_w range from 2.9 to 12. In aqueous SDS solution, however, for the same range of pH_w deviation from linearity has been observed.

In order to ascertain the fact that in the pH_w range from 0.9 to 9.0 both the protonation equilibria of MR exist we plotted absorbance versus pH_w in Figs.7.22 and 7.23. For comparison purpose we have also plotted the reported⁷ data of MR in water, aqueous SDS and aqueous CPC solutions in Fig.7.24. From the shape of these plots it is obvious that the first protonation of MR is completed in the pH_w range from about 4.8 to 4 in the case of microemulsions stabilized by SDS. For microemulsions stabilized by CPC the first protonation of MR seems to be complete in the pH range from about 4 to 3. Moreover, in the case of microemulsion

stabilized by CPC the shape of the absorbance versus pH_w curve below $\text{pH}_w \approx 4$ changes with change in R. For R=6 and 36 the curves are similar whereas for R=66 the shape of the curve is different. From these plots it appears that in benzene/CPC/propanol/water microemulsions of R=6 and 36 the second protonation of MR does not take place even upto pH_w 0.9. We have already commented above while discussing the λ_{max} of H_2MR^+ on the different behaviour of MR in these two microemulsions.

From the above type of plots of absorbance versus pH_w the pH near the completion of first protonation (which will be termed as pH_1) and also the absorbance corresponding to 100% HMR (which will be denoted by A_{al}) may be estimated. For this purpose, the region in the curve (below $\text{pH}_w \approx 5$) where absorbance becomes almost constant has been considered as the region of 100% first protonation. In those curves where absorbance does not become constant, (ME8 and ME13 media) the pH_w at which inflexion (in the pH_w range ≈ 5 to 4) occurs after the sharp increase in absorbance while moving from high pH_w to low pH_w side

has been chosen as the pH_w corresponding to 100% first protonation. Fujii et al.¹⁹ also employed a similar method for estimating from the absorbance versus pH plot the absorbance of 100% basic form of phenol red in phosphate buffer solutions. Once pH_w 's corresponding to 100% first protonation of MR are identified in the above fashion, absorbances corresponding to 100% HMR, A_{al} , can be known and hence values of D were calculated from the relation $(A_{al} - A) / (A - A_b)$ at different pH_w . By least squares fitting these data to eq 7.6 values of $pK_{app}(1)$ were computed. Using the values of $pK_{app}(1)$ thus obtained we made a second attempt to estimate more accurate values of pH_1 and A_{al} . This method is based on the fact that $pK_{app}(1)$ is equal to the pH_w at $D=1$ as apparent from eq 7.6. D becomes 1 when $A = (A_{al} + A_b) / 2$. Therefore the value of $pK_{app}(1)$ obtained above from the least squares fit is equated to pH_w and the absorbance at this value of pH_w was noted from the absorbance versus pH_w plots. Let this absorbance value be A_1 and it is equal to $(A_{al} + A_b) / 2$. Since A_b is the absorbance of 100% MR^- (absorbance at the

highest pH_w studied) which can be known with very less uncertainty, A_{al} is calculated as equal to $(2A_1 - A_b)$. Again from the pH_w versus absorbance plot the second but better value of pH_1 can be estimated as the pH_w corresponding to $A_{al} = (2A_1 - A_b)$. Using this second value of A_{al} , a new set of data for $\log D$ as a function of pH_w can be obtained which on least squares fitting to eq 7.6 provides a better value for $\text{pK}_{app}(1)$. The process may be continued to get consistent values of $\text{pK}_{app}(1)$. The values of $\text{pK}_{app}(1)$ and pH_1 obtained in this fashion are given in Table 7.5. Since the values of pH_1 , A_1 and A_{al} are obtained from the graphs (Figs 7.22 and 7.23) the error limits of the values of $\text{pK}_{app}(1)$ and pH_1 have been found to be nearly ± 0.05 and ± 0.1 , respectively. In fact, for all those systems which exhibited deviation from linearity in the plot of pH_w versus $\log D$, we replotted pH_w versus $\log D$ in the pH range from pH_1 to highest pH and very good linear plots were obtained. These plots are however not illustrated here.

From Table 7.5 it may be noted that the slope obtained by least-squares fitting pH_w and $\log D$ data to eq

7.6 is not equal to 1. Therefore, Henderson-Haselbach equation is not applicable to microemulsions in the true sense. Polyelectrolytes and dyes in microemulsion media most often exhibit such a behaviour and a modified Henderson-Haselbach equation of the form

$$\text{pH}_w = \text{pK}_{\text{app}} + n \log D \quad (7.7)$$

has been proposed by some workers.²⁰⁻²³ In the present case also eq (7.7) is applicable instead of eq (7.6) as evident from the values of n listed in Table 7.5. A similar observation was also made by Moulik et al.¹⁸ for neutral red in microemulsions stabilized by AOT. From the values of n obtained in the present study (Table 7.5) it is apparent that variation of n with R does not follow a regular trend. The values of n are found to be less as well as more than 1. Physical meaning of such value of n could not be obtained. However $n \neq 1$ is attributable to the fact that in a microemulsion the species involved in an acid-base equilibrium reside at different regions having dissimilar solvent properties.

Dependence of $pK_{app}(l)$ On R : For an acid-base equilibrium between species which do not undergo partitioning in a microemulsion and are confined to the aqueous domain Oldfield et al.¹⁴ suggested an empirical correlation between pK_{app} and R. It is of the form

$$pK_{app}(aq) = pK_0 - s_1/R^{1/2} \quad (7.8)$$

where pK_0 is the value of pK in pure water and s_1 is a constant. 'aq' indicates that the species are in the aqueous domain only.

For species which partition between the aqueous domain and the interfacial region in a microemulsion, another empirical relation was proposed by Oldfield et al.¹⁴ and is of the form

$$pK_{app} = pK_{app}(aq) - s_2 - \log R \quad (7.9)$$

s_2 is an empirical constant and $pK_{app}(aq)$ is given by eq (7.8). The empirical eq (7.9) was found to be applicable in the range $R > 15$ for p-nitrophenol in microemulsion stabilized by AOT.¹⁴ Moulik et al.¹⁸ also made attempts to correlate pK_{app} of neutral red in microemulsions stabilized by AOT to various functional forms of R and found that the

correlations suggested by Oldfield et al.¹⁴ are not applicable. Moulik et al.,¹⁸ on the other hand, reported that their data were explainable by the equation.

$$pK_{app} = pK_{AOT} + s_3 R \quad (7.10)$$

where pK_{AOT} is the pK_{app} of the indicator in excess AOT without water and s_3 is an empirical constant. However the upper limit of R values in the work of Moulik et al.¹⁸ is ~40.

In the present study the variation of $pK_{app}(1)$ of MR in benzene/SDS/butanol/water microemulsion with R has been shown in Fig.7.25. The dependence of $pK_{app}(1)$ on R is complex. A minimum exists in the plot of $pK_{app}(1)$ versus R around $R = 10$ and a maximum occurs around $R = 50$. The dependence of pK_{app} of p-nitrophenol in heptane/AOT/buffer microemulsion on R also seems to be of complex nature¹⁴ and the plot of pK_{app} versus R exhibits a maximum around $R = 10$. In the present case also the dependence of $pK_{app}(1)$ on R in the range from $R = 10$ to $R = 40$ appears to be linear as reported by Moulik et al.¹⁸ for neutral red in microemulsions containing AOT. In the case of MR in benzene /SDS /butanol /water microemulsion it

appears that $pK_{app}(1)$ decreases with increase in R in the w/o region, increases with increase in R in the bicontinuous phase region and again decreases with increase in R in the o/w region. At the minimum in the plot of $pK_{app}(1)$ versus R a change-over from w/o to bicontinuous region and at the maximum a change-over from bicontinuous to o/w region seems to take place. The dependence of $pK_{app}(1)$ on R observed by us is also different from the type of dependence reported for MR in heptane/ SDS/ butanol/ water microemulsion by Guo and Zhu.⁹ However, in the o/w region Guo and Zhu⁹ reported decrease in $pK_{app}(1)$ with increase in R which is in accordance with our observation. We also plotted $pK_{app}(1)$ versus $1/R$ in Fig.7.25 since it enables us to extrapolate the plot to $1/R = 0$ which is equivalent to water medium. It is interesting to see that $pK_{app}(1)$ in the region of high R values (o/w region) on extrapolation to $1/R = 0$ gives $pK_{app}(1) = 5.0$ which is in good agreement with the $pK(1)$ of MR in pure water.

$pK_{app}(1)$ of MR is dependent on both the

cosurfactant and surfactant systems used. Changing butanol by propanol decreases $pK_{app}^1(1)$. Same trend is observed on changing SDS by CPC.

The value of $pK_{app}^1(1)$ in a microemulsion may be considered to be controlled by three factors, viz., dielectric constant at the site of equilibrium, surface potential at the interfacial region and the partition coefficients of the acidic and basic forms of the indicator which determines the extent of their partitioning in the different regions of the microemulsion. Dependence of $pK_{app}^1(1)$ on dielectric constant and surface potential is often expressed as (cf. eq 1.34)

$$pK_{app}^1(1) = pK^i(1) - F\psi / (2.303RT) \quad (7.11)$$

The dependence of $pK_{app}^1(1)$ on dielectric constant is contained in the $pK^i(1)$ term, known as the intrinsic $pK(1)$. Dielectric constant of microemulsion may be expected to be less than that of water. From the calibration curves of $pK_{app}^1(1)$ versus dielectric constant reported by Drummond et al.¹ and using the range of $pK_{app}^1(1)$ values of MR obtained in the present work (Table 7.5), the dielectric constant of the

microemulsions used here may be roughly estimated to be in the range 40 to 50. $pK^i(1)$ of methyl red increases with decrease in dielectric constant.¹ Surface potentials of surfactants in microemulsion media required for estimating the second term of eq 7.11 are not known. However, $F\psi/(2.303RT)$ becomes -2.37 if we presume ψ to be -140mV, the value for ψ of SDS in aqueous medium.¹ Oldfield et al.¹⁴ made the attempt to correlate pK_{app} of indicator in microemulsion to the partition coefficient, K_p . For p-nitrophenol in heptane/AOT/water medium by considering partitioning of only acidic form Oldfield et al.¹ derived the expression

$$pK_{app} = pK_{app}^0(aq) + \log(1 + 1/K_p) \quad (7.12)$$

where $pK_{app}^0(aq)$ is pK_{app} of p-nitrophenol when all the species are in aqueous phase and K_p is the ratio of concentration of acidic form in the interfacial region to that in aqueous phase. Similar expression can also be written for $pK_{app}(1)$ of methyl red. Oldfield et al.¹ attributed the dependence of pK_{app} on R to the variation of K_p with R. However, to check the validity of expressions of

the form given in eq 7.12 data on K_p of indicators in microemulsion are required which are lacking now.

Second Protonation of MR : Absorbance corresponding to 100% H_2MR^+ in microemulsion is required for the estimation of $pK_{app}(2)$. Due to lack of sufficient data points values of $pK_{app}(2)$ could not be estimated. However, an attempt has been made to calculate $pK_{app}(2)$ in two o/w microemulsions, namely benzene/ SDS/ butanol/ water and benzene/SDS/propanol/water of R=66 by considering presence of 100% H_2MR^+ at pH = 0.9 and using modified Henderson-Haselbach eq 7.7 for $pK_{app}(2)$. Plots of pH_w versus $\log D$ for these two cases are shown in Fig.7.25 and the values of $pK_{app}(2)$ obtained by least squares fitting are listed in Table 7.5. These two values of $pK_{app}(2)$ of MR in o/w microemulsion is comparable to the $pK(2)$ value reported¹ in water(2.09). In fact, in dioxane-water mixtures also the values of $pK(2)$ were reported¹ to be almost independent of dioxane content. In aqueous Brij-35 solution the value of $pK(2)$ is about 1.1 and in aqueous DTAB solution also $pK(2)$ has lower value than in water.¹ On the other hand, in aqueous

SDS solutions $pK(2)$ is found to have a value which is twice the value in water.¹ It therefore appears that in o/w microemulsion second protonation of MR probably takes place at the oil/interface region rather than at the water/interface region.

Spectral Behaviours of NR : It has been reported²⁴⁻²⁶ that in pure water the spectra of neutral red as a function of pH do not exhibit a clear isosbestic point. To account for this Bartels²⁷ proposed that neutral red undergoes two acid-base equilibria with pK values of 7.38 and 5.89. Drummond et al.²⁴ however obtained well-defined isosbestic points for neutral red in dioxane-water mixtures as well as in aqueous micellar solutions and ruled out the possibility of two acid-base equilibria for neutral red. Moulik et al.¹⁸ studied the spectra of NR in w/o microemulsions stabilized by AOT and the presence of two acid-base equilibria for NR was not found.

The spectra of NR in benzene/SDS/butanol/water and benzene/SDS/propanol/water microemulsions of $R=66$ (o/w) are shown in Figs.7.26 and 7.27. Although very distinct

isosbestic point is not obtained for NR in the present work which is generally the case in microemulsions, there is no indication of two acid-base equilibria for NR. However, in comparison with the spectra of MR the spectra of neutral red have more clear isosbestic points. The shape of the plots of absorbance versus pH_w for NR (Fig.7.24) also confirms the absence of two acid-base equilibria for NR in the two o/w microemulsion media and in the pH range from 1.2 to 11.2. The shape of the spectra of NR in the two o/w microemulsions is similar. λ_{max} of the acidic form (HNR^+) of neutral red has been found to be 541 nm which is comparable with the λ_{max} value of 539 nm reported²⁴ in aqueous SDS but about 10 nm higher than the value in water. In aqueous non-ionic surfactants also λ_{max} of HNR^+ was reported to be 541 nm. The basic form (NR) of neutral red has a λ_{max} value of 459 nm. This value is higher (by 12 nm) than the λ_{max} value in water.²⁴ The λ_{max} of NR reported²⁴ in aqueous nonionic surfactants and SDS solutions is less by about 4 nm only than the present value. Moulik et al.¹⁸ reported 538 nm for λ_{max} of HNR^+ and 456 to 458 nm for λ_{max} of NR in water and

in w/o microemulsions stabilized by AOT. They did not find any effect of cosurfactant on λ_{\max} values as has been observed in the present study also. The extinction coefficients of HNR^+ and NR in the two o/w microemulsions are given in Table 7.4. On the basis of the above spectral features of neutral red the dye molecules may be considered to reside at the interfacial region.

The $\text{pK}_{\text{app}}(1)$ of NR has been calculated by least-squares fitting the pH_w dependent values of $\log D$ to eq 7.7. Values of D were calculated using absorbance data given in Table 7.6. The linear plots of $\log D$ versus pH_w are illustrated in Fig.7.21. The values obtained for $\text{pK}_{\text{app}}(1)$ of NR are 7.05 and 6.92 (Table 7.5) in benzene/SDS/butanol/water and benzene/SDS/propanol/water microemulsions, respectively. Compared to the value in water (6.5) reported by Drummond et al.²⁴ the present values are higher. On the other hand in comparison to the value in water (~7.4) reported by other workers^{18,27} the present values in the two o/w microemulsions are lower. Values of the present work for $\text{pK}_{\text{app}}(1)$ of NR are lower by nearly 2

units than the value in aqueous SDS solution,¹⁴ lower by about 0.6 unit than the value in decane/ AOT/water microemulsions and about 1.2 units higher than the value in aqueous nonionic surfactant solutions. The solvent environment experienced by neutral red in both the microemulsions used here appears to have the property midway between that exhibited by charged and uncharged interfacial regions.

Table 7.1 Composition of the different microemulsion media used for the spectrophotometric measurement.

