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Cloud point extraction for separation, preconcentration and determination zinc (ii) in different *pharmaceutical* samples

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ABSTRACT

Joining solvent extraction with cloud point extraction methods obtained a susceptible method for separation, pre-concentration, extraction and categorization of Zn (II), after forming an ion-pair association complex between Zn+2 and 4-(3-methyl phenyl azo)-4,5- diphenyl imidazole (MPADPI) with wavelength for maximum absorbance λmax.=496 Nm. This study shows optimum conditions for the formation and exaction ion-pair association complex under pH=9 and 0.5 mL Tritonx-100, 1×10-4 M (MPADPI) and heating at 80 Co for 20 minutes so that this study involved the effect of electrolyte and interferences along with the spectrophotometric determination of Zinc (II) in diverse samples.

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INTRODUCTION

As the sensitive and accurate process of cloud point extraction CPE for separation, pre-concentration and determination, many metal cations after converting their ions to suitable species can be extracted into cloud point layer, CPL intended for *numerous* industrialized, environmental, medical and *medicinal uses*. The extraction and categorization of Fe(II) in dissimilar samples has testified using safranin in HCl medium in order to create ion-pair association complex with wavelength for maximum absorbance λmax.=530 Nm. It included determination all of the optimum conditions and studied the effect of some parameter with thermodynamic study and spectrophotometric determination of Fe(II) in diverse samples (Shawket *et al.*, 2018).

Onium system joined with CPE process for separation and determination of Co (II), the supreme absorbance was at wavelength $\lambda_{max.=}$294 Nm with optimum conditions 0.8 M HCl, 0.5 mL Triton X-100, and heating the solution at 85 C^o for 15 minutes (Hayder and Jawad, 2017). Triton X-114 used in many studies for separation and extraction of different metal cations in different species by solvent extraction (Chen and Teo, 2001; Majedi *et al.*, 2014; Vatankhah *et al.*, 2018; Zhang *et al.*, 2017; Blanchet-Chouinard and Larivière, 2018; Ghasemi and Kaykhaii, 2016; Jawad and Husien, 2018). As sensitive method extraction and determined Zn (II) in diverse tasters after pinpoints all optimal conditions of the extraction method to get highly extraction efficiency several studies about separation, extraction and determination of different metal cations (Jawad and Husien, 2018; Yang *et al.*, 2017; Jalbani and Soylak, 2015; Barache *et al.*, 2018; Şatıroğlu and Arpa, 2008; Ren *et al.*, 2013; Abed, 2015).

In the present work, 4-(3-methyl phenyl azo)-4,5-diphenyl imidazole (MPADPI) was used to determine Zn (II) by CPE and preconcentration after complexation with Zn (II), ions. The method was utilizing the complexation of Zn (II), with MPADPI in the existence of Triton X-100 (non-ionic surfactant). Optimal investigational conditions were examined relating to a standard solution of the identical medium, with the intention of exploring the probability to attain the highest extraction efficiency with minimal sample treatment and minimum tentative conditions. This stands for a substitute technique for the investigation of metal ions in many samples based on their environmental importance.

MATERIALS AND METHODS

Experimental

Spectrophotometric and absorbances measurements are based on Biochrom double beam spectrophotometer (Biochromlibra 560) (A Harvard Bioscience company Cambridge UK), electrostatic water bath (Hambory 90, England). All chemical are employed as received from Authorized companies with further purification so that used deionized water is used for preparing all solutions by using a suitable volumetric flask.

Comprehensive method

Aqueous solution 10mL in volume contains optimum quantities of Zn^{2+} ion at optimum pH, TritronX-100 volume, while 1x10-4M of 4-[3-methylphenyl azo]-4,5-diphenyle imidazole (MPADPI) was heated in an electrostatic water bath at optimum temperature and time of heating until the formation of CPL. Subsequently, separate the CPL and dissolve in 5mL ethanol, and measure the absorbance of the alcoholic solution at extracted mas of ion-pair association complex. Accordingly, treat the aqueous phase according to Dithizon spectrophotometric method and return to calibration curve as inFigure 1 and calculate the remainder and transfer quantity of Zn^{+2} ion to compute Distribution ratio (D).

