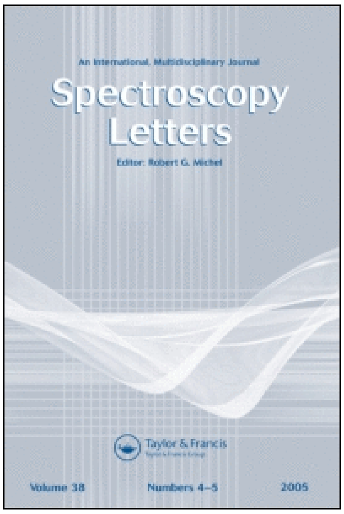

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Effect of Ethanol on the Partition Coefficient Of Cyclohexylacetate Between Bulk and Cetyltrjmethylammonium Bromide Micellar Pseudophases

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EFFECT OF ETHANOL ON THE PARTITION COEFFICIENT OF CYCLOHEXYLACETATE BETWEEN BULK AND CETYLTRIMETHYLAMMONIUM BROMIDE MICELLAR PSEUDOPHASES

Key Word : Cyclohexyl acetate ,cetyltrimethylammonium bromide , ethanol , differential absorption spectroscopic method , partition coefficient .

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ABSTRACT

Variation of the partition coefficient of cyclohexylacetate (CA) was studied by a differential absorption spectroscopic method as a function of ethanol and (CTAB) cetyltrimethylammoniumbromide concentrations. Approach used was based upon the pseudo-two phase model, including effect of ethanol concentrations on the critical micelle concentration (CMC) of CTAB.Ethanol enhanced micelle formation of CTAB at concentrations below 1% by volume, had a slight inhibitory effect at higher concentrations and totally inhibited at a concentration above 15% by volume.

Various amounts of ethanol were used with a purpose of changing the solubility of CA in water.The differential absorbance (ΔA),was almost zero at low concentrations of CTAB,however an increase in ΔA began at a certain concentration of CTAB which can accordingly be assumed to be consistent with CMC of CTAB in the presence of ethanol.As CTAB concentration increased above CMC,ΔA reached a plateau.In this plateau, ΔA can reasonably be interpreted as the saturation of CA in micellar phase.

Plateau values of ΔA decreased with increasing ethanol concentration. This showed that the fraction of CA in the micellar phase depended on the ethanol concentration in terms of changing the solubility. Partition coefficients,K_c ,were obtained from the plots of $1/\Delta A$ against $1 / [C_{CA}] + [C^{s}_{m}]$, which were linear in high CTAB concentrations.It was also seen that as ΔA, K_c decreased when the ethanol percentage were increased.In other words,the lower the solubility of CA in the bulk,the higher the partition coefficient.

INTRODUCTION

The solubility of predominantly hydrophobic molecules in aqueous solutions is enhanced by the addition of surfactants.The added surfactant molecules self assemble to form micelles which increase solubilization of sparingly soluble molecules (1). Surfactant micelles can be pictured as having a highly nonpolar core and a relatively polar interfacial region.While solubilization of very nonpolar organic substance takes place in the micellar core , relatively high polar molecules tend to be located on outer region that is solubilized in the interfacial region of the micelle .(1,2,3) This model implies that an organic substance which is almost completely insoluble in water will be solubilized by micelles while a substance which is more soluble in aqueous media would be expected to partition between aqueous and micellar phases(3). The factors that govern the distribution of nonpolar solute is of fundamental importance for understanding of the phenomenon of solubilization.

The relation between micelle-water partition and solubility of various non-polar molecules has been studied and shown that their partition coefficient aqueous solubility of non-polar molecules is inversely related to (4).

This paper reports the results obtained from a series of measurements of the partition coefficient of Cyclohexylacetate (CA) between Cetyltrimethylammonium bromide (CTAB) micelles and aqueous phase, in the presence of various amount of ethanol. The purpose of this study is to show the effect of ethanol on the partition coefficient due to the increase of solubility of CA and to find whether a correlation exists between the micelle-aqueous phase partition coefficient and its solubility in aqueous phase for the same compound.

EXPERIMENTAL

MATERIALS

Cyclohexylacetate (CA) (98% pure) and cetyltrimethylammonium bromide (CTAB) (99% pure) , ethanol (99.8%pure) were obtained from Merck , Sigma and Fluka A.G. respectively . During experimentation bidistilled water was used.