R	ϕ_w / ϕ_s	ϕ_s / ϕ_{CS}	ϕ_w	ϕ_o	Medium
S = SDS, CS = Butanol, O = Benzene					
6	0.3750	0.5	0.05	0.55	ME1
10	0.6095	0.5	0.1625	0.0375	ME2
16	1.0000	0.5	0.2	0.2	ME3
24	1.505	0.6667	0.2857	0.2381	ME4
32	2.000	0.5	0.3	0.25	ME5
36	2.2505	0.5	0.3	0.3	ME6
48	3.010	0.333	0.3158	0.2631	ME7
66	4.126	0.5	0.55	0.05	ME8
S = SDS, CS = Propanol, O = Benzene					
36	2.2505	0.5	0.3	0.3	ME9
66	4.126	0.5	0.55	0.05	ME10
66	4.126	0.5	0.579	0.0	ME0
S = CPC, CS = Propanol, O = Benzene					
6	0.3750	0.5	0.05	0.55	ME11
36	2.2505	0.5	0.3	0.3	ME12
66	4.126	0.5	0.55	0.05	ME13

Table 7.2 λ_{\max} values of the visible absorption spectra of methyl red and neutral red in different microemulsion media of varying pH at 25°C.

pH of aq. phase	λ_{\max} (nm) in different media ^{a)}				
	ME1 R = 6 [In] ^{b)} = 1.3	ME2 R = 10 [In] = 1.7	ME3 R = 16 [In] = 1.7	ME 4 R = 24 [In] = 2.5	ME5 R = 32 [In] = 2.7
<u>In : Methyl Red</u>					
0.9	519	519	520	-	-
2.7	495	503	502	502	502
3.6	495	503	501	500	500
4.0	495	503	501	500	500
4.4	495	503	501	500	500
4.8	495	503	501	500	500
5.2	495	503	501	500	500
5.6	490	500	501	500	500
6.0	420	412	420	500	500
6.4	417	412	413	420	500
6.6	-	-	-	415	415
6.8	415	412	413	-	-
9.0	415	412	413	414	415

Table 7.2 continued

pH of aq. phase	λ_{\max} (nm) in different media ^{a)}				
	ME6 R=36 [In] ^{b)} =1.7	ME7 R=48 [In]=2.8	ME8 R=66 [In]=2.7	ME9 R=36 [In]=2.2	ME10 R=66 [In]=2.9
<u>In : Methyl Red</u>					
0.9	-	-	519	-	517
2.7	502	501	510	501	510
3.6	500	498	510	500	510
4.0	500	498	510	500	510
4.4	500	498	510	500	510
4.8	500	498	510	500	510
5.2	500	498	510	500	510
5.6	500	498	510	500	510
6.0	500	498	510	500	510
6.4	495	498	510	414	414
6.6	-	495	-	-	-
6.8	493	-	413	414	414
9.0	415	-	413	414	414
12.3	-	413	-	-	-

Table 7.2 continued

λ_{max} (nm) in different media^{a)}

pH of aq. -----

phase	ME0	ME11	ME12	ME13
	R=66	R=6	R=36	R=66
	[In] ^{b)} = 2.9	[In] = 2.6	[In] = 2.6	[In] = 4.8

In : Methyl Red

0.9	517	503	511	517
2.7	510	499	501	509
3.6	510	497	500	507
4.0	510	497	500	507
4.4	510	497	500	507
4.8	510	492	500	507
5.2	510	419	494	425
5.6	510	416	420	415
6.0	505	413	414	415
6.4	-	413	414	415
6.8	410	413	414	415
9.0	410	412	413	414

Table 7.2 continued

λ_{max} (nm) in different media ^{a)}		
pH of aq. phase	ME8 R=66 [In] ^{b)} =5.8	ME10 R=66 [In]=3.4
<u>In : Neutral Red</u>		
1.2	541	541
4.5	541	541
6.0	540	540
6.4	540	540
6.8	540	540
7.2	540	460
7.6	460	460
8.0	460	460
9.5	460	460
10.7	460	460
11.2	459	459

a) Details of media given in Table 7.1

b) Indicator concentration in 10^5 mol kg^{-1}

Table 7.3 Absorbance of Methyl Red^{a)} as a Function of pH in
Microemulsions of Different R at 25^oC

Absorbance ± 0.001				
pH	ME1 R=6 $\lambda=519\text{nm}$	ME2 R=10 $\lambda=519\text{nm}$	ME3 R=16 $\lambda=520\text{nm}$	ME4 R=24 $\lambda=502\text{nm}$
<u>Water/SDS/Butanol/Benzene</u>				
0.9	0.618	0.852	0.875	-
2.7	0.379	0.586	0.589	0.827
3.6	0.382	0.578	0.517	-
4.0	0.376	0.575	0.577	-
4.4	0.362	0.551	0.566	-
4.8	0.342	0.516	0.556	-
5.2	0.300	0.432	0.495	0.741
5.6	0.238	0.288	0.402	0.649
6.0	0.160	0.143	0.249	0.499
6.4	0.112	0.069	0.127	0.327
6.6	-	-	-	0.218
6.8	0.083	0.031	0.064	-
9.0	0.052	0.014	0.029	0.104

Table 7.3 continued

Absorbance ± 0.001				
pH	ME5 R=32 $\lambda=502\text{nm}$	ME6 R=36 $\lambda=502\text{nm}$	ME7 R=48 $\lambda=502\text{nm}$	ME8 R=66 $\lambda=519\text{nm}$
<u>Water/SDS/Butanol/Benzene</u>				
0.9	-	-	-	1.484
2.7	0.857	0.662	0.900	1.143
3.6	-	0.682	-	1.074
4.0	-	0.697	-	1.060
4.4	-	0.661	-	1.045
4.8	-	0.657	-	1.025
5.2	0.787	0.648	0.836	0.998
5.6	0.719	0.623	0.793	0.919
6.0	0.602	0.556	0.678	0.780
6.4	0.460	0.445	0.582	0.552
6.6	0.357	-	0.452	-
6.8	-	0.327	-	0.367
9.0	0.175	0.115	0.045 ^{b)}	0.083

Table 7.3 continued

Absorbance ± 0.001			
pH	ME9 R=36 $\lambda=501\text{nm}$	ME10 R=66 $\lambda=513\text{nm}$	ME0 ^{c)} R=66 $\lambda=517\text{nm}$
<u>Water/SDS/Propanol/Benzene</u>			
0.9	-	1.118	1.122
2.7	0.593	0.921	0.882
3.6	0.556	0.864	0.876
4.0	0.567	0.862	0.873
4.4	0.556	0.848	0.870
4.8	0.548	0.847	0.837
5.2	0.534	0.801	0.792
5.6	0.485	0.694	0.672
6.0	0.299	0.474	0.423
6.4	0.157	0.204	-
6.8	0.054	0.070	0.043
9.0	0.046	0.093	0.028

Table 7.3 continued

Absorbance ± 0.0001			
pH	ME11 R=6 $\lambda=500\text{nm}$	ME12 R=36 $\lambda=500\text{nm}$	ME13 R=66 $\lambda=510\text{nm}$
<u>Water/CPC/Propanol/Benzene</u>			
0.9	0.6125	0.6928	1.6622
2.7	0.6334	0.6632	1.3703
3.6	0.5830	0.6330	1.2701
4.0	0.5573	0.6194	1.2126
4.4	0.4730	0.5734	1.0779
4.8	0.3714	0.5083	0.8618
5.2	0.2563	0.3889	0.5923
5.6	0.1644	0.2503	0.3801
6.0	0.1150	0.1537	0.2335
6.4	0.1085	0.1169	0.1656
6.8	0.0875	0.0822	0.1342
9.0	0.0751	0.0680	0.1034

a) Concentration of methyl red are given in Table 7.2

b) at pH = 12.3

c) without benzene

Table 7.4 Values of extinction coefficient (ϵ_e) and λ_{\max} (given in parentheses) for the different species involved in the acid-base equilibria of methyl red and neutral red in microemulsion media at 25°C
 $\left[(\epsilon_e \pm 0.1) \times 10^4 / \text{kg mol}^{-1} \text{cm}^{-1}, \lambda_{\max} \pm 1 / \text{nm} \right]$

Media ^{a)}	Species				
	MR ⁻	HMR	H ₂ MR ⁺	NR	HNR ⁺
			b)		
ME1	2.4 (415)	3.6 (495)	4.5 (519)	-	-
ME2	2.3 (412)	3.6 (503)	4.8 (520)	-	-
ME3	2.5 (413)	3.8 (502)	5.0 (520)	-	-
ME4	2.0 (414)	3.2 (502)	-	-	-
ME5	1.9 (415)	3.2 (502)	-	-	-
ME6	2.3 (415)	3.7 (502)	-	-	-
ME7	1.9 (413)	3.2 (501)	-	-	-
ME8	2.3 (413)	3.9 (510)	5.3 (519)	1.3 (459)	2.7 (541)

Table 7.4 continued

Media ^{a)}	Species				
	MR ⁻	HMR	H ₂ MR ⁺	NR	HNR ⁺
ME9	1.7 (414)	2.4 (501)	-	-	-
ME10	1.7 (414)	2.8 (510)	3.8 (517)	1.4 (459)	3.0 (541)
ME0	1.8 (410)	3.0 (510)	3.8 (517)	-	-
ME11	1.7 (412)	2.4 (499)	-	-	-
ME12	1.7 (413)	2.5 (501)	-	-	-
ME13	1.9 (414)	2.8 (509)	3.5 (517)	-	-

a) Details given in Table 7.1

Table 7.5 Values of $pK_{app}^{(1)}$ for methyl red and neutral red in the various microemulsion media at 25°C. Values of $pK_{app}^{(2)}$ for methyl red in two microemulsions are given within the parentheses

Medium ^{a)}	$pK_{app}^{(1)}$ ± 0.05	$n^{b)}$	corr. coeff.	$pH_1^{c)}$ ± 0.1
<u>Methyl Red</u>				
ME1	5.75	1.023	0.999	4.2
ME2	5.57	0.839	0.999	4.1
ME3	5.85	0.820	0.998	4.3
ME4	6.12	0.976	0.997	4.8
ME5	6.38	1.135	0.999	5.3
ME6	6.57	0.849	0.998	4.2
ME7	6.60	1.234	0.994	3.4
ME8	6.41	0.958	0.999	4.2
	(1.93)	(1.436)	(0.999)	
ME9	6.01	0.485	0.992	3.6
ME10	5.96	0.621	0.997	4.4
	(2.08)	(1.397)	(0.978)	
ME0	5.98	0.827	0.997	4.0

Table 7.5 continued

Medium ^{a)}	$pK_{app}^{(1)}$ ± 0.05	$n^{b)}$	corr. coeff.	$pH_1^{c)}$ ± 0.1
<u>Methyl Red</u>				
ME11	4.84	1.178	0.996	3.0
ME12	5.34	0.915	0.997	3.6
ME13	5.16	1.003	0.997	4.0
<u>Neutral Red</u>				
ME8	7.05	0.952	0.998	1.0
ME10	6.92	0.865	0.999	3.0

a) Details of the medium are given in Table 7.1

b) Slope of eq 7.7

c) Limiting pH at which first protonation of the indicator is complete

Table 7.6 Absorbance of Neutral Red^{a)} as a Function of pH in water/SDS/Butanol/Benzene (ME8) and water/ SDS/ Propanol/Benzene (ME10) Microemulsions at 25°C

pH	Absorbance ± 0.001	
	ME8, R=66 $\lambda = 541 \text{ nm}$	ME10, R=66 $\lambda = 541 \text{ nm}$
1.2	1.595	1.015
4.5	1.569	1.006
6.0	1.442	0.917
6.4	1.337	0.808
6.8	1.099	0.625
7.2	0.721	0.350
7.6	0.387	0.186
8.0	0.219	0.109
9.5	0.095	0.069
10.7	0.086	0.061
11.2	0.085	0.059

a) Concentrations of neutral red given in Table 7.2

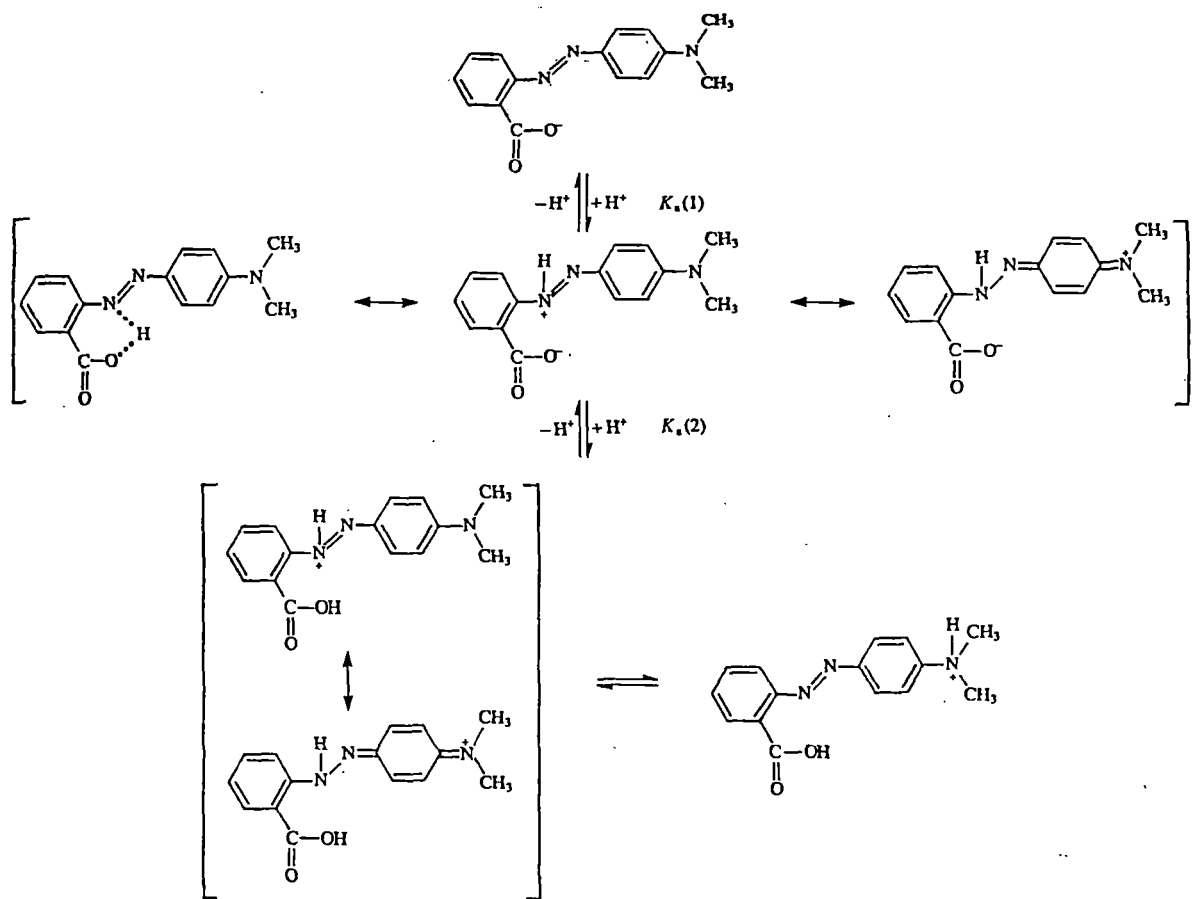


Fig 7.1 Species considered to be involved in the acid-base equilibria of methyl red in pure water, a 20 wt % 1,4-dioxane-water mixture and aqueous micellar SDS solutions. (From ref.1).