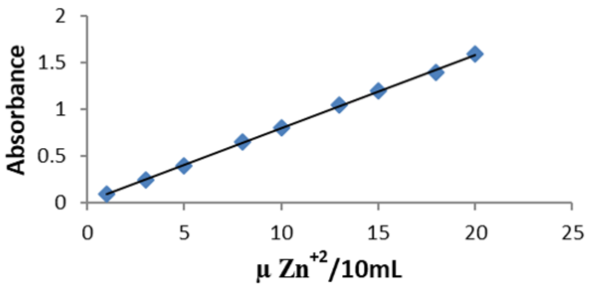

Figure 1: Calibration curve for determining Zinc(II) ion in aqueous solutions

$$D = \frac{[Zn^{2+}]cpl}{Zn^{2+}]aq}$$

RESULTS AND DISCUSSION

Spectrophotometric study of ion-pair association complex extracted into CPL shows the wavelength for the highest absorbance of the complex with ($_{mas}$= 496nm) as in Figure 2.

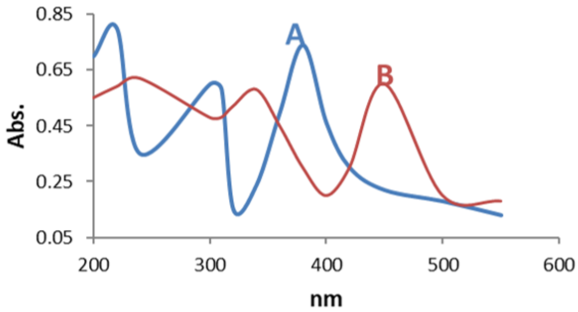

Figure 2: Absorption bands in UV-Vis region for ion-pair association complex of Zn^{2+}ion. A/ the organic reagent, B/the ion-pair complex extracted.

Variation of pH value

10mL aqueous solution contains 50 μg of Zn^{2+} ion at different pH values, in presence $1x10^{-4}$ MADPI and 0.5 mL of Triton X-100. Heat the solution in an electrostatic water bath at a suitable temperature for the exact time until forming CPL. Then, separate CPL from aqueous solution and complete the experiment as in comprehensive method to compute distribution ratio D. The results were as inFigures 3 and 4.

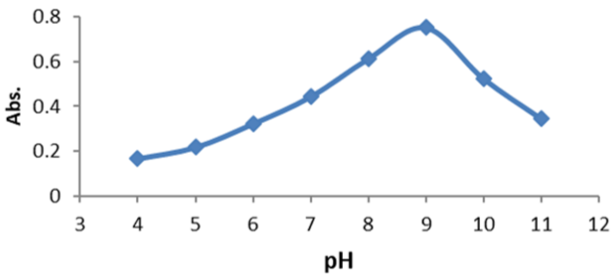

Figure 3: Influence of pH on the formation and stability of the extracted ion-pair complex

The outcomes explain that pH of 9 has the finest value of an acidic function with the higher extraction efficiency of Zn^{2+} for the reason that this pH value gives higher concentration and stability of the ion-pair complex formed. Any pH value less than the optimal value affects to decline extraction efficiency because of the decrease in binding of MPADPI

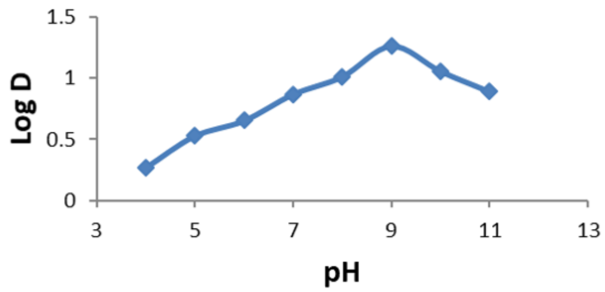

Figure 4: Effect of pH on the extraction efficiency of $Zn^{+2}$and D values

with Zn^{2+} ion so that pH value higher than optimum decline extraction efficiency also.

Variation of metal ion concentration

Aqueous solution 10mL in volume contains the intensifying amount of Zn^{2+} ion at pH=9 in existence 0.5 ml of Triton-100, and 1x10-4 of MPADPI treated these solutions consistent with the adopted comprehensive method. The resultant curves were as in Figures 5 and 6.