METHODS

Measurement of differential absorption spectra ; The partition coefficients were determined by differential absorption spectroscopic method which was described by Kawamura et ,al. (5) This approach is based on a pseudo-two phase model ,including the effect of ethanol concentration on the micellization. A CA solution with a concentration of 6.8 mmoldm^{-3} was prepared in ethanol-water mixture. All measurements were carried out at 25°C using a Perkin Elmer 554UV -V15 spectrophotometer. A portion of this solution was used as solvent for CTAB solutions. The differential absorption spectra was measured by placing CA solution in the reference side and the CTAB solution at the same ethanol and CA concentration in the sample side of the spectrophotometer.

Determination of CMC ; Measurements of surface tension of CTAB solutions with ethanol were made using Du Nouy tensiometer at 25°C.The CMC's were determined from the inflection point in the graphs between surface tension and CTAB concentration for each ethanol percentage.

RESULTS and DISCUSSION

Figure 1 shows the CMC of CTAB at 25°C as a function of ethanol percentage . The presence of ethanol at low concentrations slightly enhanced micelle formation and had inhibitory effect above 1% by volume and were totally inhibitory at the concentrations above 15% by volume. The CMC data obtained in this study, were in good agreement with the published data of the CMC of CTAB in the presence of ethanol. (6)

The process of micellization is generally explained in terms of hydrophobic interactions of surfactant with water and solvophobic interaction of surfactant with nonaqueous or mixed aqueous media, which describes an entire array of inter and intramolecular interactions involved in micellization. The driving force for micellization in mixed ethanol aqueous media is less than that of water. The effect of ethanol on the CMC of CTAB can be understood by considering the interaction between water and ethanol that results in a decrease of polarity of the media and changes in the water structure that decreases the solvophobic interaction .

The aim of this work was to find a relation between the partition coefficient that is the fraction of the solubilized CA in micelles and its solubility that is the fraction of the amount of CA in the bulk phase. CA is almost insoluble in water ,so it is almost completely solubilized in the CTAB micelles.In order to increase the solubility of CA in aqueous phase increasing amounts of ethanol was used .When it becomes more soluble by the addition of ethanol ,would be expected to partition between aqueous and micellar phases. As seen in Figure 2 absorbance of CA at a constant concentration of 6.8mmoldm^{-3} increased with increasing ethanol percentage. The spectrum of CA in aqueous CTAB solution was similar to its spectrum in ethanol, indicating that the CA molecules solubilized in the palisade layer of the micelles(3,7,8).

The distribution of CA between aqueous ethanol mixture and micellar phase is a complex phenomenon since the quaternary systems (e.g.,water-surfactant-alcohol-oil) are too complicated to study quantitatively.In this study the quaternary system contains water,ethanol,CTAB and CA.The latter may interact with CTAB monomers, micelles, ethanol and with water and also ethanol may interact with micelles. All of these will shift the CMC and influence the size and shape of the micelles and of course changes the physico-

