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JOINED CLOUD POINT EXTRACTION WITH SOLVATION FOR SEPARATION, PRECONCENTRATION AND EXTRACTION LANTHANUM (III)

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ABSTRACT

Incorporation of cloud point extraction and solvation methods are functional to accomplish very high sensitivity of separation and determination of La (III) by using 2, 4-Dimethyl pentane-3-one (2, 4-DMP) for extracting formed solvation species. This research presents a new method for determination of a La^{3+} ion in aqueous solutions by using 8-hydroxyquinoline and Safranin dissolved in chloroform. The UV-Visible spectrum of organic phase appear wavelength for the maximum absorbance of extracted solvation species was λ_{max} =259nm with Tween-20, so that the maximum absorbance of extracted solvation species to CPL has appeared at λ_{max}=293nm with Tween-80. Under optimal investigation conditions, the salting out of KNO_3 was 0.8 M in the present 100µg La^{3+} in 10 mL aqueous solution, 1×10^{-4} M 2,4-DMP and 0.5 mL Tween-20, Tween-80 and heating at 90°C for 15 min in electrostatic water bath. Additionally, this research has involved further investigations about the effect of different salting out cases, interferences and different extractants as well as the spectrophotometric determination of La (III) in different samples.

Keywords: Solvation, 2,4-Dimethyl pentane-3-one, Lanthanium(III), Salting out, Cloud Point Extraction.

INTRODUCTION

The solvent extraction of Lanthanoids La, Nd, Eu, Ho, and Lu with mixtures of the chelating extractant 1-(2-thienyl)-4, 4, 4-trifluoro-1, 3-butanedione (thenoyltrifluoro-acetone, HTTA) or 4-benzoyl-3-methyl-1-phenyl-2-pyrazoline-5-on (HP) and 4-(2-pyridylazo)-resorcin (PAR, S) in $CHCl_3$ were studied extensively. It was found that in the presence of 4-(2-pyridylazo)-resorcin, the Lanthanoids were extracted as Ln $(TTA)_{3.}S$ and $LnP_3.S$ [1]. Solvation method for separation and extraction of Zn (II) and Cd (II) from nitrate medium has been applied by using methyl stearate and determination of all optimum conditions for extraction process [2]. The complex was formed between Ni(II) chloro anion by using crown ether DB18C6 from hydrochloric acid media in presence of NaCl and Triton X-100 as well as 1×10^{-4}M DB18C6. The ion complex pair extracted to CPL has the structure 1:1 from stoichiometry experiments [3]. Solvation method can be coupled with cloud point extraction method for separation and determination of Mg^{2+} from aqueous solution in presence of KNO_3 by using 2, 4-dimethyl-3-pentanone [4]. Several N-alkyl carbonyl-substituted N-phenyl hydroxylamine has been synthesized for Ln (III) extraction. They were N-octanoyl-, N-(3, 5, 5-trimethylhexanoyl)-, N-(4-butylcyclohexanoyl)-, N-(4-butyl benzoyl) - , N-(2-propyl pentanoyl)-, and N-(2-hexyldecanoyl)-N-phenyl hydroxylamine. The distribution ratio of Ln(III) ion between CCl_4 and aqueous phases was examined as functions of the pH and R-PHA concentration at 298K and the ionic strength of 0.1 ($NaNO_3$) [5].Synergistic liquid-liquid extraction and spectrophotometric determination of Au(III) have been done by using 1-(2′,4′-dinitro amino phenyl)-4,4,6-trimethyl-1,4-dihydro pyrimidine-2-thiol[2′,4′-dinitro APTPT]. The absorbance of the complex was formed in 1, 2-dichloroethane is measured at 445 nm against reagent blank. Beer's law can be applied in the concentration range of 2.5–20.0 µg mL^{-1}, with molar absorptivity value of 8.7×10^3 dm^3 mol^{-1} cm^{-1} [6]. Cu(II) can be determined with 1-(2′,4′-dinitro amino phenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol as a chromogenic reagent, in the presence of 0.5 mol L^{-1} pyridine to give ternary complex of a molar

