

Effect of Solvent Composition on the Critical Micelle Concentration of Cetylpyridinium Chloride in Ethanol-Water Mixed Solvent Media

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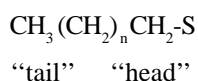
Abstract

The accurate measurement of the specific conductivity of cetylpyridinium chloride in pure water and ethanol-water mixed solvent media containing 0.10, 0.20, 0.30 and 0.40 volume fraction of ethanol at room temperature are reported. The concentrations were varied from $\sim 0.005 \text{ mol l}^{-1}$ to $\sim 0.0002 \text{ mol l}^{-1}$. The conductivity of cetylpyridinium chloride decreases with the increase in the volume fraction of ethanol. The critical micelle concentration of cetylpyridinium chloride increases with the increase in the volume fraction of ethanol.

Key words: cetylpyridinium chloride, conductivity, critical micelle concentration, ethanol-water mixed solvent media

Introduction

The chemical structures having suitable solubility properties for surfactant activity vary with the nature of the solvent system to be employed and the conditions of use. In “standard” surfactant terminology, the “head” refers to the solubilizing group—the lyophilic or hydrophilic group, in aqueous systems—and the “tail” refers to the lyophobic or hydrophobic group in water:



In water, the hydrophobic group may be, for example, a hydrocarbon, fluorocarbon, short polymeric chain, or siloxane chain of sufficient size to produce the desired solubility characteristics when bound to a suitable hydrophilic group. In aqueous systems, the hydrophilic group (the “head”) will be ionic or highly polar, so that it can act as a solubilizing functionality.

When surfactants dissolved, after they reach a certain value of concentration, molecules or ions of surfactants begin to associate and to organize themselves into more complex units, also called micelles. In colloidal and surface chemistry, the critical micelle concentration (cmc) is defined as the concentration of surfactants above which micelles

form and almost all additional surfactants added to the system go to micelles (IUPAC 1997). The concentration above which micellar aggregates begin to form in a pure surfactant solution is called critical micellar concentration, cmc (Hayakawa & Kwak 1982).

The determination of cmc is generally based on the localization of the position of a breaking point in the concentration dependencies of selected physical or chemical properties of surfactant solutions. Because of the surface activity of these substances, measurements of the surface tension of surfactant solutions represent the principal method of cmc determination. However, it is rather tedious and time-consuming procedure. In the case of ionic surfactants, the utilization of electrochemical measurement is much more convenient, especially the measurements of the electrical conductivity of their solutions with varying concentration. The conductometric method is based on the finding of a breaking point on the curves, which describe the concentration dependence of conductivity. It is well-known, that the conductivity of any solution is directly proportional to the concentration of its ions. The point, where the micelle formation starts, is indicated on the concentration dependence of specific conductivity as a breaking point. The requested value of cmc is the intercept of two linear functions

with mutually different slopes.

The presence of alcohols in water will help in breaking down of the water structure. In addition to breaking down the structure of water, alcohols lower down the dielectric constant of the water thereby contributes toward the increase in cmc. An additional complication of alcohol-water mixtures is the possibility of the alcohol to penetrate into the micelle. It is well known that the alcohol molecules orient themselves at the micelle-solvent interface with the hydrocarbon group penetrating slightly into the micelle and the hydroxyl group remaining on the micelle-solvent interface (Emerson & Holtzer 1967, Miyagishi 1974).

Cetylpyridinium chloride (CPyCl) is a cationic quaternary ammonium compound used in some types of mouthwashes, toothpastes, lozenges, throat sprays, breath sprays, and nasal sprays. It is an antiseptic that kills bacteria and other microorganisms. It has been shown to be effective in preventing dental plaque and reducing gingivitis (Asadoorian 2008). It has also been used as an ingredient in certain pesticides. CPyCl has also found its use in the washing of poultry products and beef (Bosileval *et al.* 2004). Although number of works (Varade *et al.* 2005, Mehta *et al.* 2008, Parathakkatt *et al.* 2012) have been done to study cmc of CPyCl in numerous solvent media in the presence and absence co-ions, such study in ethanol-water mixed solvent media is relatively new. Considering to the importance of CPyCl this paper deals with the measurement of cmc of CPyCl in pure water and ethanol-water mixed solvent media corresponding to range of dielectric constant at room temperature (303.15K) by conductometric method.