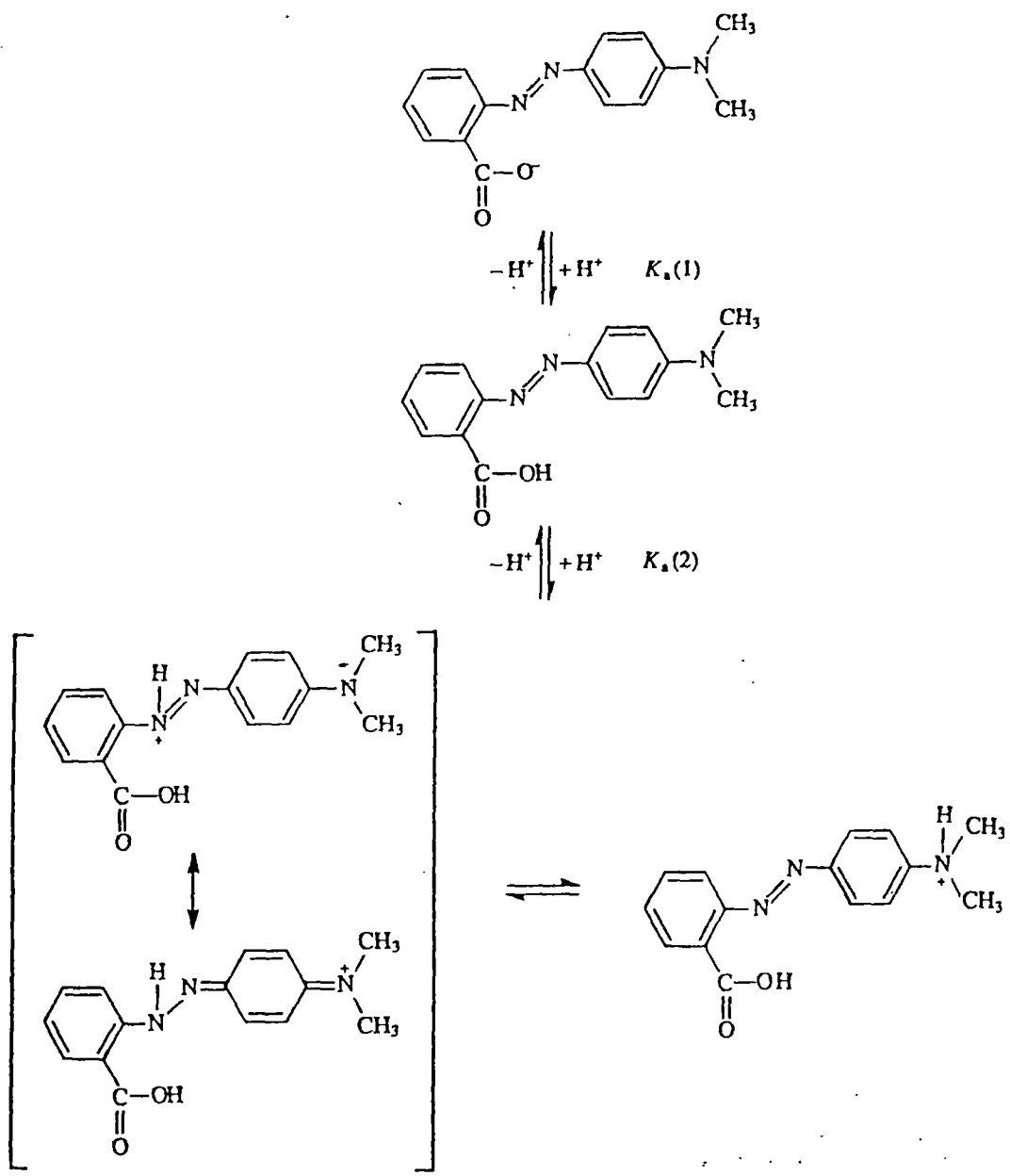


Fig 7.2 Species considered to be involved in the acid-base equilibria of methyl red in 40, 60 and 80 wt % 1,4-dioxane-water mixtures and aqueous micellar Brij-35 and DTAB solutions. (From ref. 1)

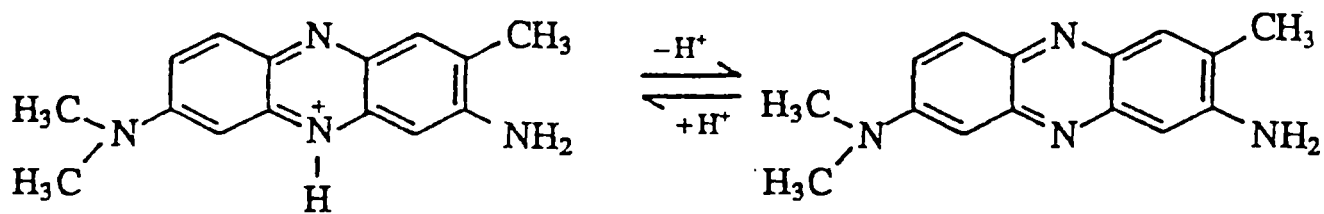


Fig 7.3 Acid-base equilibrium of Neutral Red (from ref.24).

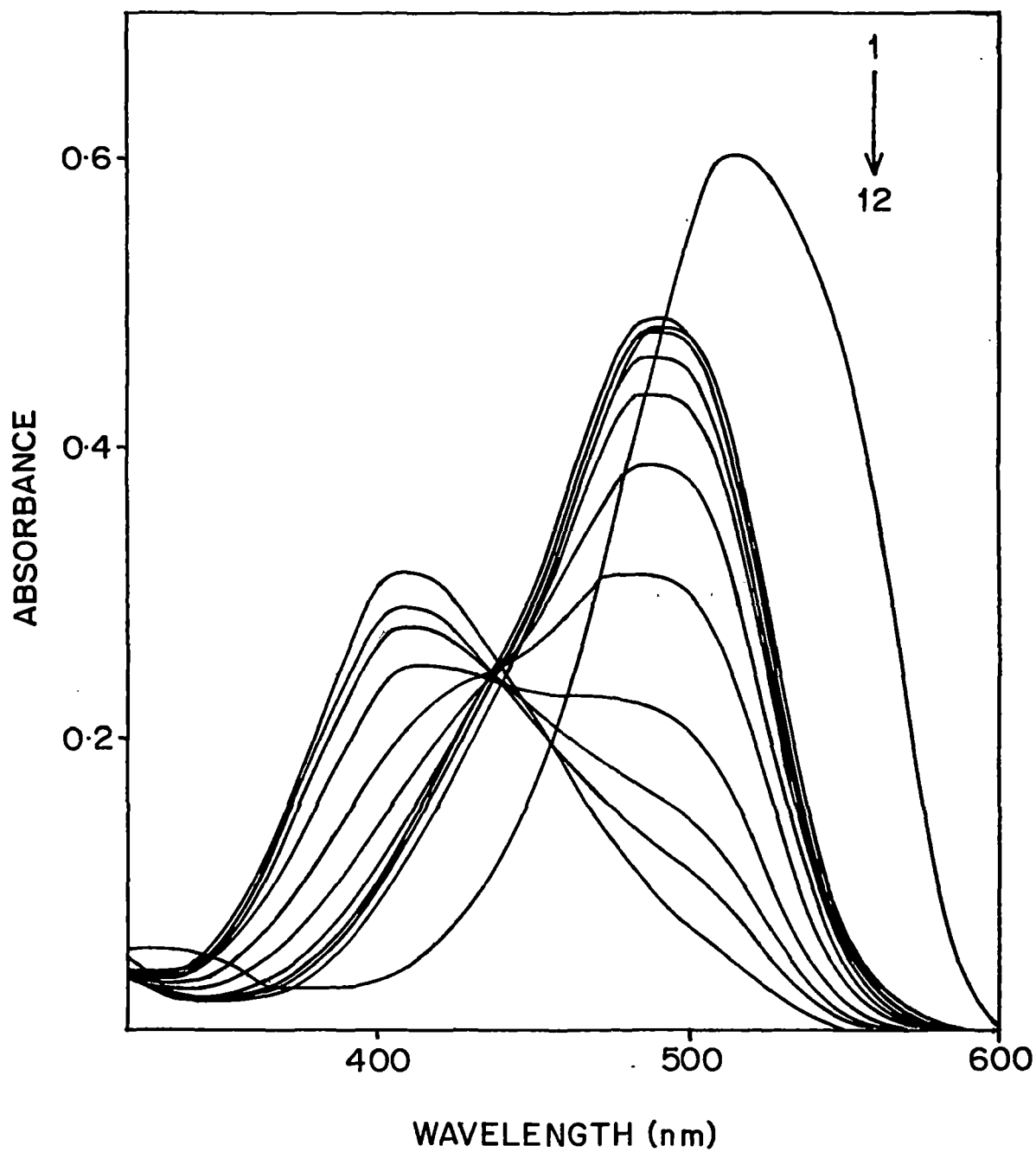


Fig 7.4 Absorption spectra of Methyl Red at 25°C in benzene/SDS/butanol/water with R = 6 (ME1). Spectra 1 to 12 correspond to pH = 0.9, 3.6, 2.7, 4.0, 4.4, 4.8, 5.2, 5.6, 6.0, 6.4, 6.8 and 9.0, respectively. (Concentration of MR = 1.3×10^{-5} mol kg⁻¹).

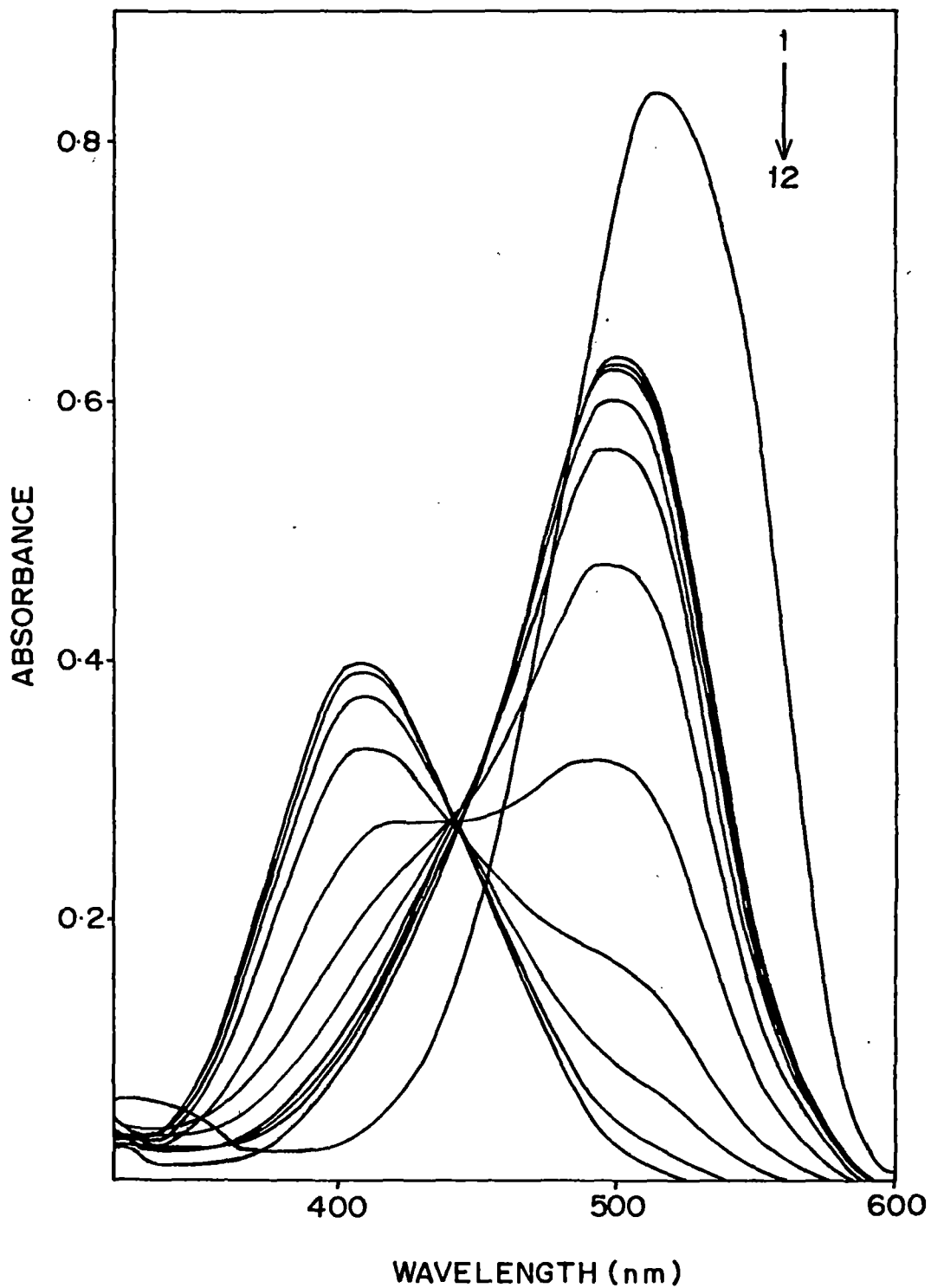


Fig 7.5 Absorption spectra of Methyl Red at 25°C in benzene/SDS/butanol/water with R = 10 (ME2). Spectra 1 to 12 correspond to pH = 0.9, 2.7, 3.6, 4.0, 4.4, 4.8, 5.2, 5.6, 6.0, 6.4, 6.8 and 9.0, respectively. (Concentration of MR = 1.7×10^{-5} mol kg⁻¹).

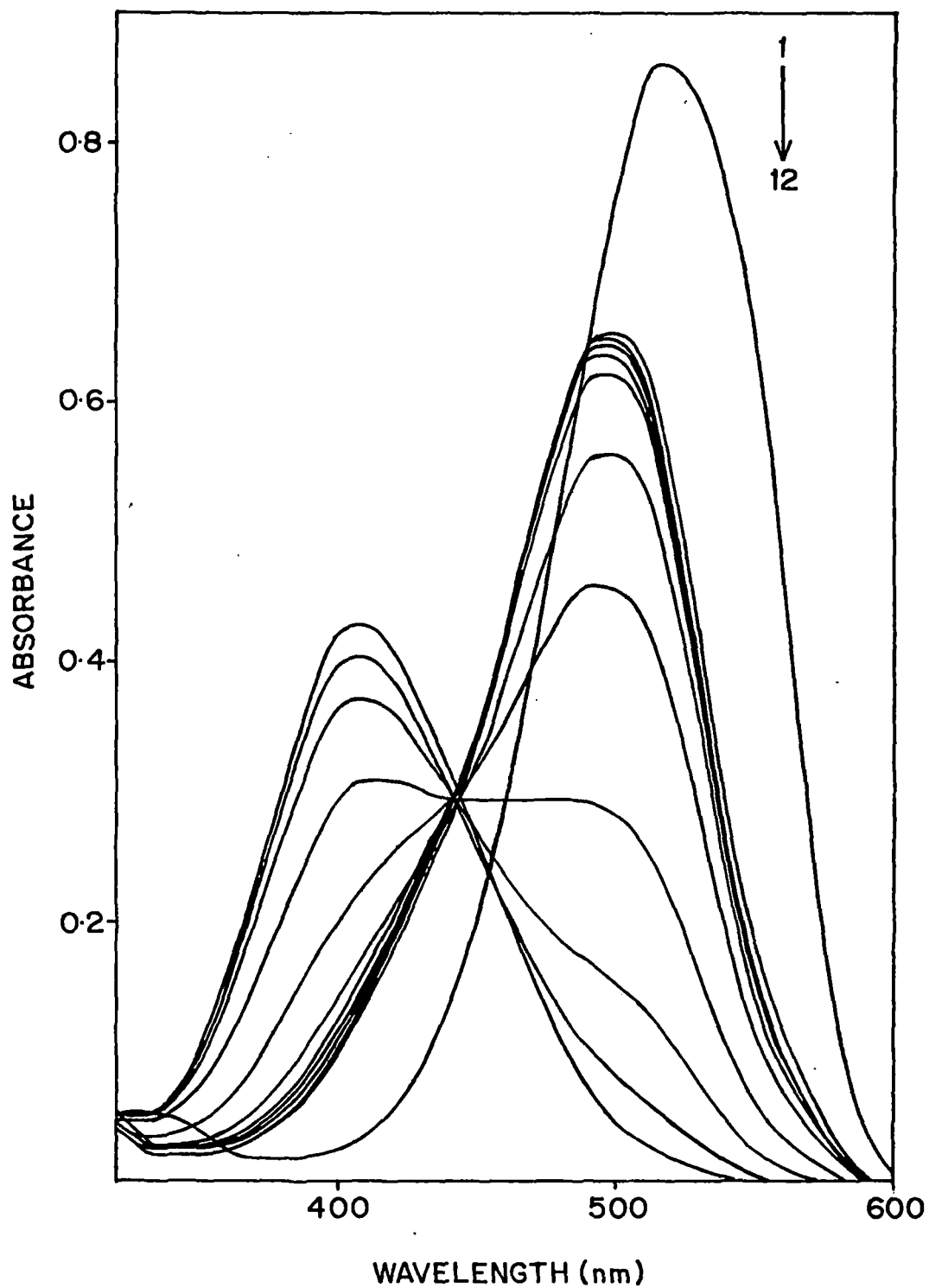


Fig 7.6 Absorption spectra of Methyl Red at 25°C in benzene/SDS/butanol/water with $R = 16$ (ME3). Spectra 1 to 12 correspond to pH = 0.9, 2.7, 4.0, 4.4, 4.8, 3.6, 5.2, 5.6, 6.0, 6.4, 6.8 and 9.0, respectively. (Concentration of MR = 1.7×10^{-5} mol kg⁻¹).

