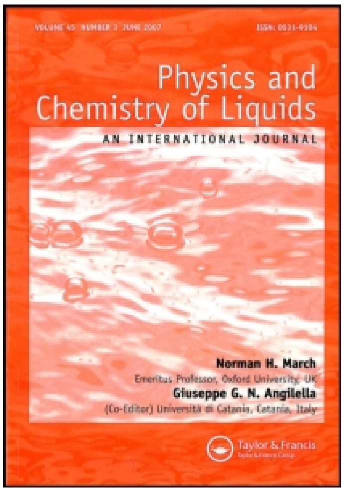

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A. A. Rafati[a]; H. Gharibi[b]; H. Iloukhani[a]
[a] Department of Chemistry, Faculty of Science, Bu-Ali Sina University, Hammadan, Iran [b] Department of Chemistry, Tarbiat Modares University, Tehran, Iran

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MICELLIZATION OF CETYLPYRIDINIUM CHLORIDE USING CONDUCTOMETRIC TECHNIQUE

A. A. RAFATI[a,*], H. GHARIBI[b] and H. ILOUKHANI[a]

[a]*Department of Chemistry, Faculty of Science, Bu-Ali Sina University, Hammadan, Iran;* [b]*Department of Chemistry, Tarbiat Modares University, Tehran, Iran*

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Conductometric technique has been used to investigate the equilibrium properties of cetylpyridinium chloride (CPC) in the presence of a series of aliphatic alcohols. The dependence of conductivity of surfactant solution in the presence of particular amount of alcohol has been studied. According to the experimental results, ethanol cause to decrease the dielectric constant and conductivity of micellar solution. Alcohols with longer chain may change the conductivity of solution depend on concentration of surfactant. At low concentration of CPC near critical micelle concentration (cmc) region, the minimum value of conductivity can be observed. This minimum value can be controlled by decreasing of free monomer concentration and also increasing degree of dissociation of micelle because of penetration of alcohols in micellar core. Using Conductometric technique cmc and α (degree of dissociation of counterion) of CPC were evaluated. The micelle formation of CPC has been considered in ethylene glycol (E.G)/water and glycerol/water mixtures. It has been shown, the logarithm of cmc is directly depended on the ratio of E.G/water or glycerol/water.

Keywords: Surfactant; Aliphatic alcohols; Conductivity

1. INTRODUCTION

Surfactant molecules are associated into micelles above the critical micelle concentration (cmc). Micelle formation of ionic amphiphile molecules in aqueous solution is dynamic associations of surfactant

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*Corresponding author.

molecules that achieve segregation of their hydrophobic portions from the solvent *via* self assembly [1]. Both attractive, as hydrophobic associations, and repulsive, as electrostatic interactions, forces govern the micellization of ionic amphiphiles [2, 3]. It is well known that the micelle formation to be affected by a number of environmental factors such as pH, ionic strength, temperature and the presence of various additives. The effect of organic additives on micellization of anionic and cationic surfactants has been well studied [4–8]. To quantitative understanding of solvent effects on aggregation process, it is necessary to distinguish between three classes of organic materials that markedly affect the cmc of aqueous solution of surfactants: (I) those in which give rise to solvophobic interactions, *i.e.*, the nonpolar portions of the amphiphiles are shielded from solvent upon aggregation; (II) electrostatic interactions are primarily responsible for aggregation and the amphiphiles polar head groups are shielded from solvent; (III) those in which aggregation does not occur.

Addition of alcohols and other organic additives to a solution of an ionic surfactant is known to affect the micellar properties by changing the structure of the solvent and of the surfactant aggregates. It has been shown that additive may be distributed between aqueous and micellar phases and may accumulate both in the polisade layer and inside the micelle hydrophobic core, thus favoring the stability of the system. The solubilization process of additives in micelles has been studied by considering the nature of both the additive and the surfactant [9–15]. Moreover, more attention has been paid attention to polar additives rather than to nonpolar ones because the latter have very low solubility in water.

To our knowledge no data are available on the (cmc), degree of dissociation of counterion (α) and behavior of CPC in nonaqueous solvents. In the present work we analyzed the micellar behavior of CPC in a number of aliphatic alcohol and two solvents that have a highly hydrogen-bonded structure, *i.e.*, ethylene glycol (E.G) and glycerol. To determining cmc and α, we used conductometric technique at constant temperature.