ratio 1:2:2 (M:L:Py) in the pH range 8.7–10.5 [7]. Extraction of Ag (I) using 1-(2′, 4′-dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydro pyrimidine-2-thiol, in presence of 0.5 mol L⁻¹ pyridine. The corresponding complex has λ_{max} of 440nm [8]. A synergistic spectrophotometric method was used for the determination of Co (II) with 1-(2′, 4′-dinitro aminophenyl)-4, 4, 6-trimethyl-1, 4-dihydropyrimidine-2-thiol [2′, 4′-dinitro APTPT] in the presence of pyridine at pH range of 9.5–10.2 [9]. Bi (III) was determined by using complexing reagent of 4-(4'-chlorobenzylideneimino)-3-methyl-5-mercapto-1, 2, 4-triazole (CBIMMT) in dichloromethane from HCl-KCl buffer medium having pH of 2.0 [10].Spectrophotometric determination of Pd (II) can be realized by using 4-(4'-fluorobenzylideneimino)-3-methyl-5-mercapto-1, 2, 4-triazole,(FBIMMT). In HCl medium, Pd (II) instantly forms 1:1 complex with FBIMMT at room temperature. The extracted Pd (II)-FBIMMT species showed that λ_{max} is 390 nm against reagent blank [11]. Cu (II) has been determined by using 4-(4′-chlorobenzylideneimino)-3-methyl-5-mercapto-1, 2, 4-triazole [CBIMMT]. The Cu (II) complex with ligand is instantly extracted into chloroform and it shows a maximum absorbance at 414 nm [12].

EXPERIMENTAL

Biochrom Libra S60 model, Cambridge CB40FJ spectrophotometer with 1.00cm quartz cell was used for the absorbance measurements. The temperature of heating was controlled by using an electrostatic water bath (WNB7-45, England).

All chemicals have been received and used by the commercial company without any furthermore purification. A stock solution of La⁺³ ion (1mg/mL) was prepared by dissolving 0.3116g of La(NO₃)₃.6H₂O in 100mL distilled water that contains 1mL of nitric acid HNO₃ and other working solutions prepared by dilution with distilled water. In all preparation of solutions, volumetric flasks were used, so that 1% 8-Hydroxy quinolone can be dissolved in ethanol. Also, 1×10^{-2} M 2, 4-DMP was prepared by dissolving 0.1142 g in 100mL distilled water and other working solutions were prepared by dilution process with distilled water in suitable volumetric flasks.

Comprehensive Metal

Aqueous solution 10mL in volume contains 100µg La³⁺. The optimum concentration of salting out is of KNO₃ and 1×10^{-4}M 2, 4-Dimethyl pentane-3-one (2,4DMP), while optimum volume is of Tween-20 and Tween -80. Firstly, heat these solutions for suitable optimum temperature and time in an electrostatic water bath until formed cloud point layer CPL. Then, separate this layer from aqueous solution and dissolve it in 5mL ethanol, then measure the absorbance of the alcoholic solution at λ_{max}=259nm with Tween-20 and λ_{max}=293nm with Tween-80 against blank prepared at the same manner in the absence of metal ion La³⁺. But, the aqueous solution was treated according to the new spectrophotometric determination method 8-Hydroxy quinoline and Safranin. After that, return to the calibration curve in Figure-1 to determine reminder quantity of La³⁺ in the aqueous phase. After extraction process, subtract this quantity from the original quantity of La³⁺ in aqueous solution before extraction to determine the transferring quantity of La³⁺ to the organic phase to form solvation species. Lastly, calculate the distribution ratio (D) by:

$$D = \frac{[La^{3+}]_{org.}}{[La^{3+}]_{aq.}}$$

RESULTS AND DISCUSSION

For spectrophotometric determination of La³⁺ ion in aqueous solutions, the new spectrophotometric method was included by setting the pH of the aqueous solution that contains La³⁺ ion to 10mL by diluting ammonia solution, adding a 5mL solution of 0.25M 8-HQ and dissolved 1×10^{-4}M Safranin in chloroform and shaking it for 10min. Afterward, separate the chloroform solution that contains ion-pair association complex, prepare UV-Visible absorption spectrum against blank and make it ready in the same manner without La³⁺ ion. The results were illustrated in Fig.-1.The spectrum exhibits λ_{max} of 529nm. A calibration curve can be prepared to determine reminder quantity of La³⁺ ion in the aqueous phase after extraction.