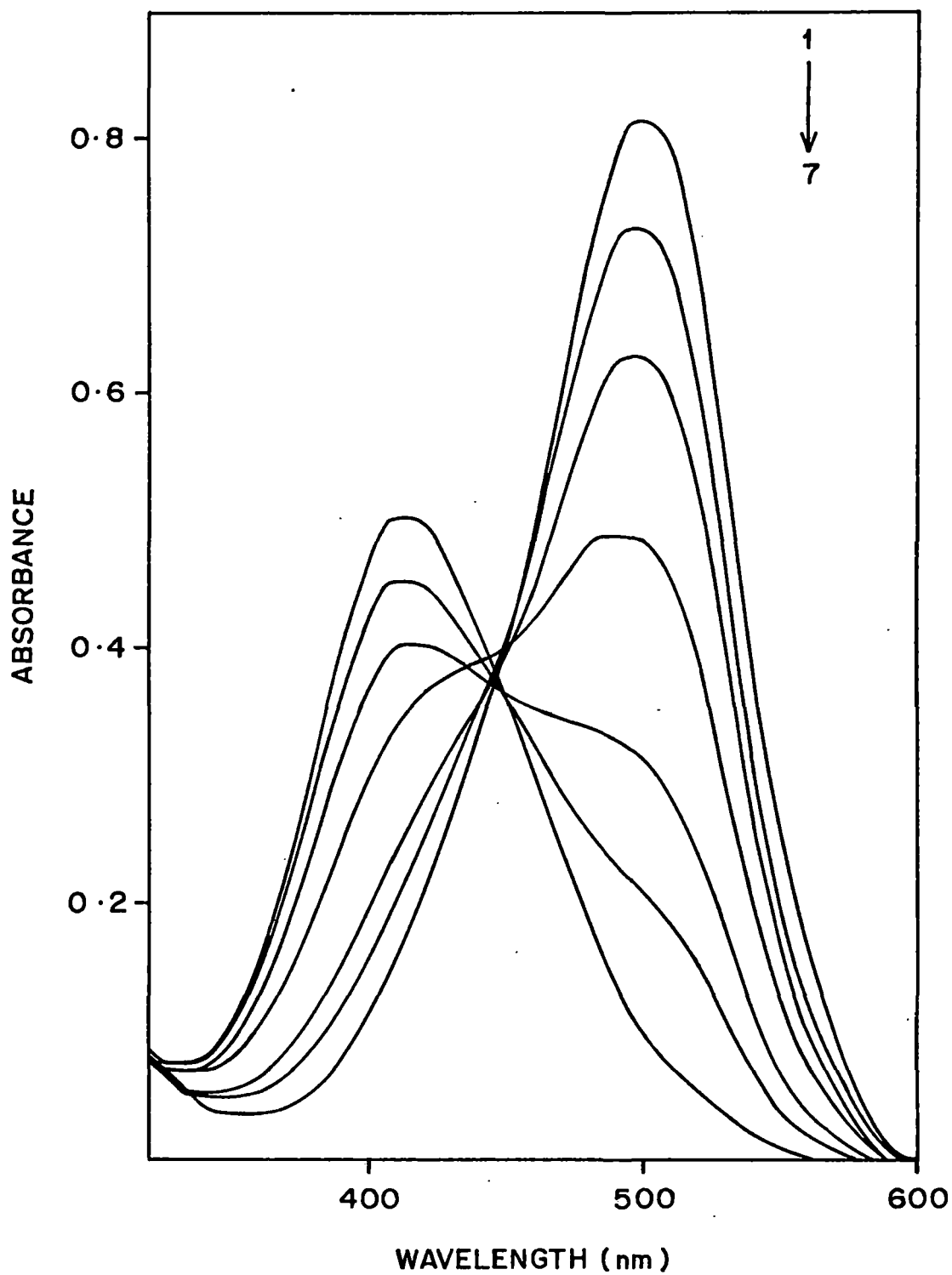


Fig 7.7 Absorption spectra of Methyl Red at 25°C in benzene/SDS/butanol/water with $R = 24$ (ME4). Spectra 1 to 7 correspond to pH = 2.7, 5.2, 5.6, 6.0, 6.4, 6.6 and 9.0 respectively. (Concentration of MR = 2.5×10^{-5} mol kg⁻¹).

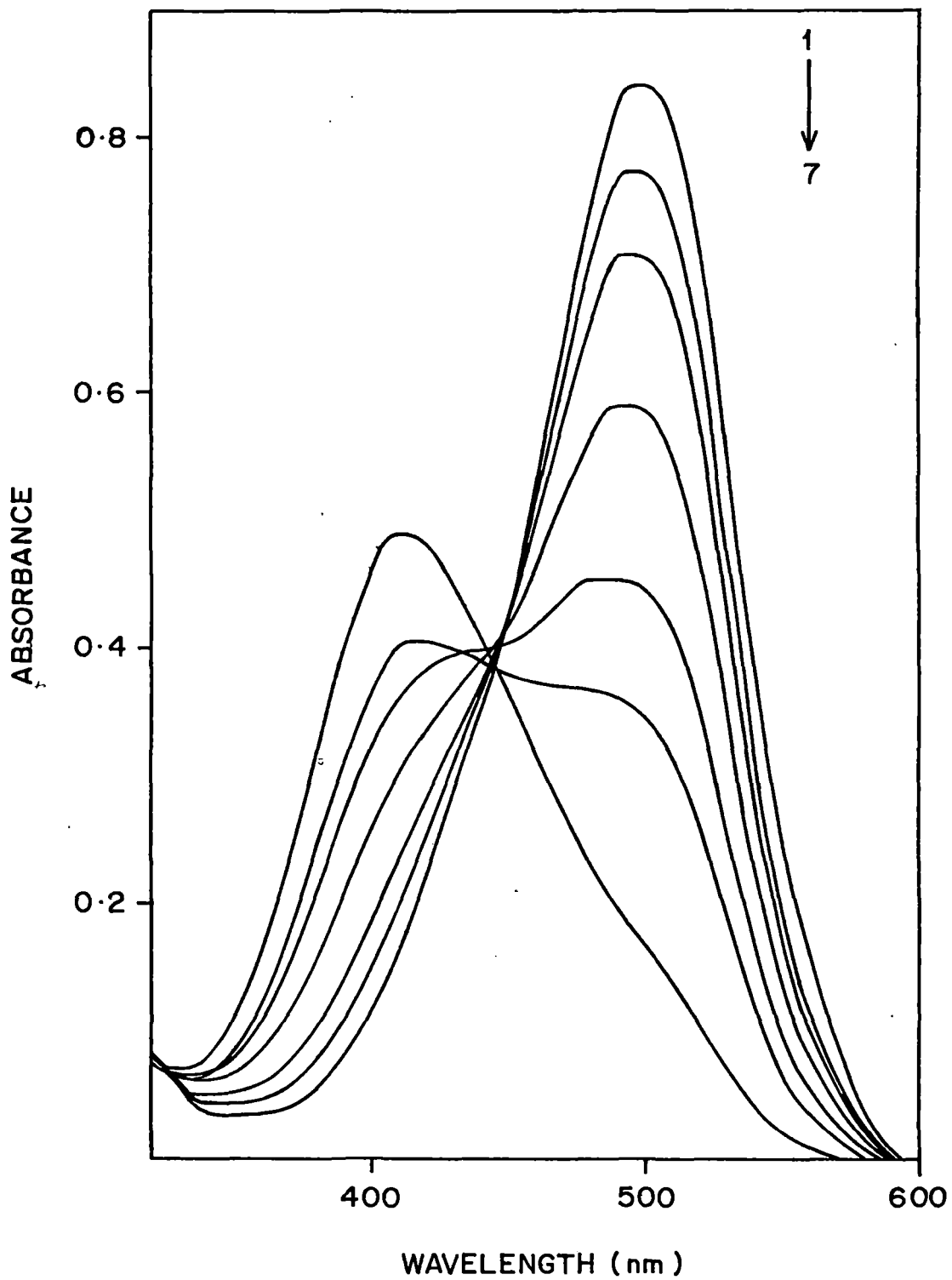


Fig 7.8 Absorption spectra of Methyl Red at 25°C in benzene/SDS/butanol/water with $R = 32$ (ME5). Spectra 1 to 7 correspond to pH = 2.7, 5.2, 5.6, 6.0, 6.4, 6.6 and 9.0, respectively. (Concentration of MR = 2.7×10^{-5} mol kg⁻¹).

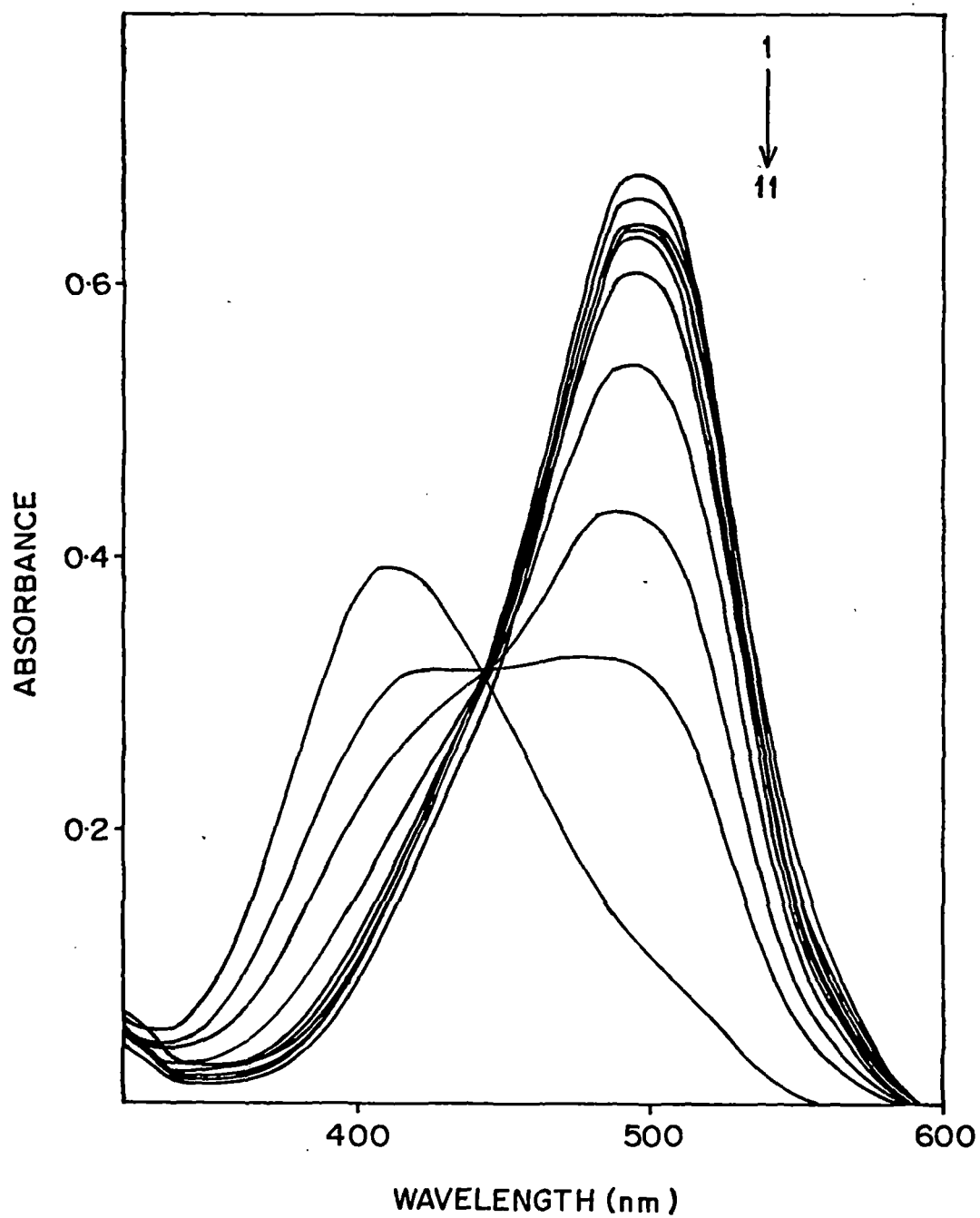


Fig 7.9 Absorption spectra of Methyl Red at 25°C in benzene/SDS/butanol/water with R=36 (ME6). Spectra 1 to 11 correspond to pH = 4.0, 3.6, 2.7, 4.4, 4.8, 5.2, 5.6, 6.0, 6.4, 6.8 and 9.0, respectively. (Concentration of MR = 1.7×10^{-5} mol kg⁻¹).

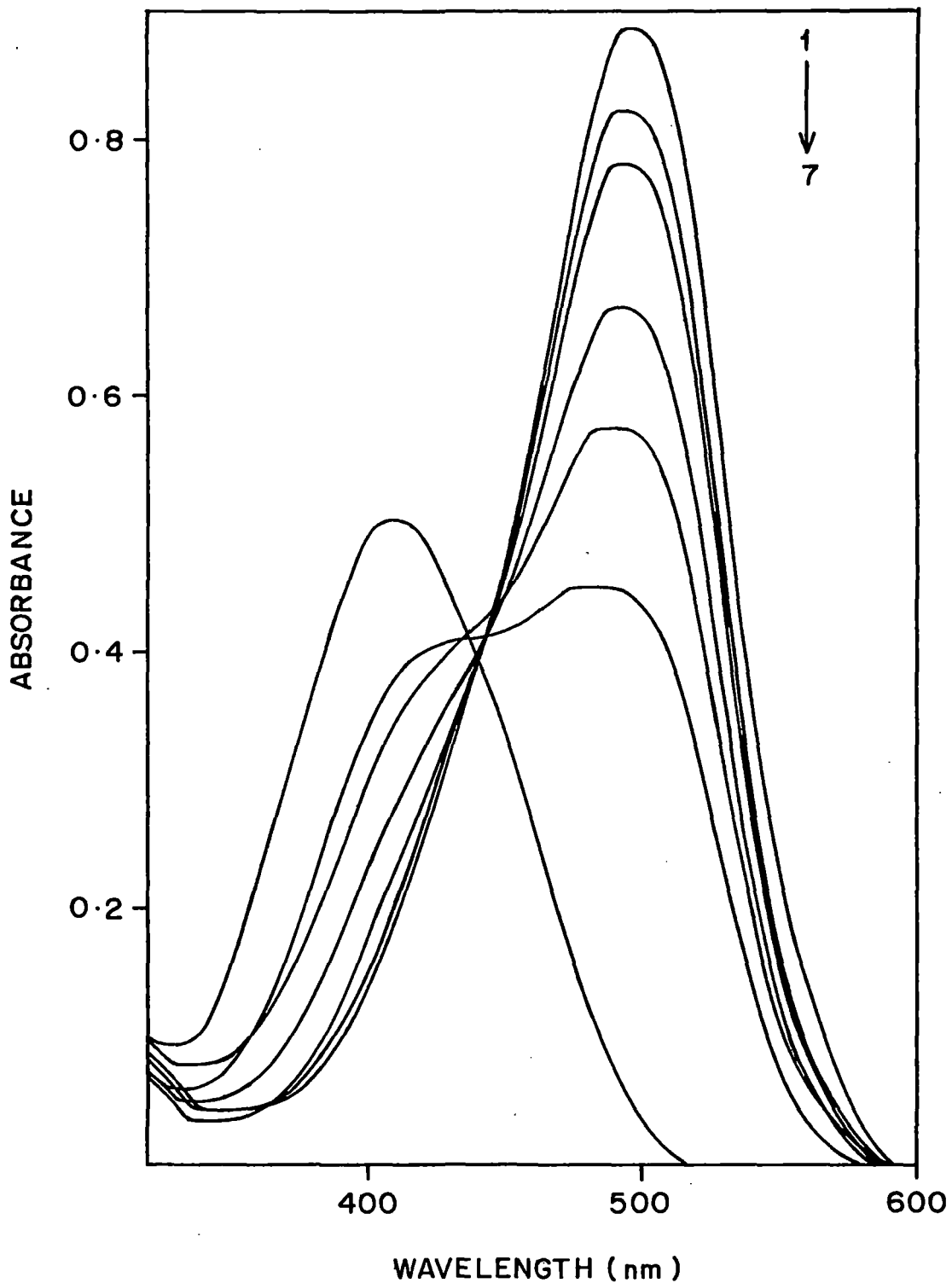


Fig 7.10 Absorption spectra of Methyl Red at 25°C in benzene/SDS/butanol/water with $R = 48$ (ME7). Spectra 1 to 7 correspond to pH=2.7, 5.2, 5.6, 6.0, 6.4, 6.6 and 12.3, respectively. (Concentration of MR= 2.8×10^{-5} mol kg⁻¹).