2. EXPERIMENTAL SECTION

Cetyl pyridinium chloride (CPC) was obtained from Aldrich Chemical Co. (purity > 98%). The additives (ethanol, *n*-propanol, *n*-butanol, *n*-pentanol, ethylene glycol and glycerol) were all Merck products and were used as received. All solutions were prepared in double distilled water. The conductance was measured by using Genway conductometer (model 4020) and the conductivity cell was calibrated with KCl solution in the appropriate concentration range. The measuring cell was immersed in a thermostat bath, keeping the temperature constant within ± 0.1 K.

3. RESULTS AND DISCUSSION

The change in the electrical conductance of aqueous ionic surfactant solution at the cmc is due to the different degree of surfactant ionization below and above the cmc. The specific conductivity, k, of surfactant solutions can easily be calculated in terms of the molar ionic conductivities of ions, λ_i. Electrical conductivity below cmc is written as:

$$k = \lambda_{s^+}[S^+]_f + \lambda_{c^-}[C^-]_f \tag{1}$$

below the cmc

$$[S^+]_f = [C^-]_f = C_f$$

where $[S^+]_f$ and $[C^-]_f$ are the concentration of free surfactant and its counterion, respectively and λ_{s^+} and λ_{c^-} are corresponding to molar ionic conductivities. The perfect dissociation of ionic surfactant is assumed below the cmc [16]. The slope (S_1) of molar conductivity becomes:

$$S_1 = k/C_t = \lambda_{s^+} + \lambda_{c^-} \tag{2}$$

Above the cmc, the specific conductivity is expressed as:

$$k = \lambda_{s^+}[S^+]_f + \lambda_{c^-}[C^-]_f + \lambda_m[C]_m \tag{3}$$

where $[C]_m$ and λ_m are the concentration and ionic molar conductivity of micelle, respectively. Above the cmc, concentration of free counterion, $[C^-]_f$, is expressed as:

$$[C^-]_f = \text{cmc} + \alpha[M]_m \tag{4}$$

where $[M]_m = C_t - \text{cmc}$; and above the cmc, $[S]_f$ is assumed to be constant and equal to cmc. Combining Eqs. (3) and (4), one obtains:

$$k = (\lambda_s + \lambda_c)(\text{cmc}) + \lambda_c\alpha[M]_m + \lambda_m[C]_m \tag{5}$$

Taking into account that $[C]_m = (C_t - \text{cmc})/N_{\text{agg}}$ and assuming that the contribution of the micelle to the conductance is the same as that of an equivalent number of monomeric ions, the sum of whose charges equals the micellar charge, then $\lambda_m = \alpha N_{\text{agg}} \lambda_s$ and Eq. (5) becomes:

$$\begin{aligned} k &= (\lambda_s + \lambda_c)(\text{cmc})(1 - \alpha) + (\lambda_s + \lambda_c)\alpha C_t \\ k &= k_o + S_2 C_t \end{aligned} \tag{6}$$

where S_2 $(= \alpha S_1)$ is the slope of the linear plot of k *vs.* C_t above the cmc, and k_o is the corresponding intercept.

Plot of specific conductivity, k, against of total concentration of CPC in water at 303 K is illustrated in Figure 1. The cmc value can then be determined as the cross point of the two straight lines defined by Eqs. (2) and (6). The degree of dissociation of counterion (or degree of micellar ionization), α, can be obtained as the ratio of the slopes of conductance *vs.* C_t above and below the cmc; that is:

$$\alpha = S_2/S_1 \tag{7}$$

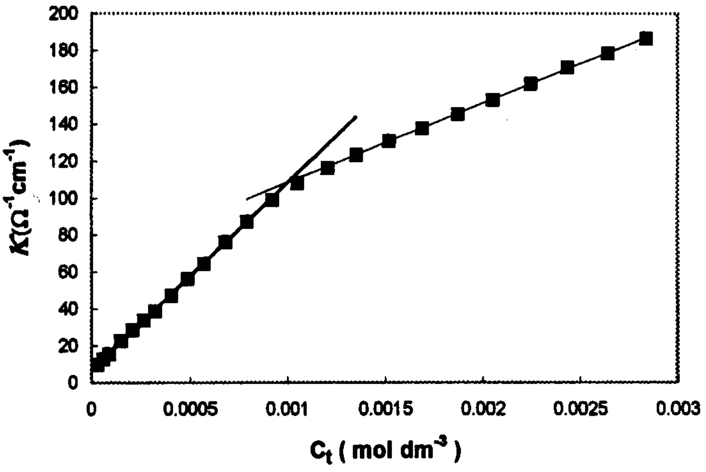

FIGURE 1 Specific conductivity *vs.* total concentration of CPC in water at 303 K.

3.1. Effect of Aliphatic Alcohols on Properties of Micellar Solutions of CPC

Figure 2 shows the specific conductivity of aqueous CPC solution in the presence of various concentration of ethanol. These plots show how the cmc is affected by a range of ethanol concentrations.

At low concentration of alcohol, the cmc is found to decrease with addition of more alcohol whilst at higher concentration it is found to be increased (Fig. 3). The results for used alcohols are reported in Table I. We believed that the addition of alcohols thermodynamically stabilizes the micelle at lower alcohol concentration and destabilize at higher alcohol concentration. The values of cmc of CPC have been determined in various type of alcohols with changing in carbon number by Shinoda [17]. These results indicate a linear relationship between the change of cmc and carbon number of alcohols. As the chain length of the alcohol becomes longer a larger part of the chain can enter the hydrophobic core [18]. Short-chain alcohols are usually known as cosolvents which are highly miscible with water, while the larger one are known as cosurfactants which soluble in micellar phase.

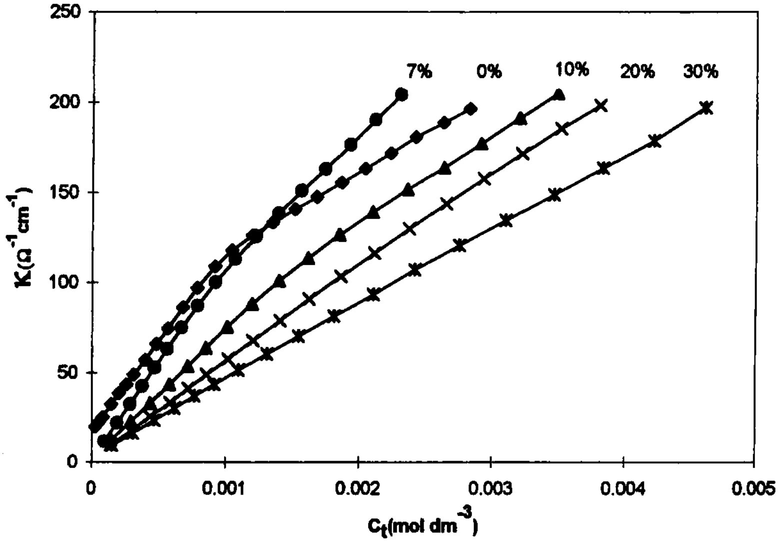

FIGURE 2 Conductivity, *k* *vs*. total concentration of CPC in various concentration of ethanol at 303 K.

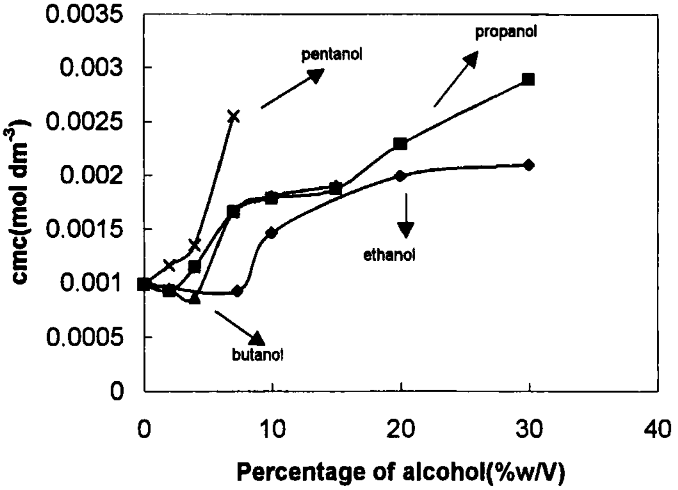

FIGURE 3 The cmc of CPC in mixed solvent as a function of alcohol concentration at 303 K.