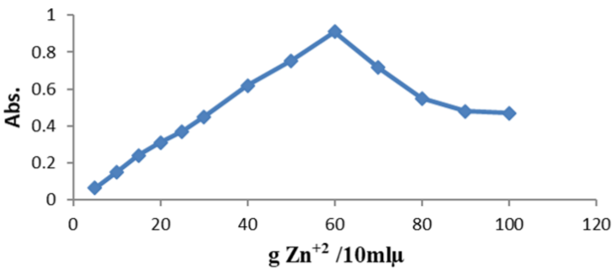

Figure 5: Effect of Zn^{+2} ion concentration on formation and stability of ion-pair extraction complex

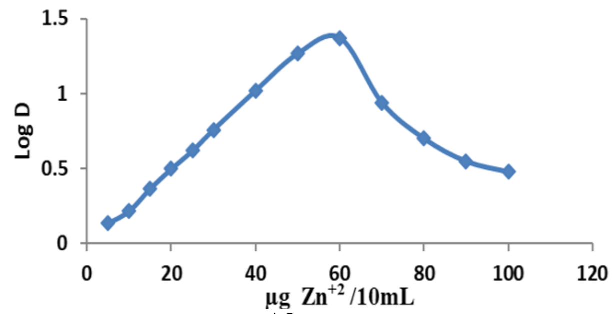

Figure 6: Effect of Zn^{+2} ion concentration on the extraction efficiency of Zn^{+2} and D values

The consequences explain that 60 μgZn^{2+}/10mL as been the best concentration necessary for thermodynamic equilibrium to form ion-pair association complex with higher concentration and stability. Any focus is lower than optimal value inadequate to reach proper thermodynamic equilibrium, so that metal ion Zn^{2+} concentration of higher than optimal value influences to drop extraction efficiency according to mass action law.

Effect of Tritonx-100 Volume

Sequences of aqueous solutions 10mL in volume have been employed with 60μg of Zn^{2+} ion at pH=9 in existence of different volumes of Tritonx-100 and 1x10-4M MPADPI. These solutions have heated in an electrostatic water bath at a suitable temperature and time. The task has completed based on the comprehensive method. The corresponding results have been depicted in Figures 7 and 8.

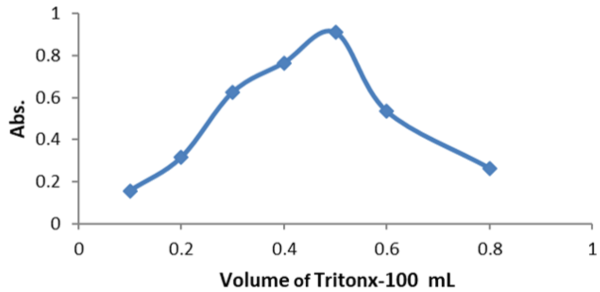

Figure 7: Influence of Tritonx-100 volume on formation CPL with high properties

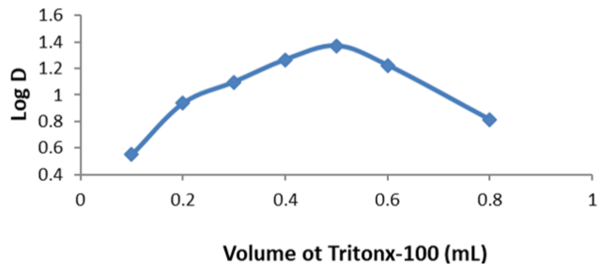

Figure 8: Influence of Tritonx-100volume on extraction efficiency of Zn^{2+} ion

The results explained that 0.5mL of Tritonx-100 was the best volume, which achieves our status of critical micelles concentration (CMC) to form the best CPL with minor volume and greater density to extract a higher concentration of ion-pair association complex of Zn^{2+} ion. Any volume higher than the finest value influences upturn diffusion of micelles in aqueous solution and lessen properties of CPL and extraction efficiency.

Effect of temperature

A sequence of aqueous solutions 10mL in volume has employed with 60μg of Zn^{2+} at pH=9 in presence 0.5mL of Tritonx-100 and $1x10^{-4}$M (MPADPI). These solutions are heated in an electrostatic water bath, but at different temperature for a suitable time until forming CPL and complete the experiment as in the comprehensive method, the consequences were as in Figures 9 and 10.