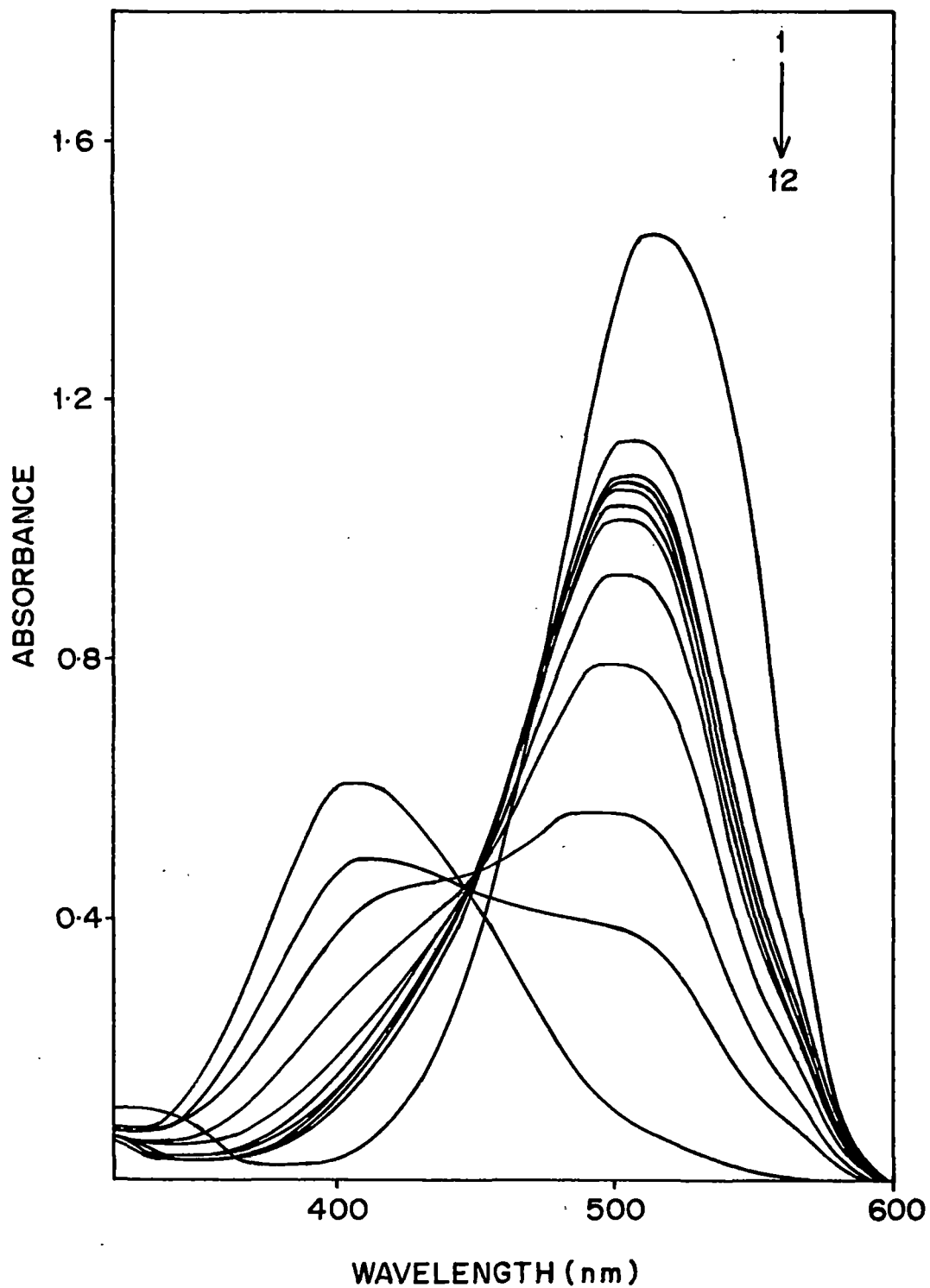


Fig 7.11 Absorption spectra of Methyl Red at 25°C in benzene/SDS/butanol/water with $R = 66$ (ME8). Spectra 1 to 12 correspond to pH = 0.9, 2.7, 3.6, 4.0, 4.4, 4.8, 5.2, 5.6, 6.0, 6.4, 6.8 and 9.0, respectively. (Concentration of MR = 2.7×10^{-5} mol kg⁻¹).

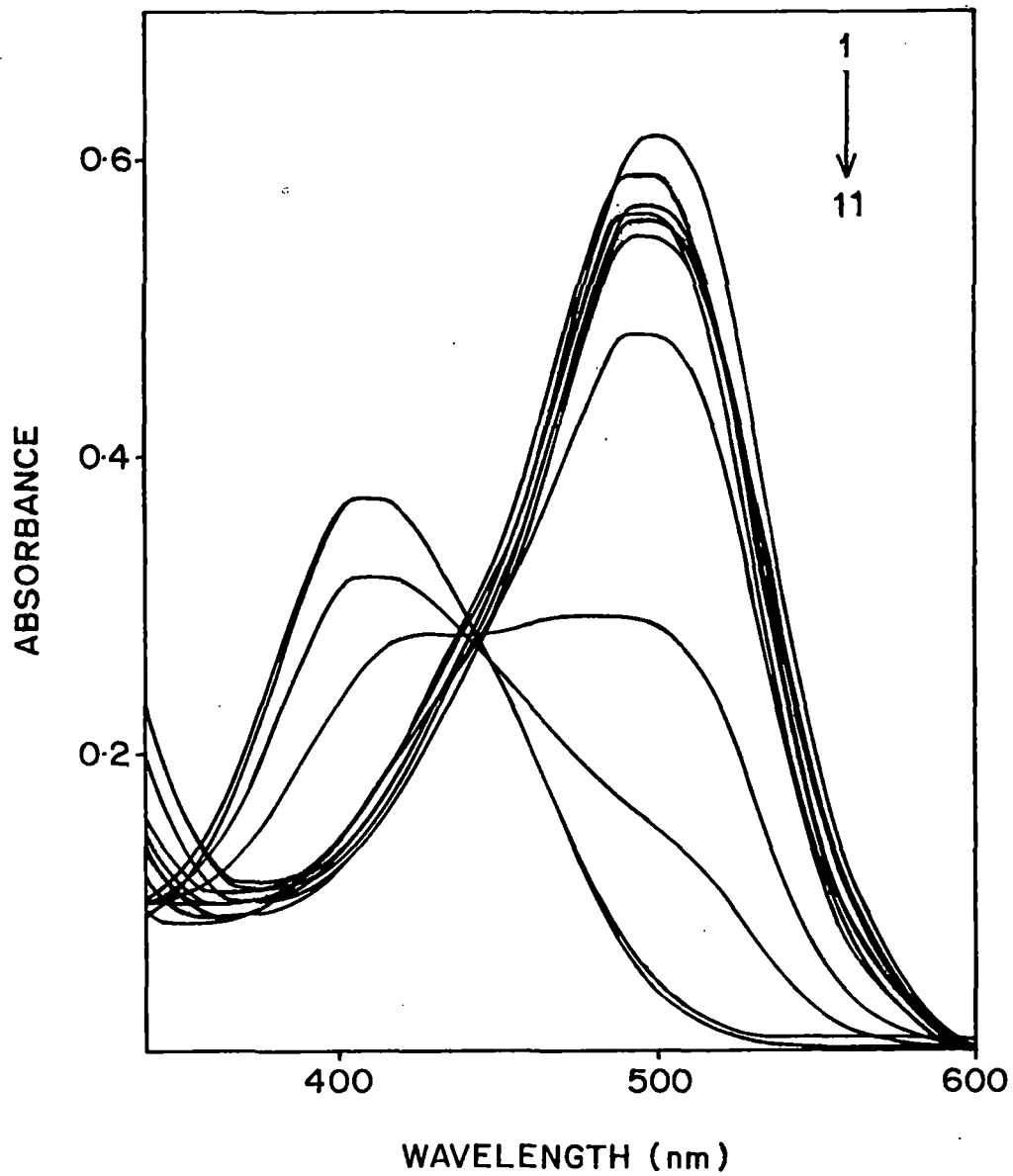


Fig 7.12 Absorption spectra of Methyl Red at 25°C in benzene/SDS/propanol/water with $R = 36$ (ME9). Spectra 1 to 11 correspond to pH = 2.7, 4.0, 3.6, 4.4, 4.8, 5.2, 5.6, 6.0, 6.4, 6.8 and 9.0, respectively. (Concentration of MR = 2.2×10^{-5} mol kg⁻¹).

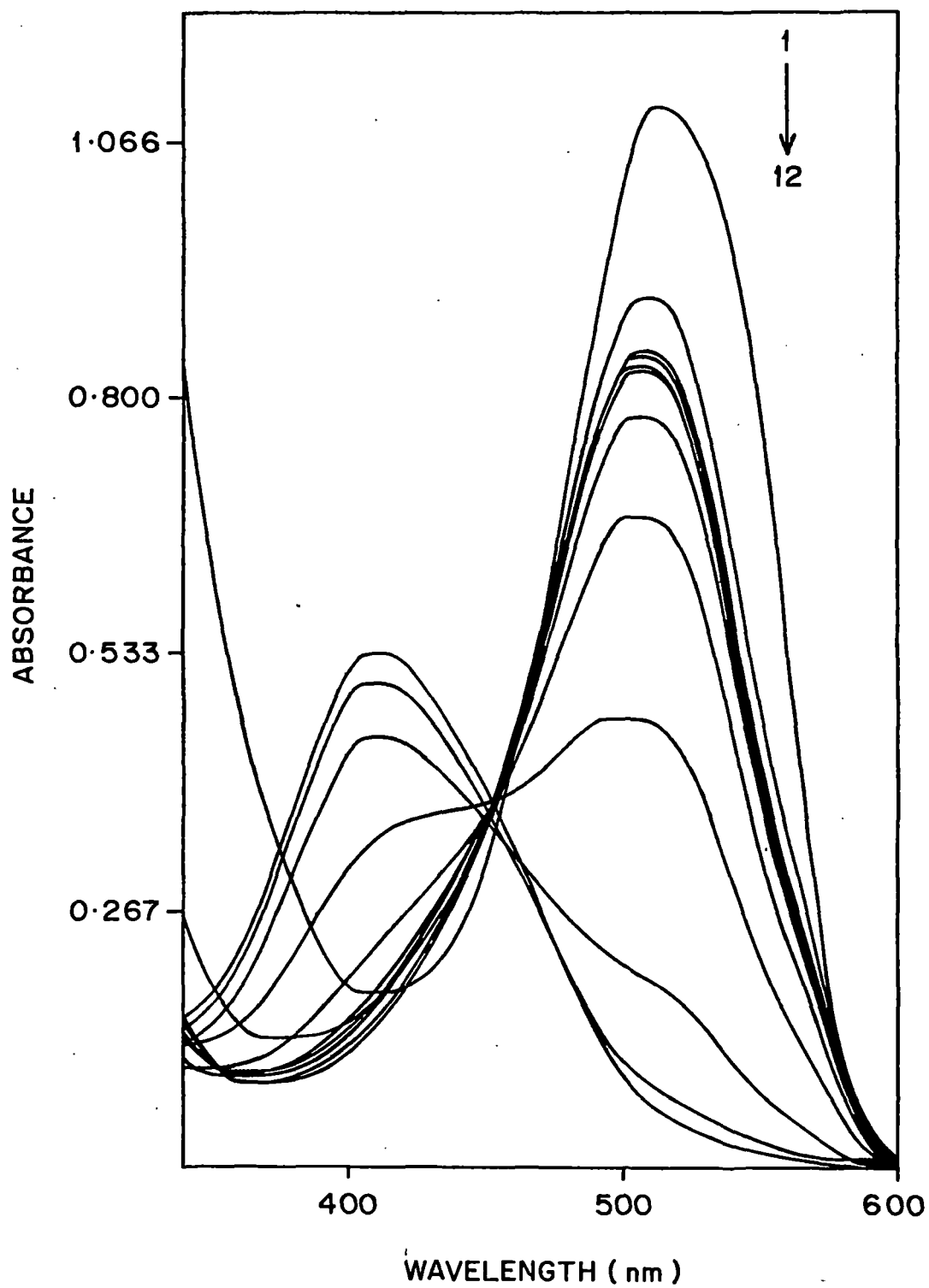


Fig 7.13 Absorption spectra of Methyl Red at 25°C in benzene/SDS/propanol/water with R = 66 (ME10). Spectra 1 to 11 correspond to pH = 0.9, 2.7, 3.6, 4.0, 4.4, 4.8, 5.2, 5.6, 6.0, 6.4, 9.0 and 6.80, respectively. (Concentration of MR = 2.9×10^{-5} mol kg⁻¹).

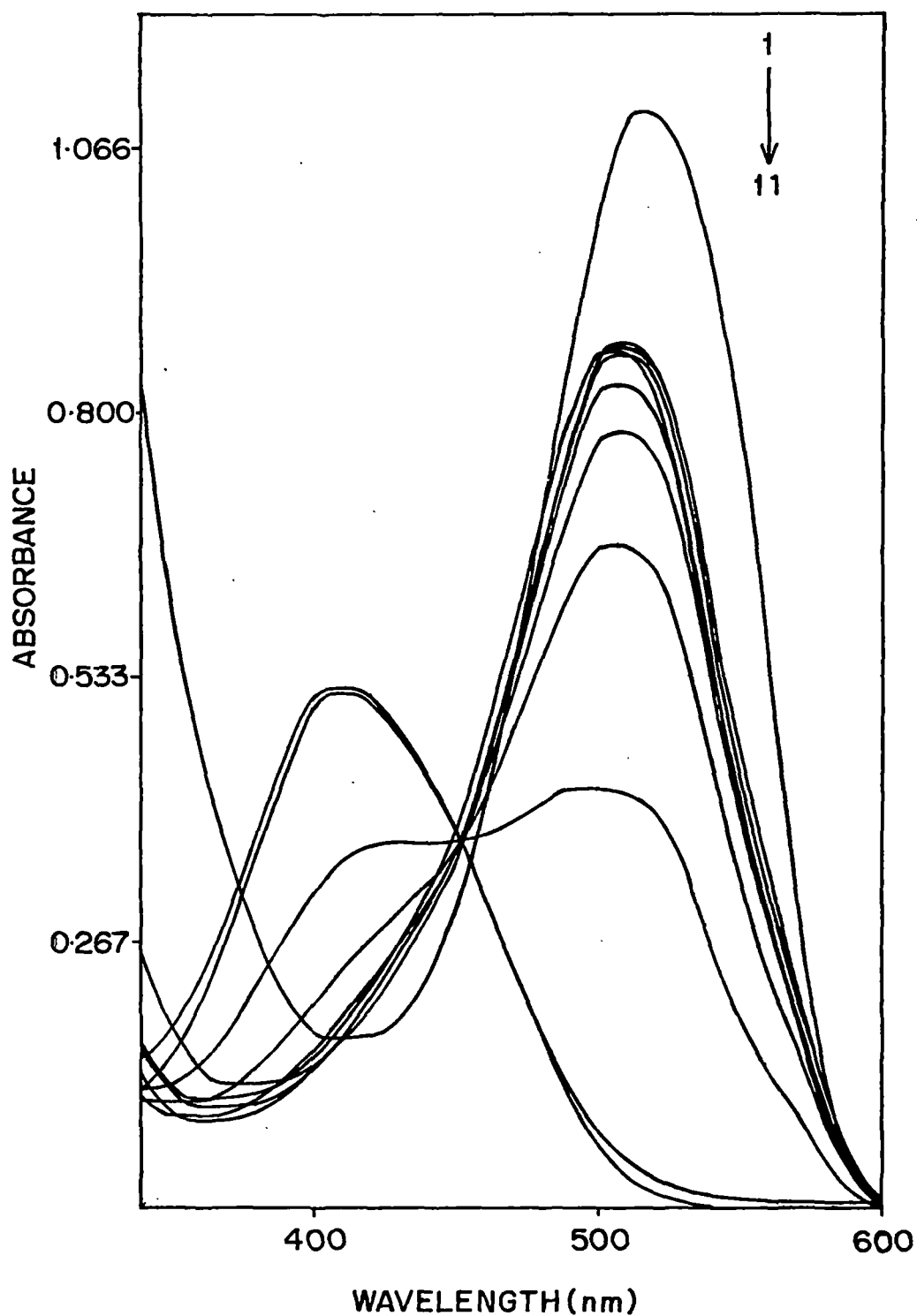


Fig 7.14 Absorption spectra of Methyl Red at 25°C in SDS/ propanol/water with R = 66 (ME0). Spectra 1 to 11 correspond to pH = 0.9, 2.7, 3.6, 4.0, 4.4, 4.8, 5.2, 5.6, 6.0, 6.8 and 9.0, respectively. (Concentration of MR = 2.9×10^{-5} mol kg⁻¹).