Extracted La^{3+} ion from 10mL aqueous solutions contains rising quantity of La^{3+} ion by following the spectrophotometric method detailed above. The result was demonstrated in Figure-2.
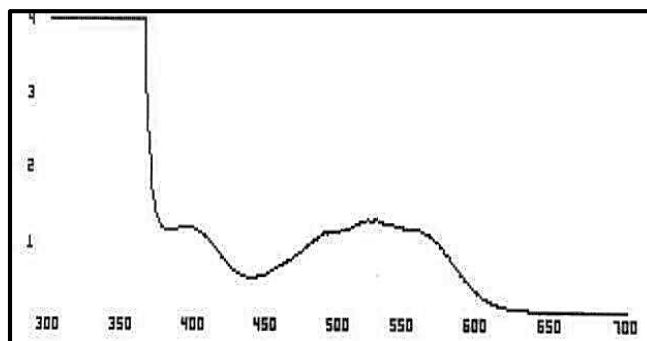

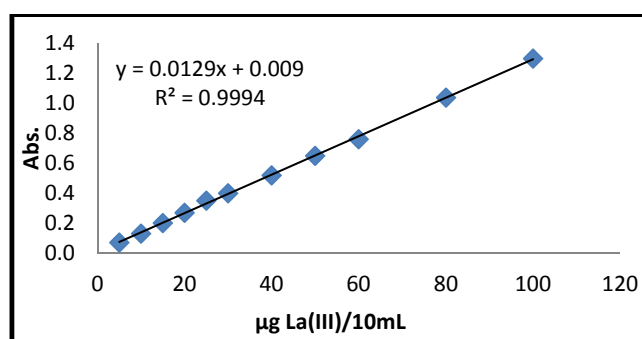Fig.-1: UV-Visible spectrum for ion-pair association complex extracted

y = 0.0129x + 0.009
R^2 = 0.9994

Fig.-2: Calibration curve for determination La^{3+} ion in aqueous solutions.

According to the comprehensive method, extract 100µg of La^{3+} in 10mL aqueous solution in the presence of 0.5mL of Tween-20 or Tween-80 and 0.25M 8-HQ, 1×10^{-4}M 2,4-DMP and heat the solution at 90^0C for 15min. Then, until formed cloud point layer CPL, separate this layer, dissolve it in 5mL ethanol and take the UV-Visible spectrum for this solution against blank at the same manner preparation without La^{3+} ion. The results have been demonstrated in Figure -3:
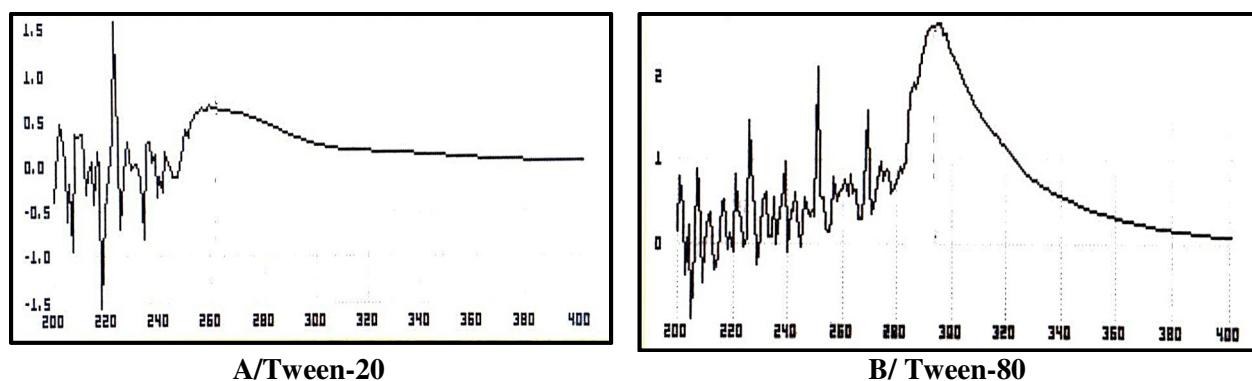
A/Tween-20   **B/ Tween-80**
Fig.-3: UV-Visible absorption spectrum of solvation species extracted of La^{3+} ion by using
The spectrum has a wavelength of maximum absorbance for solvation species at λ_{max}=259nm by using Tween-20 and λ_{max}=293nm by using Tween-80.