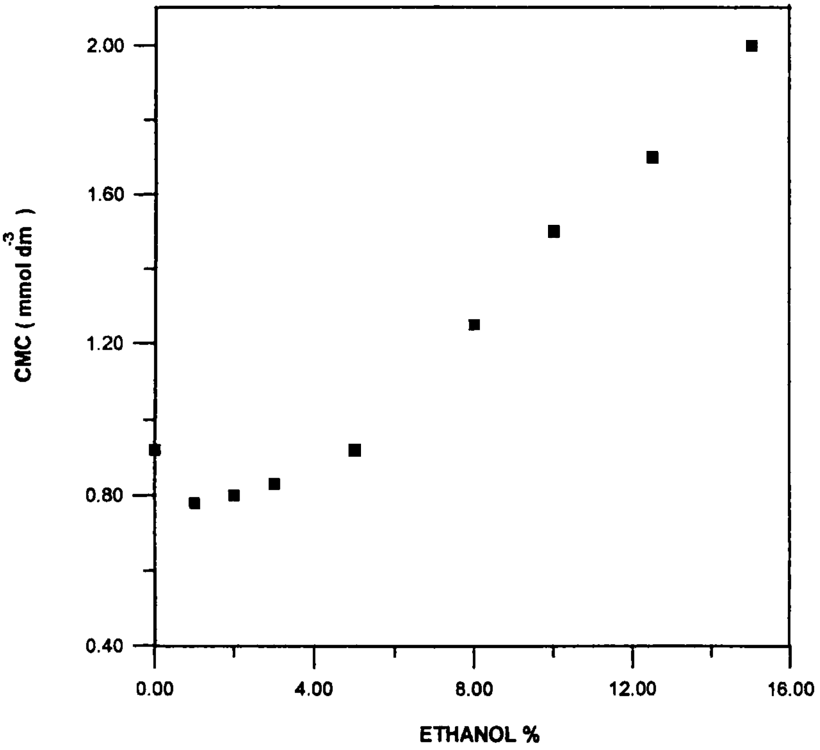

Figure 1. Variation of CMC of CTAB as a function of ethanol concentration.

chemical properties of the bulk .(4) Up until now, there has not been any published studies which consider all these effects together. However, most of the studies investigated each effect separately. For example , Christian et al.(9), De Lisi et al. (10,11,12) Hetu et al. (4) and Kawamura et al. (5) have concentrated on the distribution of solute between aqueous medium and the micelles, while Treiner (13) ,Ionesco et al. (6) and Leund et al. (14) have studied the influence of the solute on the CMC.

In this study, it was assumed that the inclusion of the CA molecules into the CTAB micelles was independent of the ethanol molecules already transferred and the transfer of CA did not cause a change in the micellar aggregation number. In order to understand the solely effect of ethanol, CA concentration was held constant to eliminate its influence.

Figure 3 shows the relation between the differential absorbance , ΔA of CA at the same concentration,and CTAB concentration for each ethanol percentage. As seen from

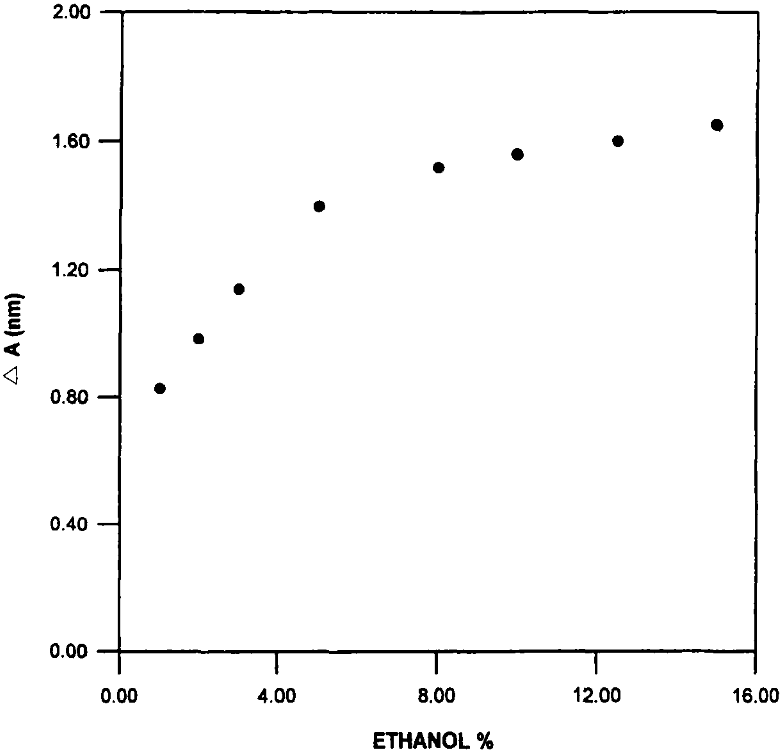

Figure 2. Absorbance of CA (6.8 mmoldm^{-3}) as a function of ethanol concentration.

Figure 3, ΔA was almost zero at low concentrations of CTAB, however an increase in ΔA was observed at a certain concentration of CTAB which accordingly would be assumed to be coincident with CMC of CTAB in the presence of ethanol. The increase of ΔA can be attributed to an increase in the amount of solubilized CA in the micelles. Further addition of CTAB, increased ΔA until it reached a plateau at which it remained almost constant. The plateau implies mutual solubility equilibrium of CA between micelle and bulk phases. This pointed out an equilibrium between the portion of CA solubilized in the micelles (concentration,C_{CA}^{m}) and the rest (concentration,C_{CA}^{b}) still remained in the bulk aqueous phase ,the total concentration C_{CA} equals to C_{CA}^{m} plus C_{CA}^{b}.