Methodology

Ethanol (E. Merck, India) was used for the experimental works. The purified solvent had a density of $0.78097 \text{ g.cm}^{-3}$ and a co-efficient of viscosity of 0.9490 mPa.s at 303.15 K these values are in good agreement with the literature values (Lange & Dean 1967). Distilled water with a specific conductance less than $10^{-6} \text{ S.cm}^{-1}$ at 303.15 K was used for the preparation of the mixed solvents. The physical properties of Ethanol-Water mixed solvents used in this study at 303.15K were taken from the published works (Lee & Lee 1988, Bhattarai & Sah 2011, Harned & Owen 1957).

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of

2000 Hz using a dip-type cell with a cell constant of 1.15 cm^{-1} and having an uncertainty of 0.01%. The cell was calibrated by the method of Lind and co-workers (Lind *et al.* 1959), using aqueous potassium chloride solution. The measurements were made at room temperature (303.15K). The details of the experimental procedure have been described earlier (Das & Hazra 1992, Das & Hazra 1995). In order to avoid moisture pickup, all solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed in three replicates.

Results and Discussion

Conductivity measurements of CPyCl were performed in pure water and water-ethanol mixed solvent media at 303.15 K. The critical micellar concentrations (*cmc*) of CPyCl were determined from conductometry. These were obtained from the inflections in the plots of specific conductivity versus surfactant concentration. The data points above and below the inflection were fitted to two linear equations, and the cmcs were obtained from the intersection. This method is found to be reliable and convenient for the present system because of the significant variations of specific conductivity with surfactant concentration in the pre- and postmicellar regions which allowed us to draw two unambiguous straight lines above and below the *cmc*. The experimental specific conductivities of CPyCl as a function of its molar concentration at 303.15 K of pure water and four different Ethanol-water mixtures (containing 0.10, 0.20, 0.30, 0.40 volume fractions of ethanol) are depicted in figures 1-5.

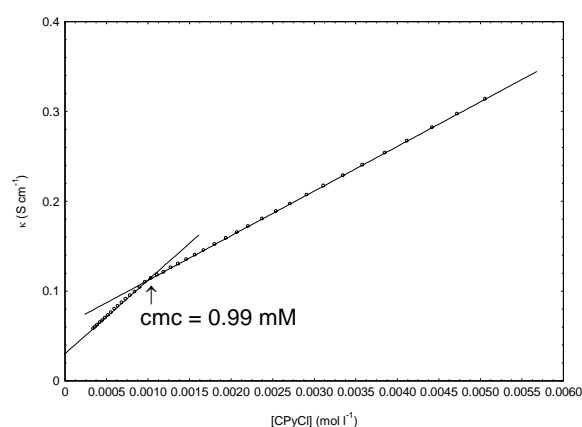


Fig. 1. Specific conductivities of CPyCl as a function of the surfactant concentration in 303.15 K: opened circles represent pure water

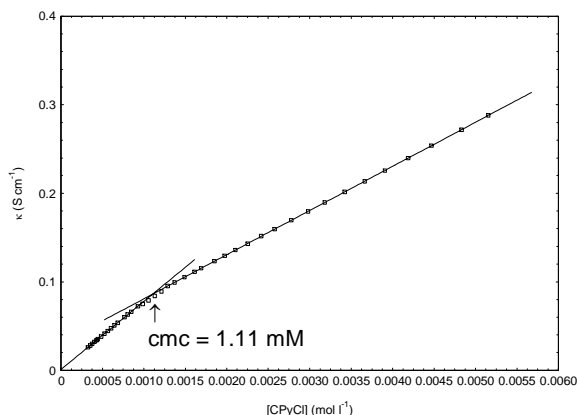


Fig. 2. Specific conductivities of CPyCl as a function of the surfactant concentration in 303.15 K: opened squares represent 0.10 volume fractions of ethanol in the solvent mixture

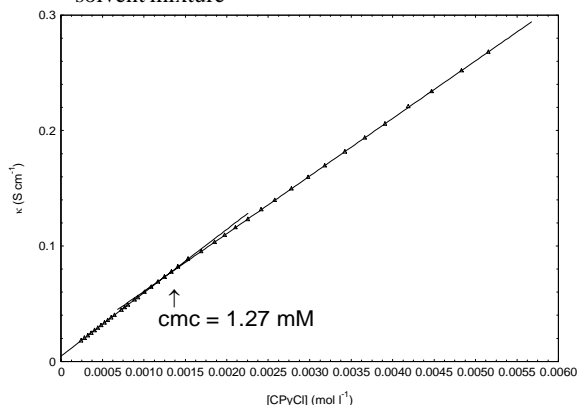


Fig. 3. Specific conductivities of CPyCl as a function of the surfactant concentration in 303.15 K: triangles represent 0.20 volume fractions of ethanol in the solvent mixture