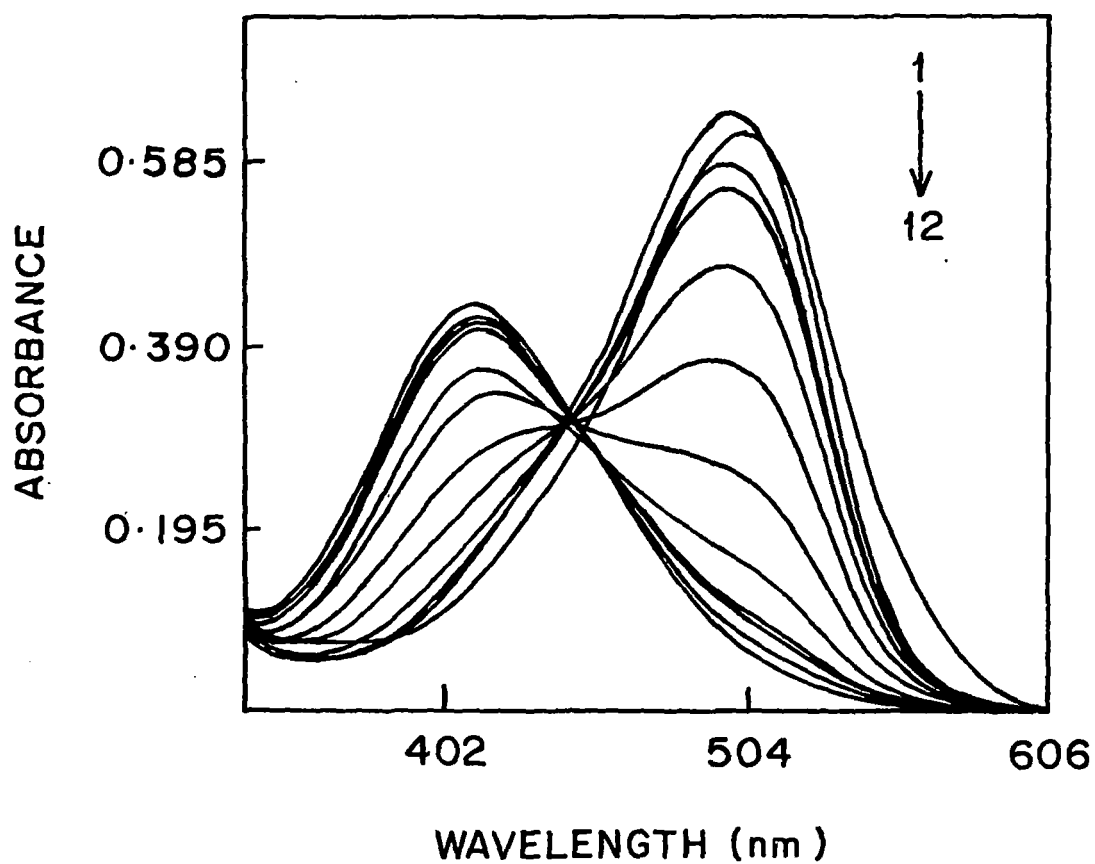


Fig 7.15 Absorption spectra of Methyl Red at 25°C in benzene/CPC/propanol/water with $R = 6$ (ME11). Spectra 1 to 12 correspond to pH = 2.7, 0.9, 3.6, 4.0, 4.4, 4.8, 5.2, 5.6, 6.0, 6.4, 6.8 and 9.0, respectively. (Concentration of MR = 2.6×10^{-5} mol kg⁻¹).

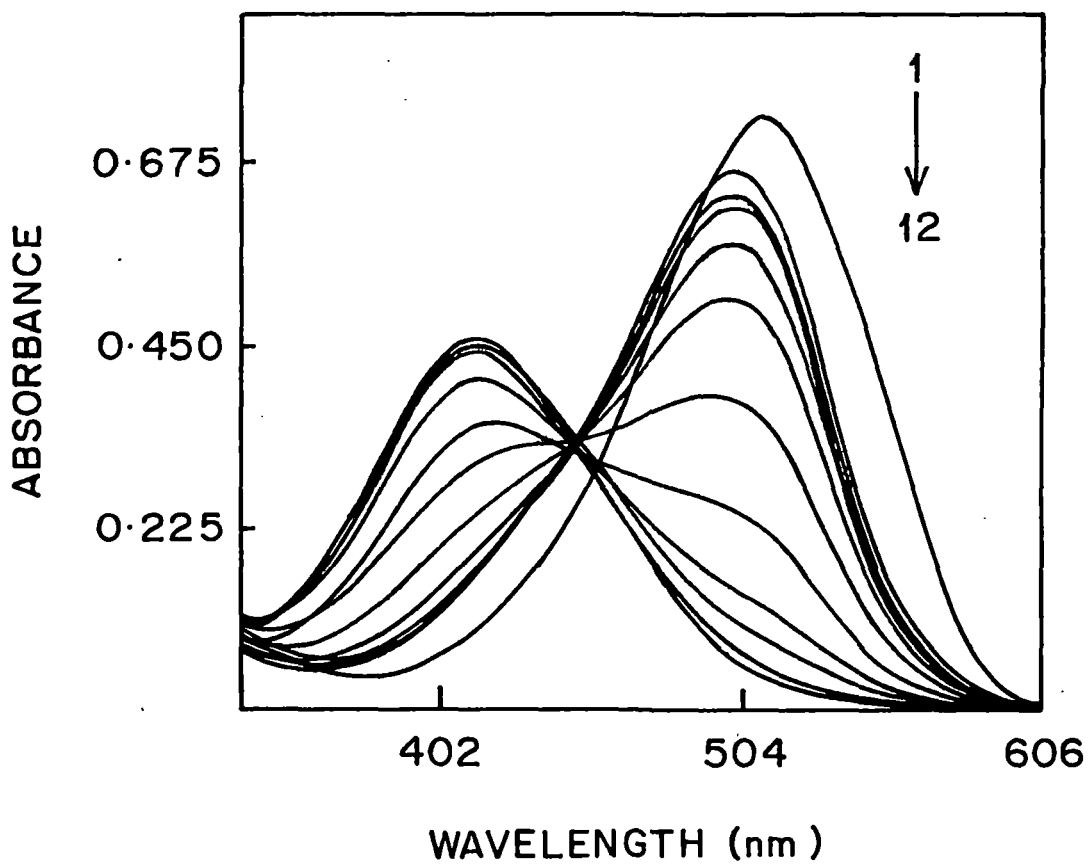


Fig 7.16 Absorption spectra of Methyl Red at 25°C in benzene/CPC/propanol/water with R =36 (ME12). Spectra 1 to 12 correspond to pH = 0.9, 2.7, 3.6, 4.0, 4.4, 4.8, 5.2, 5.6, 6.0, 6.4, 6.8 and 9.0, respectively. (Concentration of MR = 2.6×10^{-5} mol kg⁻¹).

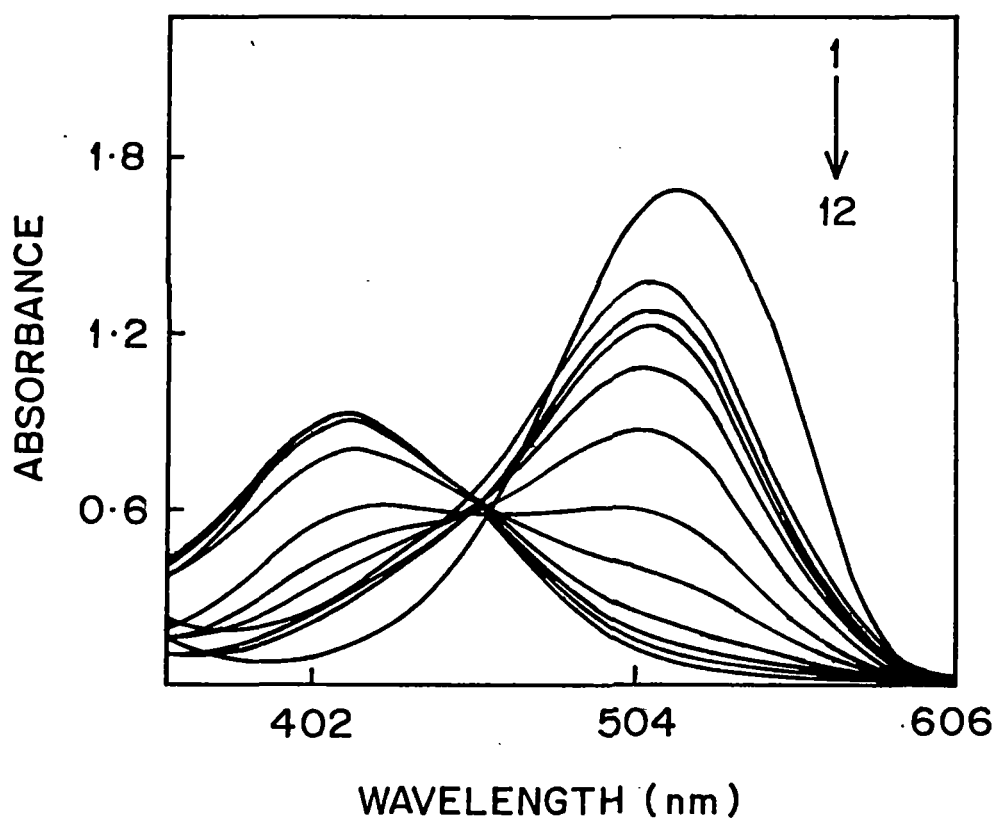


Fig 7.17 Absorption spectra of Methyl Red at 25°C in benzene/CPC/propanol/water with R=66 (ME13). Spectra 1 to 12 correspond to pH = 0.9, 2.7, 3.6, 4.0, 4.4, 4.8, 5.2, 5.6, 6.0, 6.4, 6.8 and 9.0, respectively. (Concentration of MR = 4.8×10^{-5} mol kg⁻¹).

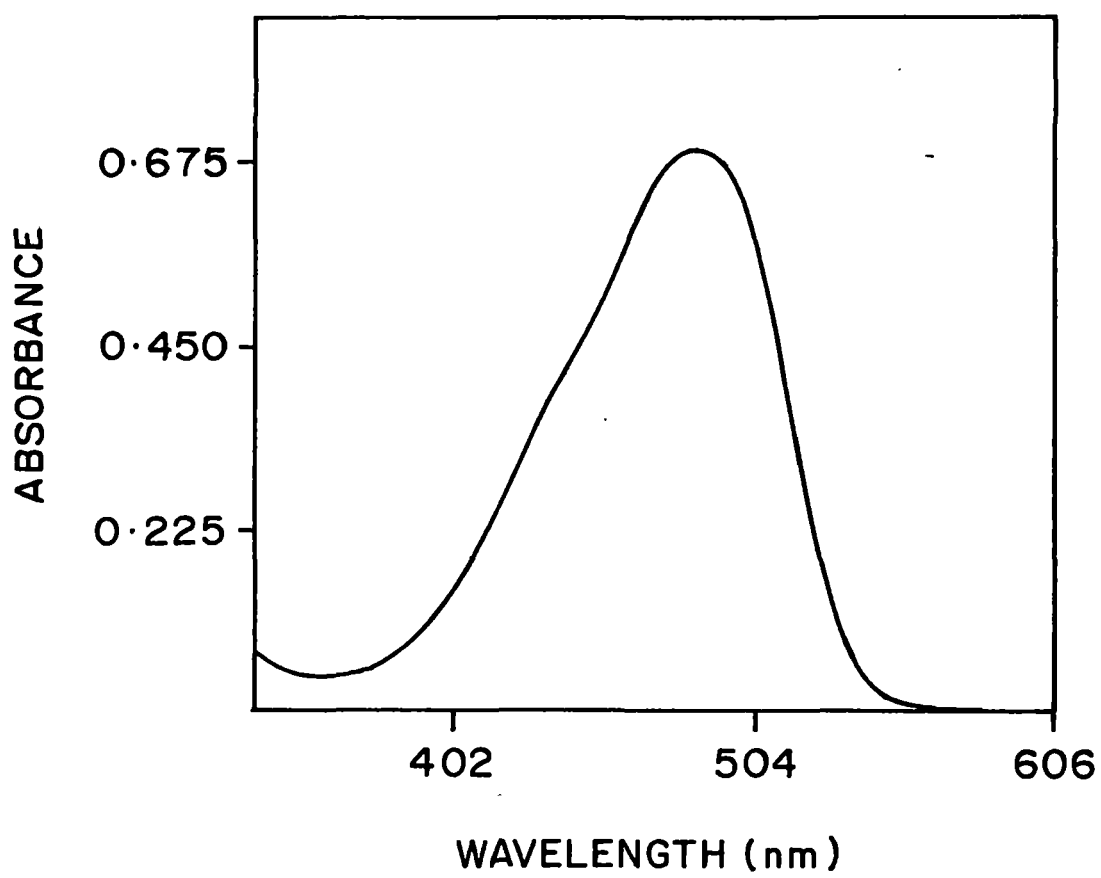


Fig 7.18 Absorption spectra of Methyl Red in benzene at 25°C.

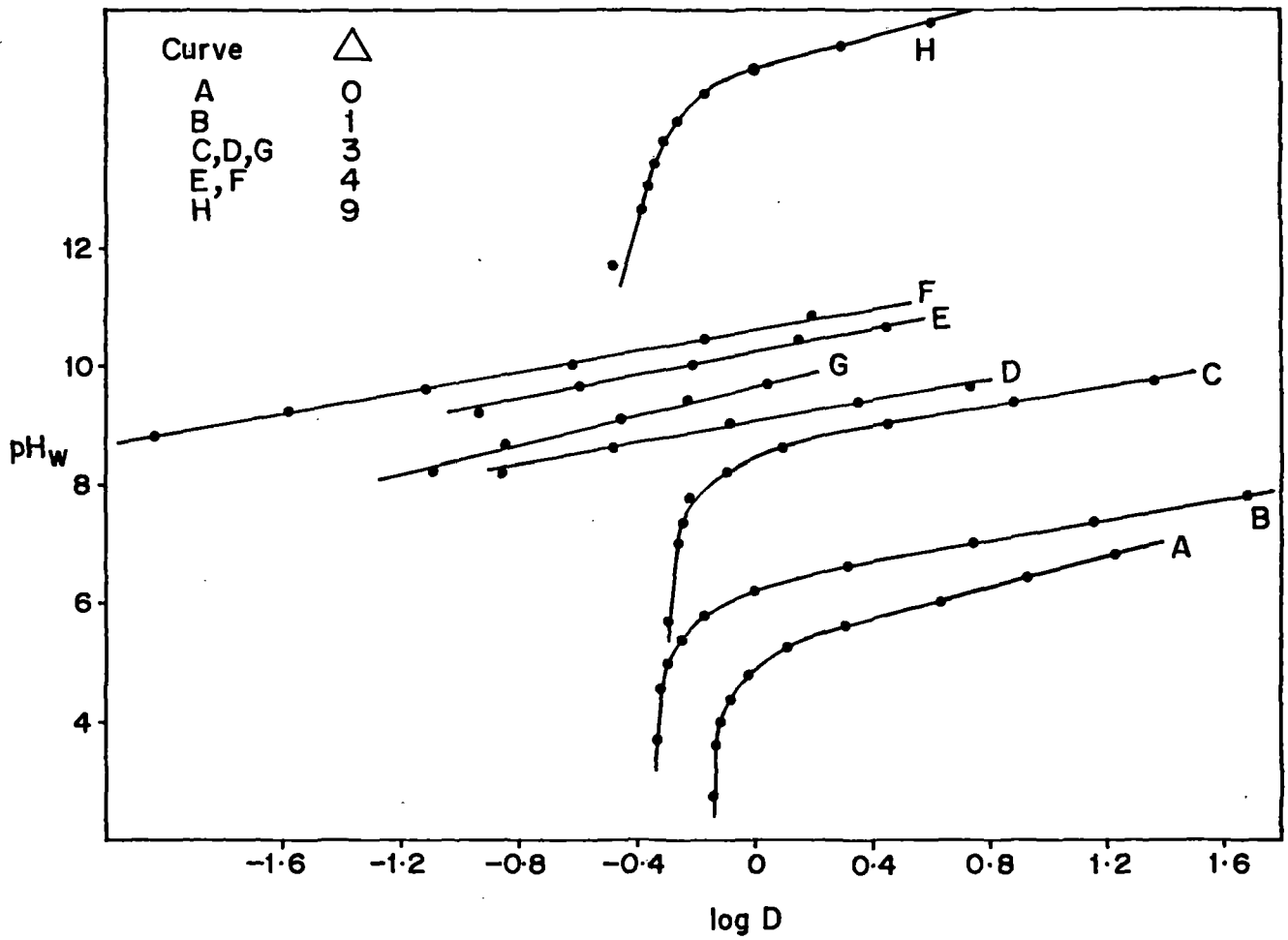


Fig 7.19 Plots of pH_w versus $\log D$ for MR in benzene/SDS/butanol/water microemulsion of different R values. Curves A-H: R = 6, 10, 16, 24, 32, 36, 48 and 66, respectively. Δ indicates upward shift in the ordinate scale.