Afterwards, calculate extraction constant K_{ex} at different temperatures by applying the relation below.

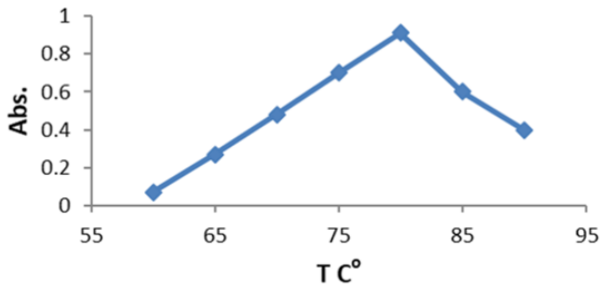

Figure 9: Effect of temperature on formation CPL

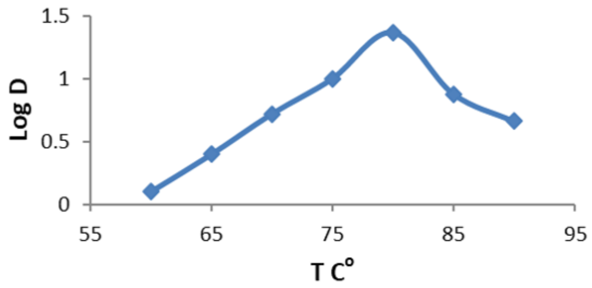

Figure 10: Influence of temperature on extraction efficiency of Zn^{2+} ion

The fallouts are depicted inFigure 11.

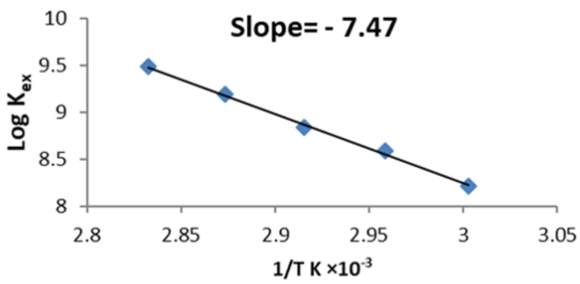

Figure 11: Influence of Temperature on extraction constant values

From the slope of the straight-line relation in Figure 9 and the thermodynamic relation below, the results are clarified in Table 1.

Table 1: Thermodynamic data for extraction constant of Zn^{2+}

ΔH_{ex}	ΔG_{ex}	ΔS_{ex}
0.143 KJ.mol^{-1}	-64.106 KJ.mol^{-1}	182.008 J.$mol^{-1}K^{-1}$

$$\frac{\triangle \log k_{ex}}{\triangle 1/T} = slope = \frac{-\triangle H_{ex}}{2.303R}$$

$$\triangle G_{ex} = -R\,T\,\ln\,K_{ex}$$

$$\triangle G_{ex} = \triangle H_{ex} - T \triangle S_{ex}$$

The optimum temperature for higher extraction efficiency was 80°C, at this temperature formed best cloud point layer (CPL) with food properties for extraction higher concentration of ion-pair association complex of Zn^{2+} ion.

Effect of heating time

A sequence of an aqueous solution of 10mL in volume with 60μg Zn^{2+} at pH=9 has employed in the existence of 0.5mL Tritonx-100 and 1x10-4M (MPDPI). Heat these solutions in an electrostatic water bath at 80 C° for a different time until forming CPL. Then, separate CPL from aqueous solution and dissolve in 5ml ethanol. Afterwards, measure the absorbance of the alcoholic solution at λmax 496nm vis blank prepared at the identical routine in the absence of Zn^{2+} ion and treat the aqueous solution according to Dithizone spectrophotometric technique (Vatankhah *et al.*, 2018) as in comprehensive method. The outcomes were as inFigures 12 and 13.