Effect of Salting Out
In this stage, extract 100µg of La^{3+} in 10mL aqueous solution in the presence of rising concentrations of salting out of KNO_3 and 1×10^{-4}M 2, 4-DMP, and 0.5mL of Tween-20 or Tween-80. Afterward, heat the

solutions in an electrostatic water bath at 90^0C for 15min. Then, until formed cloud point layer CPL, complete the procedure as in the comprehensive method. The results have been depicted in Figures -4 and 5:
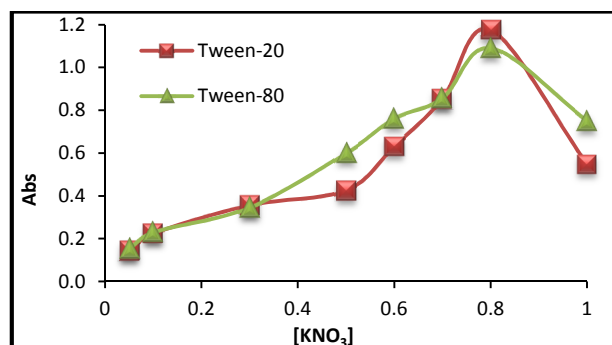

Fig.-4: Effect of KNO_3 concentration on formation and stability of solvation species.
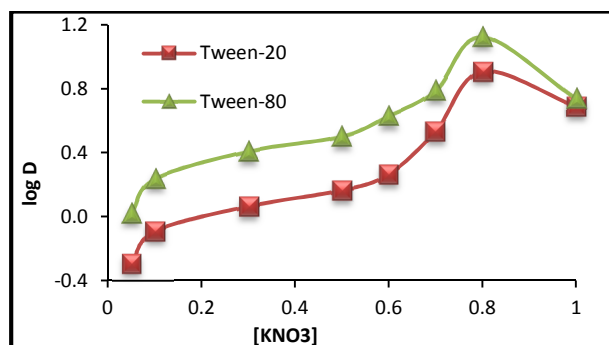

Fig.-5: Effect of KNO_3 concentration on extraction efficiency and D values

Accordingly, these results show that 0.8M KNO_3 was the optimum concentration favorable to formed solvation species with high stability. Also, it has a powerful effect to give the best dehydration of micelles to aggregate and form CPL with smaller volume and higher density. More hydrophobicity can be acquired to motivate transferring solvation species quantitatively to appear higher extraction efficiency:

$$La^{3+} + 3NO_3^- + 2,4\text{-DMP} \longleftrightarrow 2,4\text{-DMP:}La(NO_3)_3$$
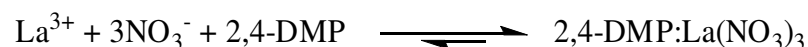
Any concentration of KNO_3 less than optimum value is not enough to reach to the best thermodynamic equilibrium. Consequently, it gives less hydration and not a good aggregation of micelles. Additionally, any concentration of KNO_3 more than optimum value has a huge effect to decline extraction efficiency as well as the effect of mass action law and electrophoretic effect.

Effect of La^{3+} Concentration
From 10mL aqueous solution, extract rising concentration of La^{3+} as in comprehensive method and at optimum conditions. The results were as in Figures -6 and 7:
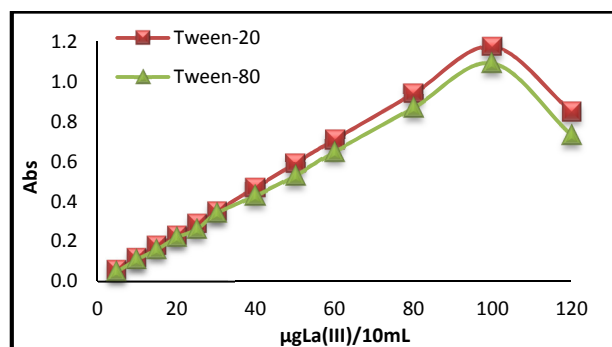