TABLE I The value of cmc of CPC in water–alcohol mixtures at 303 K

%*w*/*V*	2%	4%	7%	10%	15%	20%	30%
C_2H_5OH			0.92	1.46		1.99	2.10
C_3H_7OH	0.92	1.14	1.66	1.78	1.87	2.29	2.89
C_4H_9OH	0.94	0.87	1.84	1.66	1.84		
$C_5H_{11}OH$	1.16	1.35	2.55				

Cosolvents which lower the dielectric constant of water increase the counterion binding and hence decrease the conductance of the solution, but this prediction seems only valid for few additives. This behavior was observed for ethanol, while the conductance was passed through a minimum or maximum, depends on concentration of CPC, for longer alcohols (Figs. 4 and 5). The alcohols that have not highly miscibility with water penetrate into micelles [19]. Also the addition of alcohols may affect the structure of the stern layer in two ways: the amount of water molecules can become larger and this will lead to a decrease of the cmc and an increase of the aggregation number. The second way is inserting of alcohol molecules between the head groups of the surfactant molecules that will screen the electrostatic repulsion of the head groups less than the water molecules they replace and this

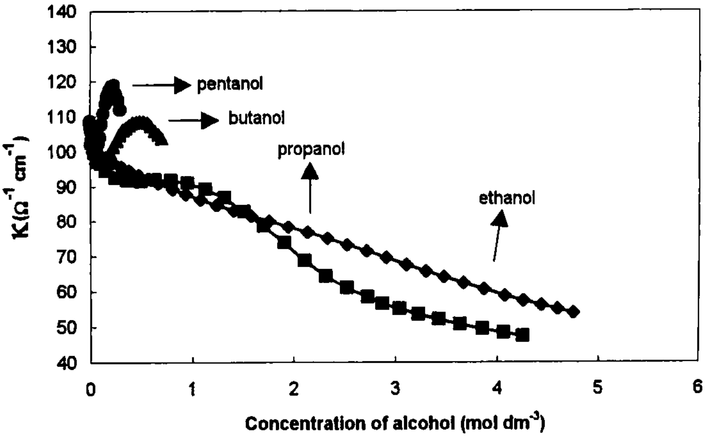

FIGURE 4 Variation of the conductivity of 10 mmol dm^{-3} CPC solution as a function of alcohol concentration at 303 K.

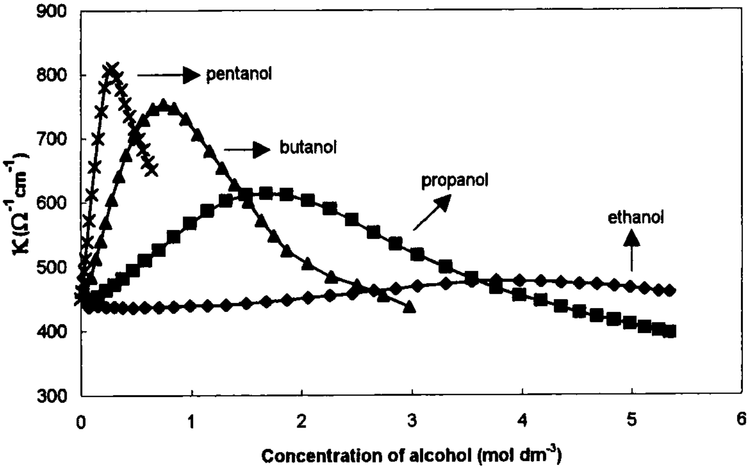

FIGURE 5 Variation of the conductivity of 100 mmol dm^{-3} CPC solution as a function of alcohol concentration at 303 K.

leads to an decrease of the charge density at the micellar surface. Conductivity measurements indicate that α increases upon addition of alcohols (Tab. II).