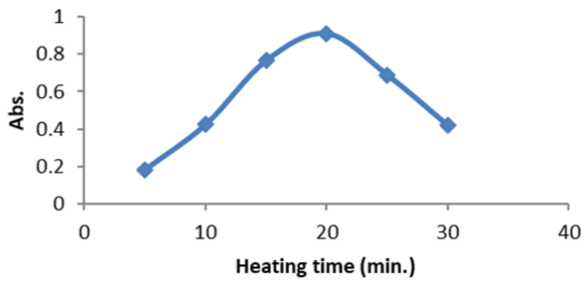

Figure 12: Influence of heating time on formation CPL

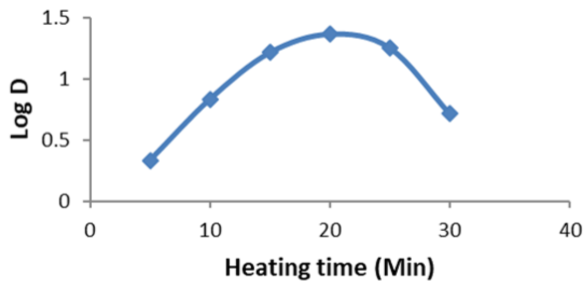

Figure 13: Influence of heating time on extraction efficiency of Zn^{+2} ion

The results have shown that 20 minutes was the optimal heating time necessary to form CPL with the highest features to reach higher extraction efficiency, this time allows us to reach thermodynamic equilibrium for creating the best CPL. Any heating time greater than optimal effect to increase diffusion micelles of TritonX-100 and drop aggregation of micelles and decrease dehydration that is mean decrease in extraction efficiency.

Effect of electrolyte

Aqueous solutions of 10mL in volume have used with 60μg of Zn+2 ion at pH= 9 in presence 0.5mL Tritonx-100, 1x10-4M MPDPI and 0.1M of different electrolytes. Heat these solutions in an electrostatic water bath at 80°C for 20 minutes up to the formation of CPL. Then, separate CPL from aqueous solution, dissolve in 5mL ethanol and record the absorbance of alcoholic solutions at ;mas of 469nm in contradiction of blank organised by the identical manner without Zn^{2+} ion. The aqueous solutions have treated as in comprehensive method to compute D-values, and the results have been detailed inTable 2.

Table 2: Influence of Electrolyte on the extraction efficiency of Zn^{2+} ion

Electrolytes	Abs. 469nm	D
LiCl	1.24	54.56
NaCl	0.985	42.87
KCl	0.956	83.19
NH_4Cl	0.921	28.22
$MgCl_2$	1.08	46.55
$CaCl_2$	0.972	40.58
$AlCl_3$	0.944	31.43

The results have depicted an enhancement in extraction efficiency in the existence of electrolyte in aqueous solution since electrolyte has an effect to lessen dielectric constant and polarity of an aqueous solution, and terminate the hydration shell of Zn^{2+} ion. Namely, there is an increase in binding of metal ion Zn^{2+} with MPDPI to increase ion-pair association complex extracted into CPL. According, there is a dissimilar effect with diverse electrolytes due to the different behaviour of electrolytes in aqueous solution.

Influence of interferences

A series of aqueous solutions 10mL in volume contain 60Mg of Zn^{2+} ion at pH=9 in existence 0.5mL Tritonx-100, 0.1M NaCl, 1x10-4M MPDPI, complete the work as in the comprehensive method, the results were as in Table 3.

The results have demonstrated the presence of these foreign metal cations in aqueous solution effect decrease extraction efficiency of Zn^{2+} ion, for the reason that these metal ions participate Zn^{2+} ion to form ion-pair association complex and this behaviour motivate consumption of some reagent MPDPIs that are in effect to increase the rate of dissociation direction in thermodynamic equilibrium and lessen ion-pair association complex of Zn^{2+} ion extracted to CPL. Hence, these metal cations have different behaviours in aqueous solution to exhibit diverse effect as interferences.

Table 3: Influence of interferences on the extraction efficiency of Zn^{2+} ion

Interferences	Abs. 496nm	D
Cd^{2+}	0.543	23.40
Ni^{2+}	0.616	28.16
Co^{2+}	0.667	31.54
Hg^{2+}	0.533	18.46
Cu^{2+}	0.481	13.66

Table 4: Statistical treatments for the calibration graphs

Analytical parameters	Value
Molar absorptivity ($L.mol^{-1}.cm^{-1}$)	10696.168
RSD%	0.135%
Sandell's Sensitivity ($\mu g/cm^2$)	0.00596
Detection limit (μg/mL)	0.0041

Table 5: Quantities of Zn(II) in different samples

Samples	ppm Zn(II)
Celery	55
Leeks	54
Metal	46
Beef	42
Chicken meat	45
Fish	38

Stoichiometry

With the intention of getting the most feasible structure of ion-pair association complex of Zn^{2+} ion with MPDPI. Based on followed mole ratio and method, the results have shown in Figures 14 and 15.