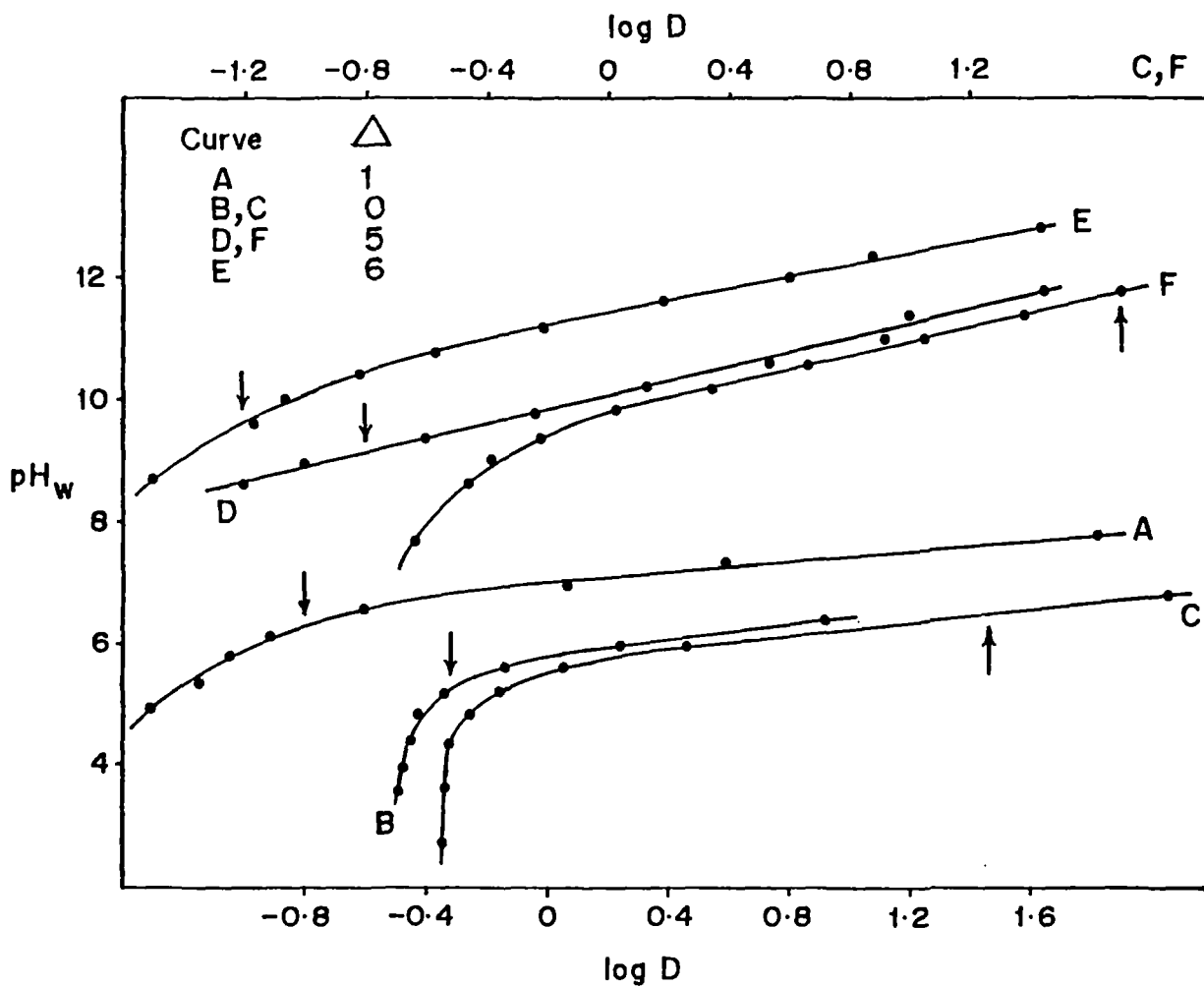


Fig 7.20 Plots of pH_w versus $\log D$ for MR. in benzene/SDS/propanol/water (A:R = 36, B:R = 66). Δ indicates upward shift in the ordinate scale.

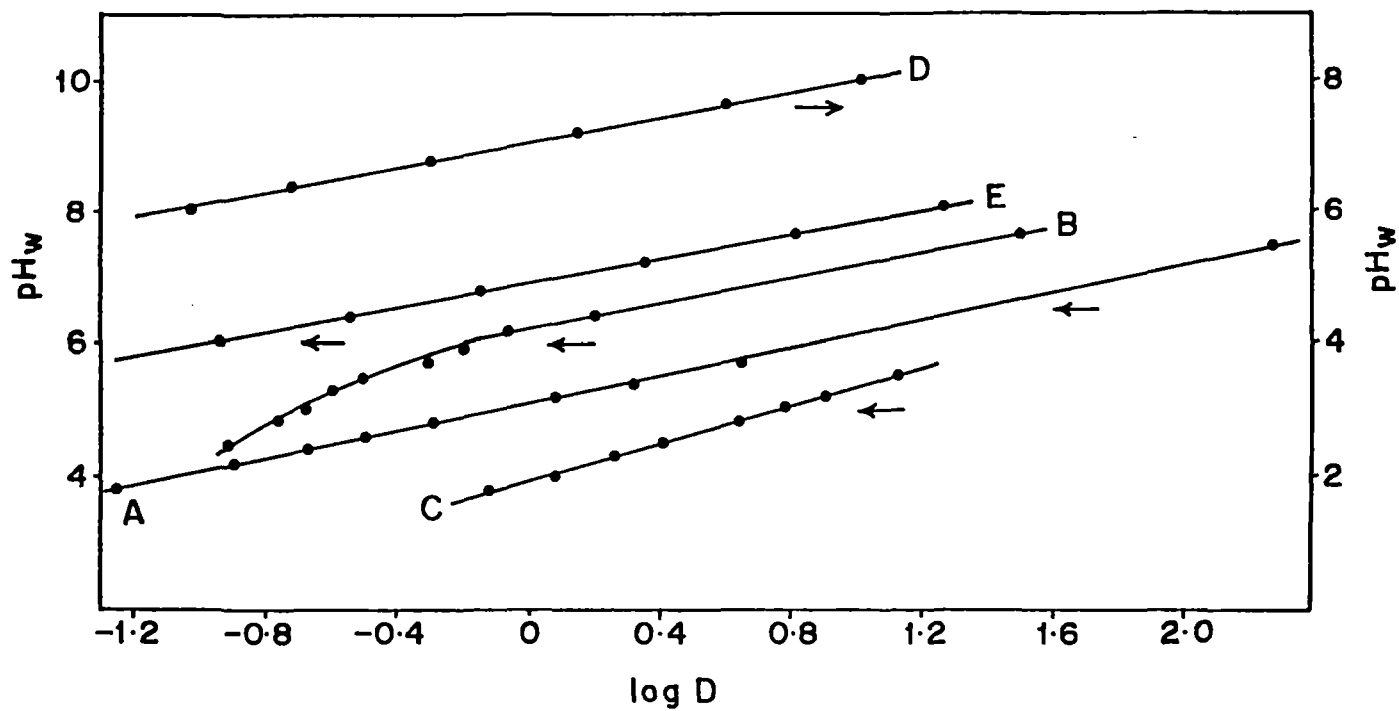


Fig 7.21 Plots of pH_w versus $\log D$ for MR [A:in water, B:in aqueous SDS solution, C:in aqueous CPC solution (data from ref.7)] and for NR [D:in benzene/SDS/butanol/water, $R = 66$ and E:in benzene/SDS/propanol/water, $R = 66$].

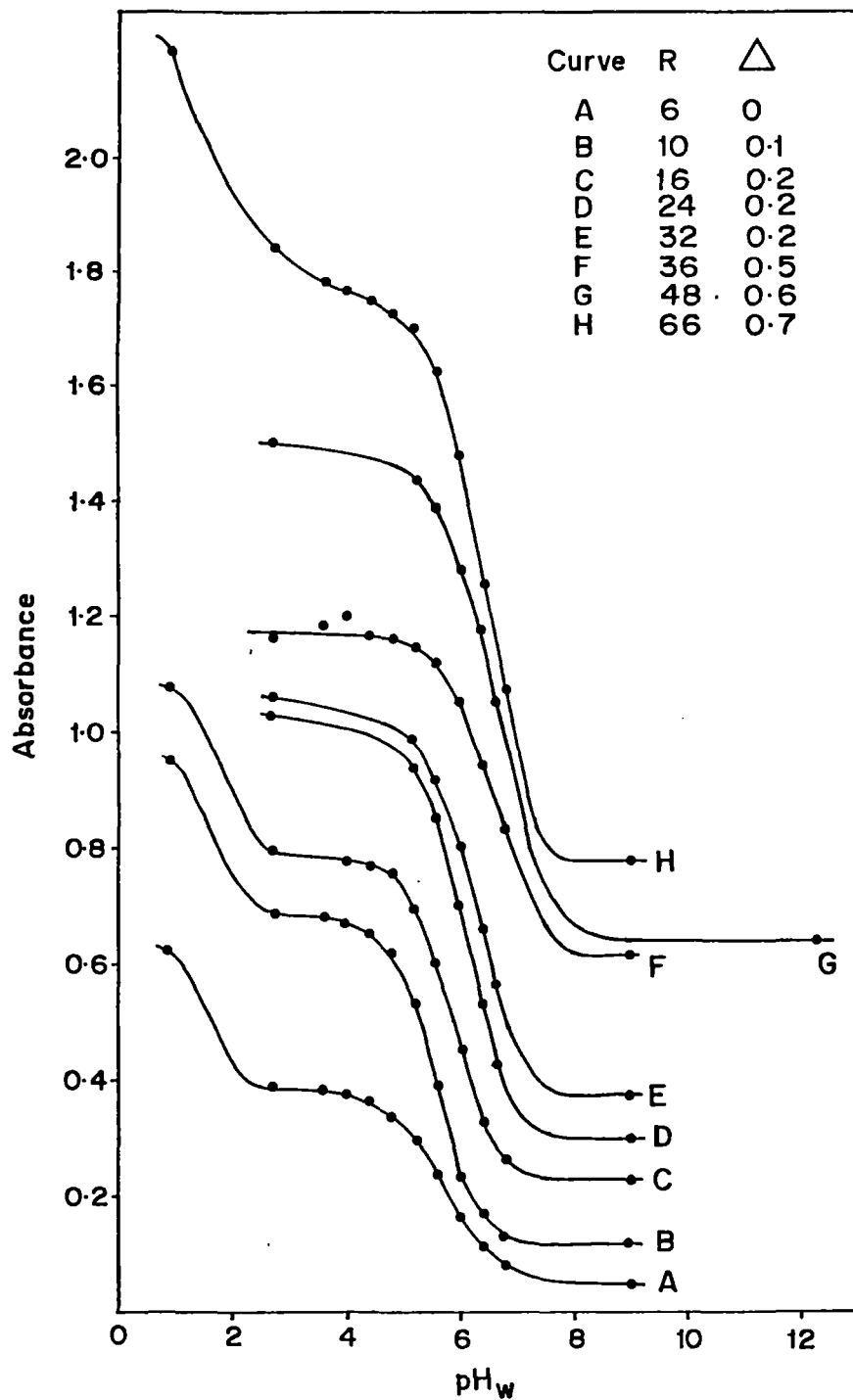


Fig 7.22 Plot of absorbance of MR in water/SDS/butanol/benzene microemulsions versus pH. Absorbances are at wave lengths (in nm): 519(A), 519(B), 520(C), 502(D), 502(E), 502(F), 502(G), 519(H). Δ indicates the upward shift in the ordinate scale for the different curves.

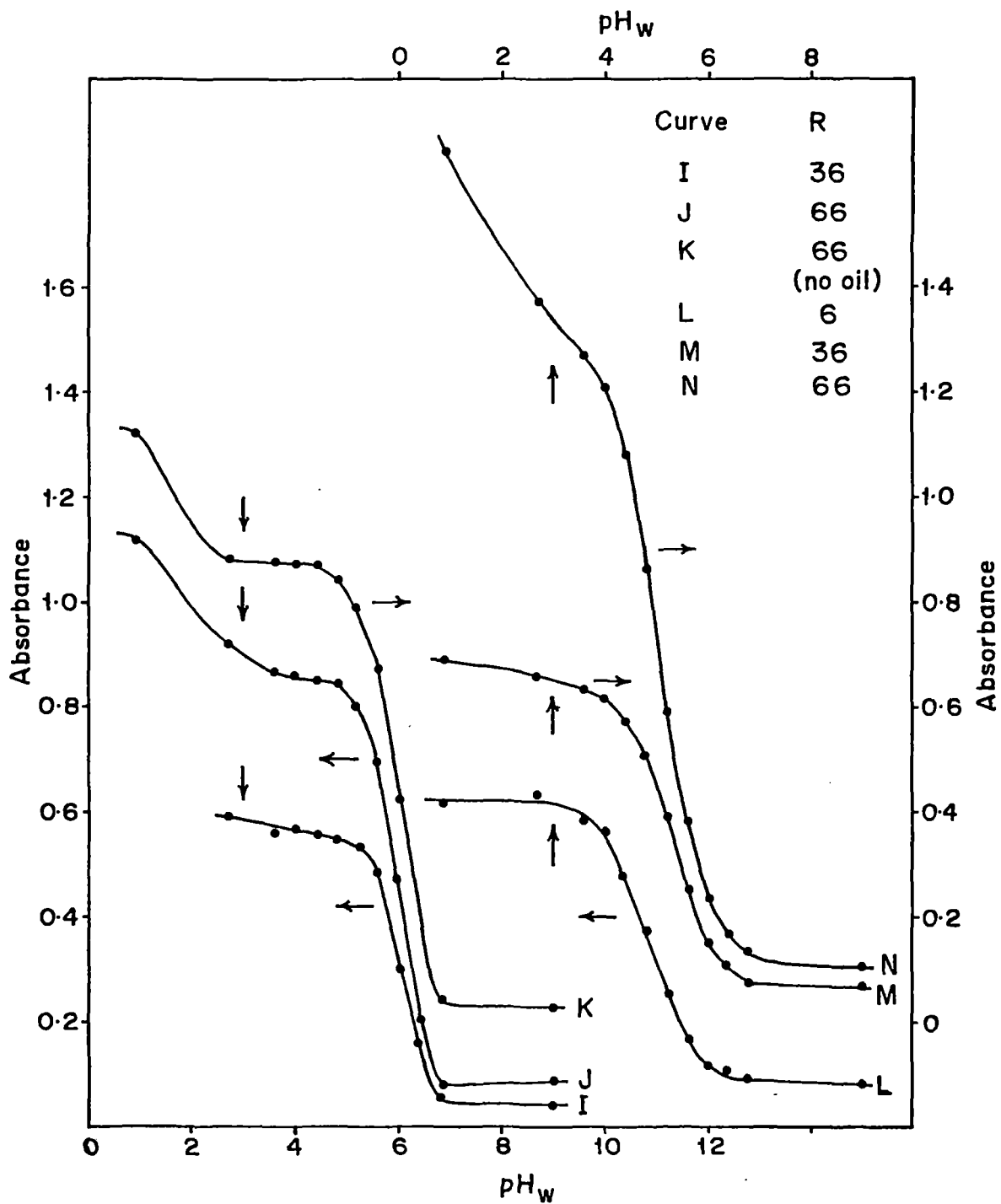


Fig 7.23 Plot of absorbance of MR in water/SDS/propanol/benzene (curve I,J,K) and water/CPC/propanol/benzene (curves L,M,N) microemulsions versus pH. Absorbances are at wavelengths (in nm) : 501(I), 513(J), 517(K), 500(L), 500(M), 510(N)