Figures 4 and 5 show the change of conductance as a function of alcohol concentration. These results can be interpreted in terms of the

TABLE II The values of α of CPC in water–alcohol mixtures at 303 K

%*w*/*V*	2%	4%	7%	10%	15%	20%	30%
C_2H_5OH			0.63	0.65		0.77	0.90
C_3H_7OH	0.54	0.68	0.82	0.73	0.92	0.95	0.92
C_4H_9OH	0.62	0.74	0.76	0.92	0.76		
$C_5H_{11}OH$	0.80	0.96	0.90				

comicellization effect. Since the penetration of alcohol into micelles can decrease the cmc and hence the surfactant monomer concentration [20] and increase the degree of dissociation of micelles [21], the addition of alcohols into micellar solutions is expected to decrease the conductance contributed by the surfactant monomers, while increase the conductance by the micelles and their counterions. At low alcohol concentration, the decrease of conductance with increasing of alcohol can be attributed to the decrease of the cmc upon the addition of alcohols [22]. As alcohol concentration increases, the increase in conductance is due to the increasing degree of dissociation of micelles. The direct increase in conductance observed in Figure 5 indicate that the conductance of a micellar solution at higher surfactant concentration is indeed dominated by the micelles, and hence the effect of cmc depression can not be detected by the conductance measurement. On the other hand, the cmc depression at low alcohol fractions can also be partly ascribed to the structure promotion of water [19–23]. At higher alcohol concentrations, the cmc was increased and micelles break down that correspond to the disruptive effect of alcohols on the structure of water.

3.2. Micellization in E.G/Water Mixture

In the present work the values of cmc and α for CPC has been measured in the range 0.0–50.0%w/V of E.G. As has been shown in Figure 6, the cmc of CPC is increased as the concentration of E.G is increased. Also the α value in this media are presented in Table III. These observations can be attributed to the structure-breaking nature of E.G in water, reducing the hydrophobic interactions which are the main driving force for micelle formation. Moreover, the increase in cmc value with increase in E.G content (Fig. 6) in E.G/water systems can be explained on the basis of a decrease in cohesive energy density

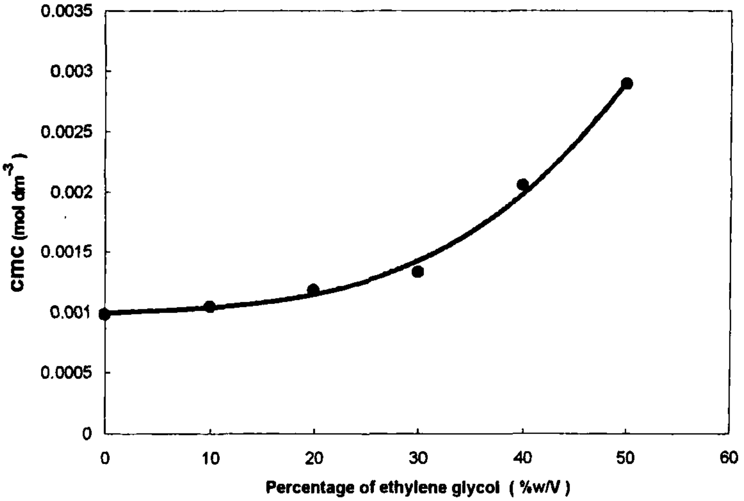

FIGURE 6 Plot of cmc *vs.* concentration of ethylene glycol in water at 303 K.

TABLE III The values of cmc and α of CPC in different concentration of (E.G) at 303 K

%w/V	10	20	30	40	50
cmc (mM)	1.05	1.18	1.32	2.04	2.89
α	0.422	0.456	0.466	0.474	0.573

which increases the solubility of hydrocarbon chain of the surfactant monomers.

3.3. Effect of Glycerol on Micellization of CPC

The solubility of glycerol in hydrocarbons is very small and it is therefor expected that this additive will not penetrate into the micellar interior. Since glycerol has three hydrogen bonding centers in its structure it is very likely to form hydrogen bonded network structures. It is generally believed that there is an increase in ordering of the water surrounding the nonpolar parts of the solute. This is a result of hydrogen bonding and on the formation of the hydrophobic bond this order is diminished so that there is a positive entropy change. In a similar way Ray [24] reported that there are solvophobic interactions in several nonaqueous polar solvents such as glycerol, E.G *etc.*

It has been suggested that solvophobic interactions seen to be most pronounced in water, and to a slightly smaller extent in glycerol. Both water and glycerol have very high concentration of OH groups per unit volume, so it can be argued that the solvophobic interaction is caused by an incompatibility of the OH groups of the solvent molecules with the hydrocarbon parts of the nonpolar solutes.