The fraction " J" of the solubilized CA in the micellar phase may be defined as:

$$J = \frac{C_{CA}^{m}}{C_{CA}} \qquad (1)$$

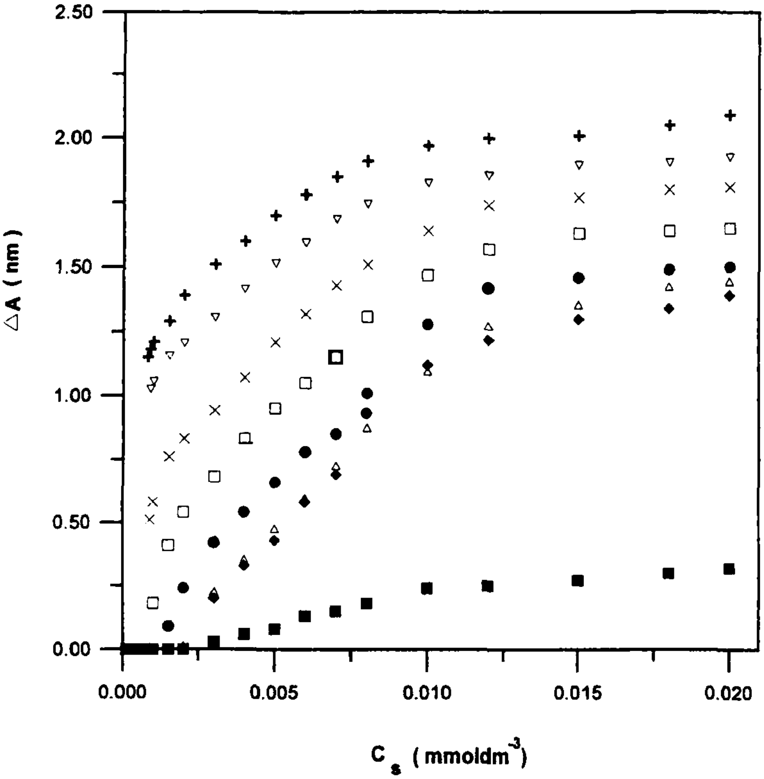

Figure 3.Differantial Absorbance (ΔA) of CA (6.8 mmoldm^{-3}) as a function of CTAB concentration at various ethanol percentages.(+) 1% ,(▽) 2 %,(×) 3 % ,(□) 5 % ,(●)8% (△) 10 %, (◆) 12.5 %, (■)15 %.

At a certain $C_{CA,}$ it is equal to zero in nonmicellar region and increases with increasing CTAB concentration and approaches unity as CTAB concentration increases up to infinity.It is related to a differential absorbance as

$$J = \frac{\Delta A}{\Delta A_\infty} \qquad (2)$$

where ΔA_∞ represents ΔA at infinity of CTAB concentrations.

The solubilization equilibrium constant or partition coefficient of an organic solute in an aqueous micellar solution (K_c) is defined as the ratio of molar organic solute in the micellar phase to the molar concentration of the unsolubilized organic solute in the aqueous phase. The approach for the determination of K_c has been described previously by