The results show the most likely structure of the ion-pair association complex was 1:1 (metal ion: MPDPI).

Spectrophotometric determination of Zn(II)

To determine Zn (II) in different samples, the calibration graph for Zn(II) was obtained by the procedure described previously in which a series of standard solutions were analyzed in triplicates to test the linearity. And all of the samples

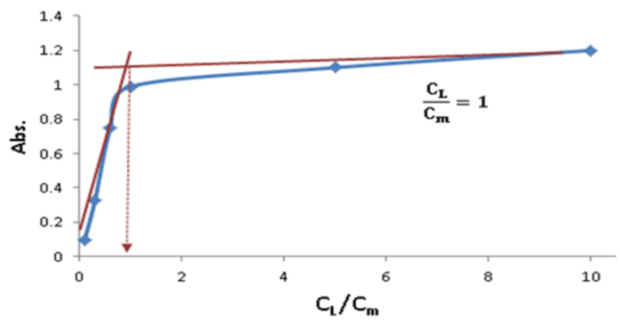

Figure 14: Mole ratio method

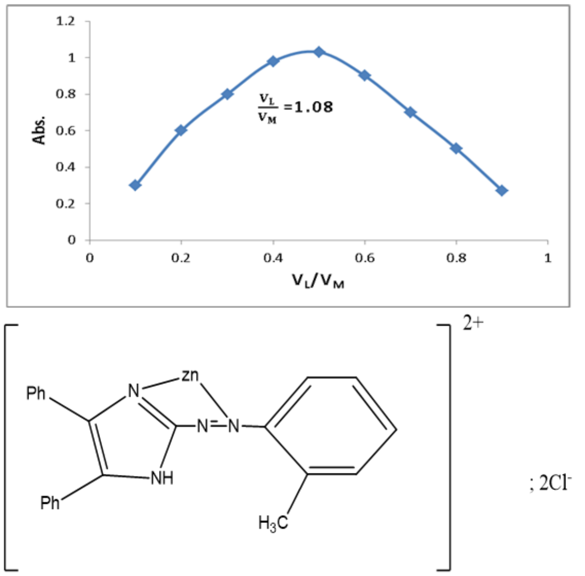

Figure 15: Continuous variation method(job method). Ion-pair association complex

were prepared according to the previous scientific sources (Reddy *et al.*, 2007; Admasu *et al.*, 2016; Bahar and Babamiri, 2014). The results and statistical treatments for the calibration graphs were as in Figure 16,Table 4 and Table 5.

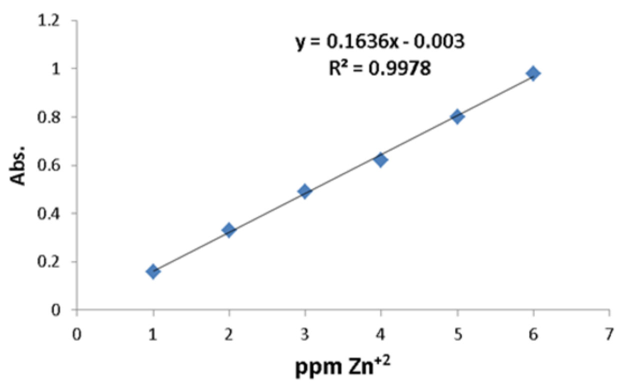

Figure 16: Calibration curve for spectrophotometric determination of Zn(II)

CONCLUSION

The paper presents a simple, very sensitive and cost-effective cloud point extraction coupled with a spectrophotometric technique to evaluate Zn (II) ion that can be useful for biological and *pharmaceutical* samples. Also, it clarifies that a cloud point extraction is an investigative tool that has unlimited capacity to be investigated in the enhancing detection limits and other analytical features over of the spectrophotometric analytical methods. It is a useful option for preconcentration and separation processes owing to its flexible recoveries and concentration factors.

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