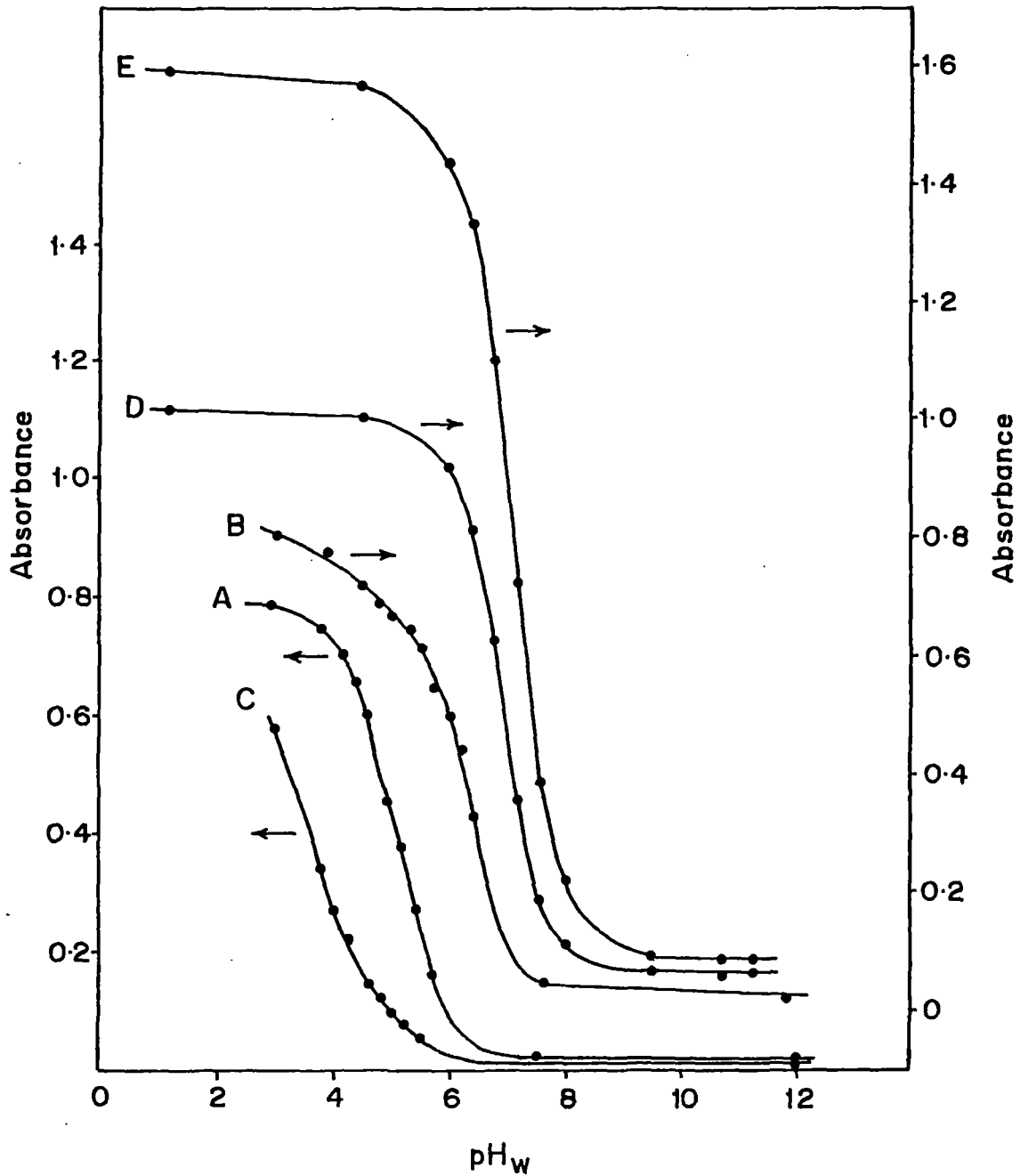


Fig 7.24 Plot of absorbances of MR (curves A,B,C) and NR (curves D,E) versus pH. A:in water, B:in aqueous SDS, C: aqueous SDS, C:aqueous CPC, D: water/SDS/propanol/benzene of $R = 66$, E: water/SDS/butanol/benzene of $R = 66$. For aqueous A,B,C wave length in 520 nm (data from ref.7) and for curves D,E wavelength in 541 nm.

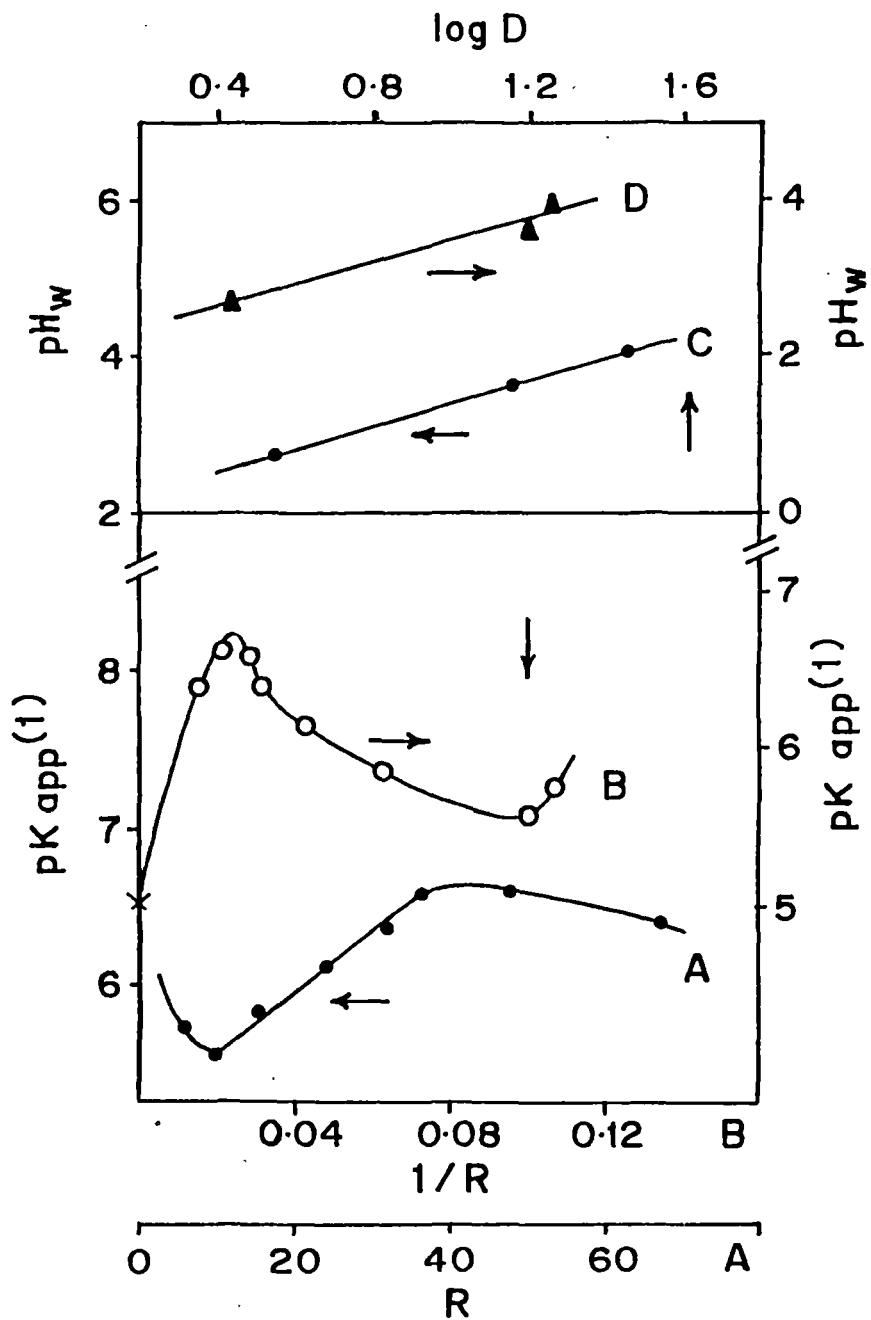


Fig 7.25 Plots of $\text{pK}_a(1)$ of MR versus R (curve A) and versus $1/R$ (curve B) and of pH_w versus $\log D$ for MR in ME8 (line C) and ME10 (line D) media in second protonation region.

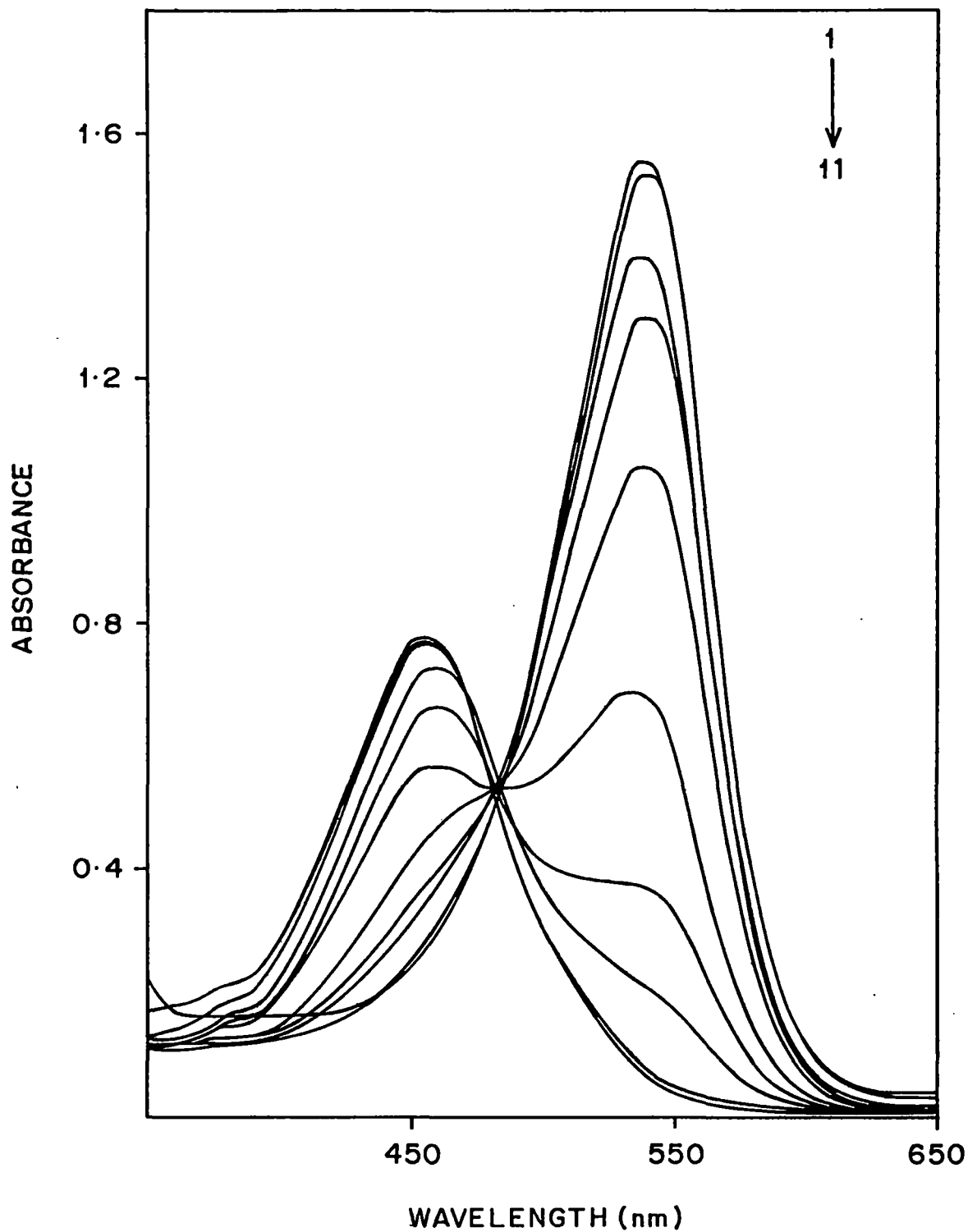


Fig 7.26 Absorption spectra of Neutral Red at 25°C in benzene/SDS/butanol/water with R = 66 (ME8). Spectra 1 to 11 correspond to pH = 1.2, 4.5, 6.0, 6.4, 6.8, 7.2, 7.6, 8.0, 9.5, 10.7 and 11.2, respectively. (Concentration of NR = 5.8×10^{-5} mol kg⁻¹). 10 & 11 in the region > 470nm overlap

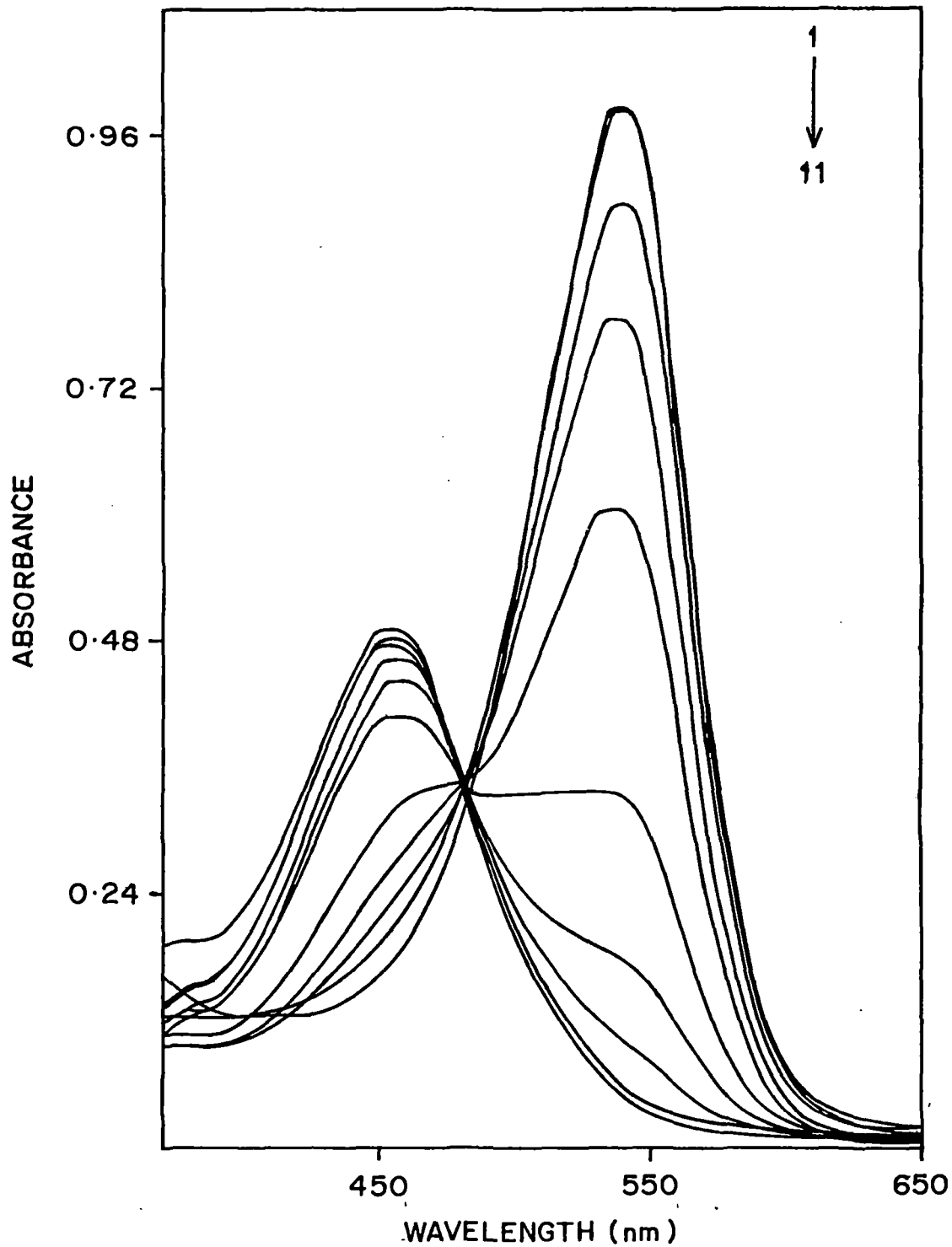


Fig 7.27 Absorption spectra of Neutral Red at 25°C in benzene/SDS/propanol/water with $R = 66$ (ME10). Spectra 1 to 11 correspond to pH = 1.2, 4.5, 6.0, 6.4, 6.8, 7.2, 7.6, 8.0, 9.5, 10.7 and 11.2, respectively. (Concentration of NR = 3.4×10^{-5} mol kg $^{-1}$). 10 & 11 in the region > 470 nm overlap

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