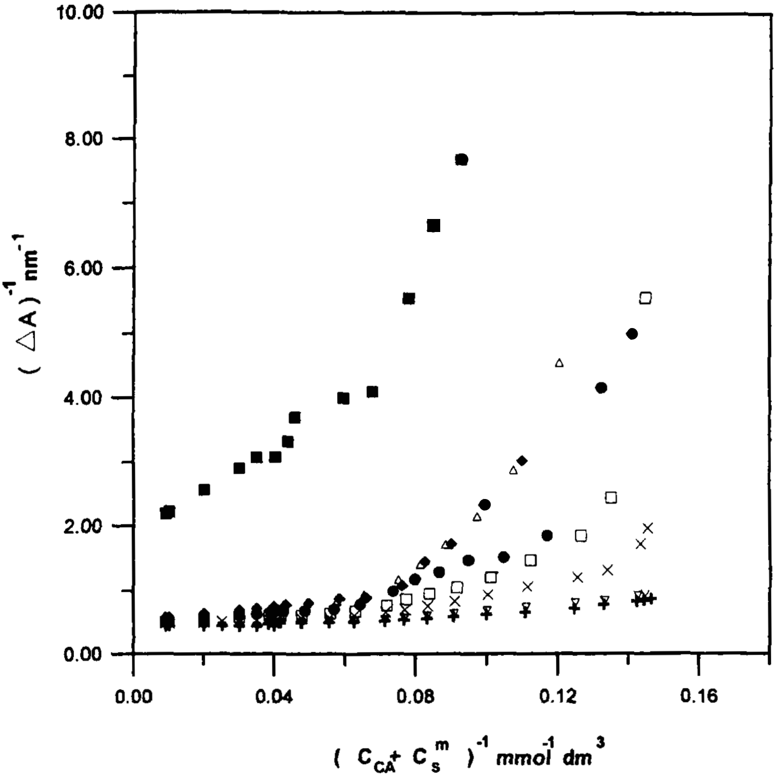

Figure 4a. Relation between $(\Delta A\ )^{-1}$ and $(C_{CA}\ + C_s^m\ )^{-1}$ for CTAB at various ethanol concentration. Straight line was determined by the least squares method. (✚) 1% , (▽)2 %, (×) 3 % ,(□) 5 % ,(●) 8% ,(△) 10 %, (◆) 12.5 %, (■)15 %.

Kawamura et al. which is based on the pseudo phase equilibrium model.(5,6) This model treats the surfactant and dissolved organic solute in the micelles as being analogous to a separate condensed phase which is thermodynamically in an equilibrium with the bulk aqueous phase.

K_c , for an organic solute between bulk aqueous and micellar phase can be defined as

$$K_c = \frac{C_{CA}^m / (C_{CA}^m + C_s^m)}{C_{CA}^f} \qquad (3)$$

where, C^m_s represents the concentration of CTAB in micellar state. As the concentration of CTAB approaches infinity.C^m_{CA} and C^m_s approach C_s and C_s^{mo} respectively and

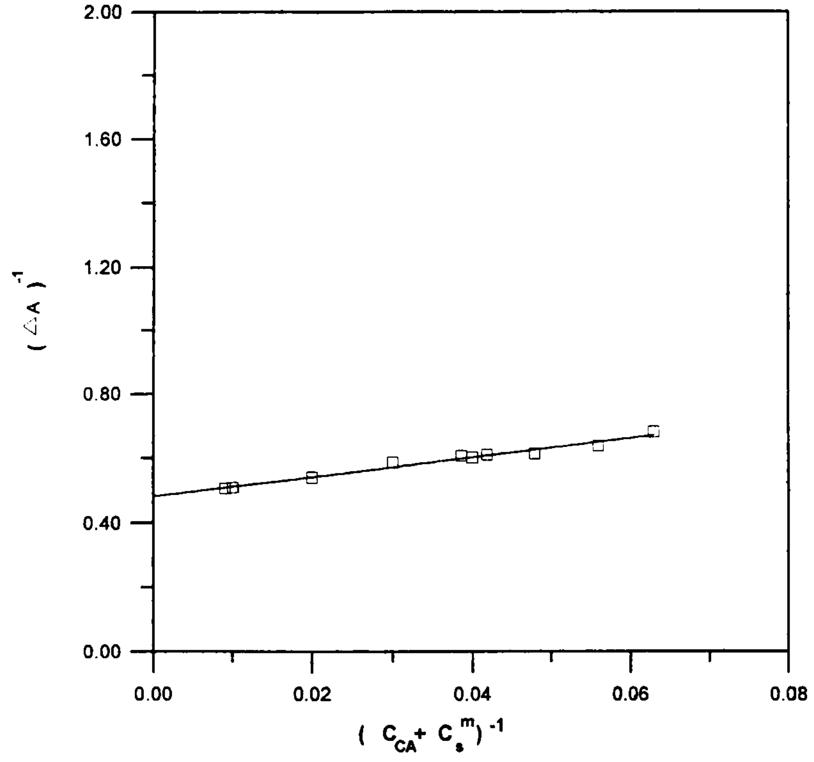

Figure 4b. Relation between $(\Delta A)^{-1}$ and $(C_{CA} + C_s^m)^{-1}$ for CTAB at 5 % ethanol concentration was given as an example.