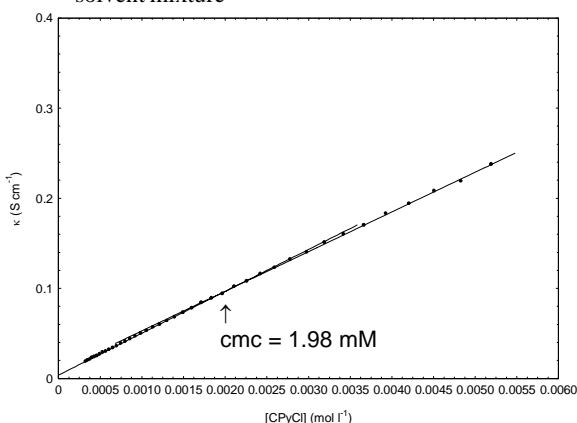


Fig. 4. Specific conductivities of CPyCl as a function of the surfactant concentration in 303.15 K: closed circles represent 0.30 volume fractions of ethanol in the solvent mixture

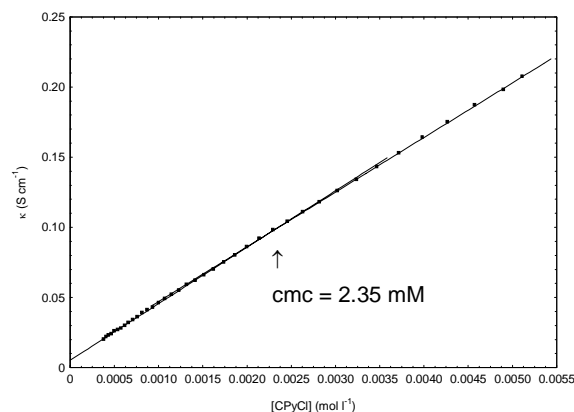


Fig. 5. Specific conductivities of CPyCl as a function of the surfactant concentration in 303.15 K: closed squares represent 0.40 volume fractions of ethanol in the solvent mixture

The *cmc* of CPyCl in pure water was found 0.98 mM by Varade *et al.* 2005 at 303.2 K which also supports to our *cmc* data of pure water (Table 1). It was also observed that *cmc* of CPyCl increase with the increase in the volume fraction of ethanol (Table 1). Similar trend

Table 1. The critical micellar concentration (*cmc*) obtained from conductometry of cetyl pyridinium chloride in pure water and ethanol-water mixed solvent media containing 0.10, 0.20, 0.30 and 0.40 volume fraction of ethanol at 303.15 K.

T(K)	Water <i>cmc</i> (mM)	0.10 volume fraction of ethanol <i>cmc</i> (mM)	0.20 volume fraction of ethanol <i>cmc</i> (mM)	0.30 volume fraction of ethanol <i>cmc</i> (mM)	0.40 volume fraction of ethanol <i>cmc</i> (mM)
303.15	0.99	1.11	1.27	1.98	2.35

has been observed in experiment related to other surfactant in methanol-water mixed solvent medium (Shah *et al.* 2012). Two factors must be considered to explain this significant influence of ethanol on the *cmc* value of CPyCl: (a) the presence of ethanol decreases the cohesive energy density, or the solubility parameter, of water, thus increasing the solubility of the monomeric form of the surfactant and hence the *cmc*, and (b) the cosolvent causes a reduction in the relative permittivity of the aqueous phase, favouring the mutual repulsion of the ionic heads in the micelle, thus opposing micellisation and increasing the *cmc*. It

is also well known that addition of solvent which acts as water structure breakers decrease the hydrophobic effect result in to the increase in the cmc value of ionic surfactants (Gracie *et al.*1996).

The relative permittivity of the medium decreased at a given temperature with the increase in the ethanol content and this trend has also been seen in the conductivity study (Bhattarai & Raut 2011, Bhattarai and Sah 2011). The conductance decreases with increase of alcohol content for the studied ethanol-water mixed solvent system (Fig. 2-5). The presence of ethanol reduces the dielectric constant of the solvent phase and makes easier for the formation of ion-pairs in the solution phase. In other words, in solvents of low dielectric constants, having small ionizing effect on the electrolytes, the electrostatic forces between oppositely charged ions would be appreciable and conductance value will be small. However, solvents with high dielectric constants yield more conducting solutions.

The following conclusions have been drawn from the above results and discussion. Experimental result for the conductivity of CPyCl solution in pure water and ethanol- water mixed solvent media has been presented as a function of salt concentration and different percentage composition of ethanol-water mixed solvent media. The cmc of CPyCl are found to increase with the increase in the volume fraction of ethanol in ethanol-water mixed solvent media.

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A. Bhattarai *et al.*/Effect of Solvent.....

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