To understand the effect of glycerol on the micellization of CPC, different concentrations of glycerol (10, 20, 30, 40, 50 and 60%w/V) have been studied. Figure 7 shows the plot of *k* as a function of CPC concentration. In the case of 10% glycerol the value of cmc does not change and is similar to the magnitude of cmc in water. An increase in concentration of glycerol from 10%w/V to 60%w/V leads to increasing in cmc value. The values of cmc of CPC in glycerol/water system listed in Table IV.

As shown in Table IV the degree of dissociation of CPC in the presence of glycerol is increases with increasing in percentage of

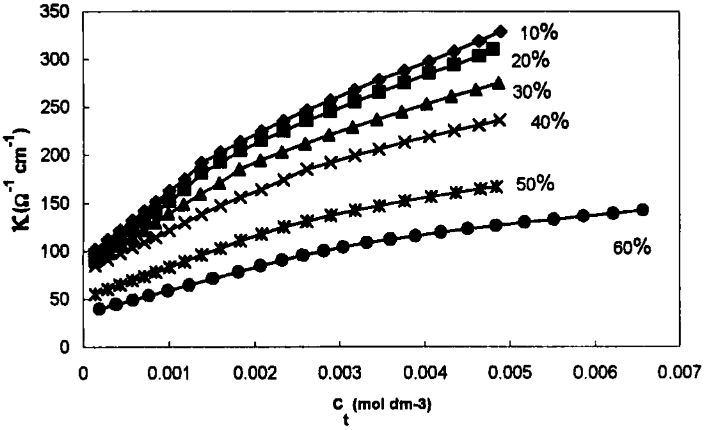

FIGURE 7 Conductivity *k*, *vs.* total concentration of PCP in various glycerol/water percentage at 313 K.

TABLE IV The values of cmc and α of CPC in different concentration of glycerol at 313 K

%*w*/*V*	10	20	30	40	50	60
cmc (mM)	1.66	1.78	2.01	2.60	2.63	3.26
α	0.532	0.499	0.478	0.483		

glycerol. At higher concentration of glycerol (50% and 60%) because of problem in the determination of the slope below and above the cmc, the value of α can not be measured perfectly.

Another factor which may be important in the determination of α is the dielectric constant of glycerol which is 42.5 compared to 78.5 for water [24] on this basis we predict that the dielectric constant is an unimportant factor in the determination of α, because it decrease as the concentration of glycerol is increased. As we reported earlier [25], the cmc normally increased logarithmically with the concentration of additive (cosolvent) according to the following relation:

$$\log(\mathrm{cmc})_{\mathrm{mix}} = \log(\mathrm{cmc})_o + KC_{\mathrm{alc}} \qquad (8)$$

where $(\mathrm{cmc})_{\mathrm{mix}}$ and $(\mathrm{cmc})_o$ are critical concentration of surfactant in mixed solvent and water, respectively. Also C_{alc} is the solvent/water ratio in wt% and K is a constant. The plot of $\log(\mathrm{cmc})_{\mathrm{mix}}$ against C_{alc} for glycerol and E.G/water mixtures is shown in Figure 8. The values of K for glycerol/water and E.G/water mixture are 0.00583 and 0.0112, respectively. This is indicating that the effect of E.G on micellization of CPC in comparison with glycerol is predominant.

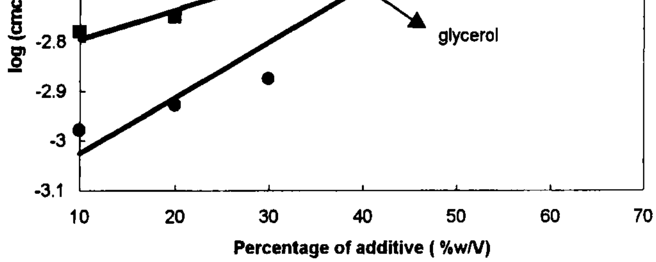

FIGURE 8 Plot of log (cmc) *vs.* concentration of cosolvent in water.

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