$C_s^{mo} = C_s - CMC'$. (CMC' is the CMC of CTAB in the presence of various amount of ethanol.) Using these equations a simple linear relation is obtained as,

$$\frac{1}{\Delta A} = \frac{1}{K_c \Delta A_\infty (C_{CA} + C_s^{mo})} + \frac{1}{\Delta A_\infty} \qquad (4)$$

So, K_c and ΔA_∞ can be obtained from the plot of $1/\Delta A$ versus $1 / (C_{CA} + C^{mo}_s)$.As can be seen in Figure 4a, the linear relation of the Eq. 4 was valid in a high C_s region below which the curve bend upwards with decreasing C_s in agreement with Kawamura et al (5). Changes in $(\Delta A)^{-1}$ values were close to each other at various ethanol percentages. Straight lines for each ethanol percentages were determined by the least-square method where the linear relation exist . Only 5 % ethanol-water mixture was shown as an example in Figure 4b . The intercept and the slope of the linear relation provide ΔA_∞, and K_c . The results summarized in Table I. and the dependence of K_c on the ethanol concentrations studied was shown in

TABLE 1: The values of K_c and ΔA_∞ at various ethanol concentration.

Ethanol %	K_c ($dm^3 mol^{-1}$)	ΔA_∞
1	399.11	2.278
2	305.40	2.188
3	212.17	2.159
5	156.42	2.092
8	109.37	2.080
10	99.90	1.953
12.5	92.40	1.912
15	54.81	0.532

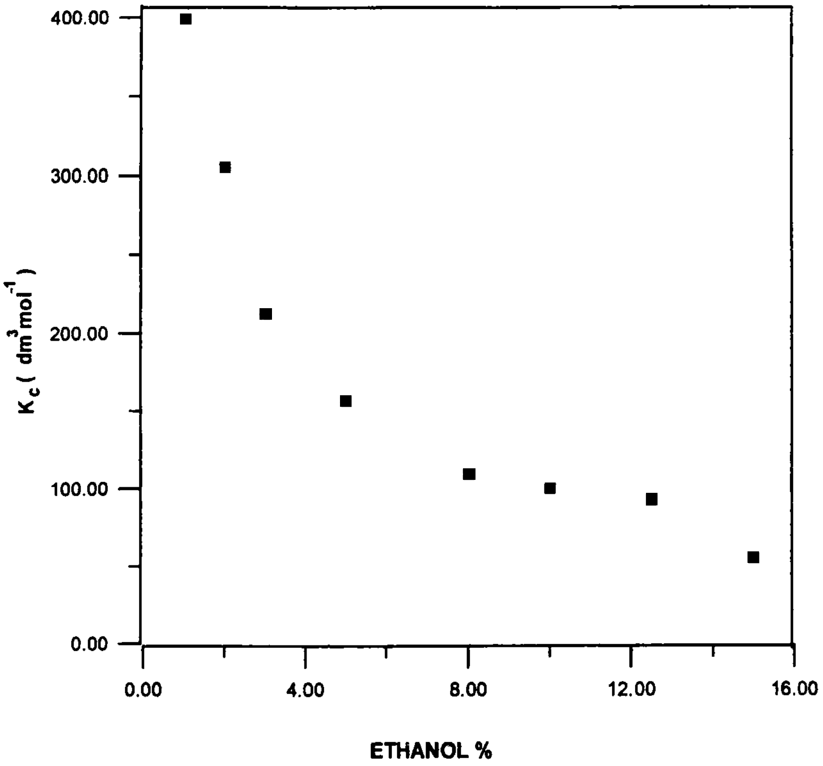

Figure 5. Dependence of K_c on the ethanol concentration.

Figure 5. The K_c values were treated as ideal constants since all the causes of non-ideality resulting from all kind of interactions takes place in the system were ignored.

It was seen that as more ethanol present in the quatemary system the fraction of CA existing in the micelles declined with addition of ethanol as the solubility of CA in the bulk increased. K_c was found to be inversely proportional to the solubility of CA. The solubility of CA in the aqueous phase was very low and it was almost completely solubilized by the micelles and when CA became more soluble in higher percentages of ethanolic -water mixture it partitioned between bulk and micellar phase. Increasing ethanol addition also affects the aqueous phase by decreasing its dielectric constant causing it to be more hydrophobic. The equilibrium balance was found to be preferentially directed towards the aqueous phase with an increase in the ethanol percentage. Therefore, the tendency of CA to distribute itself in micelles depends on not only its hydrophobicity but also on the hydrophobicity of the medium. This could be considered as an another factor resulting lower K_c with increasing ethanol concentration.

As a conclusion, it can be said that a correlation between the micelle-aqueous phase partition coefficient and its solubility in aqueous phase should exist for the same compound.

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