Fig.-6: Effect of La(III) concentration on formation and stability of solvation species extracted
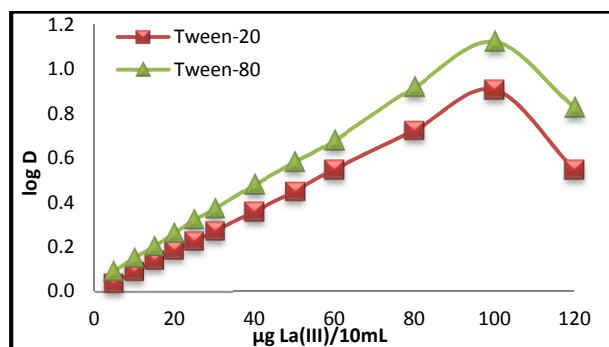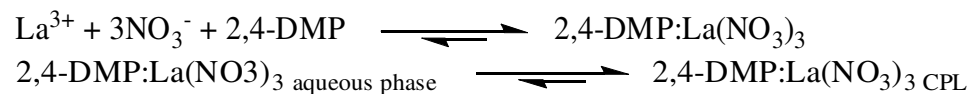

Fig.-7: Effect of La(III) concentration on extraction efficiency and D values

The results demonstrate the straight-line relation between absorbance and D values against the concentration of metal ion La^{3+} and show the linearity relation to 100µg La^{3+} in 10mL aqueous solution. The results explain an increase in absorbance and D values as a function of La^{3+} ion concentration according to thermodynamic relation to formation and stability of extracted solvation species that stands

for an increase in the rate of the forward direction of thermodynamic equilibrium of formed solvation species because the concentration of metal ion is a thermodynamic parameter:

$$La^{3+} + 3NO_3^- + 2,4\text{-DMP} \longrightarrow 2,4\text{-DMP:La(NO}_3)_3$$

$$2,4\text{-DMP:La(NO3)}_{3 \text{ aqueous phase}} \longrightarrow 2,4\text{-DMP:La(NO}_3)_{3 \text{ CPL}}$$

So, any concentration of La^{3+} more than optimum value has a consequence to decline extraction efficiency and solvation species extracted according to mass action law [13, 14].

Effect of 2,4-DMP Concentration

100µg of La^{3+} ion has been extracted from 10mL aqueous solutions by using Tween-20 and Tween-80 at optimum concentrations for each surfactant according to the comprehensive method. The results were as in Figures -8 and 9:
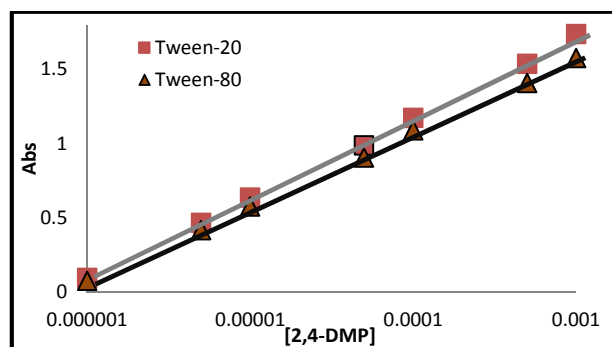

Fig.-8: Effect of 2,4-DMP concentration on formation and stability of solvation species extracted
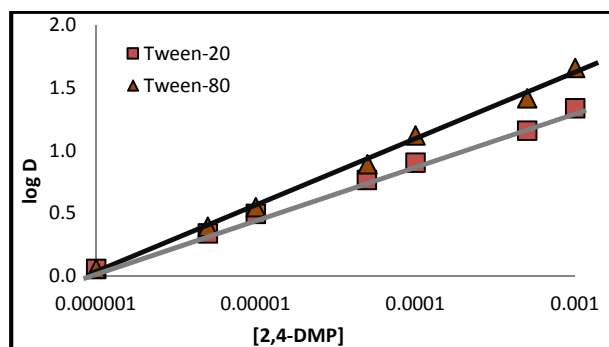

Fig.-9: Effect of 2,4-DMP concentration on extraction efficiency and D values

The results show a linear relation for 2,4-DMP concentration with formation and stability of solvation species as well as extraction efficiency, whereas the concentration of 2,4-DMP represents thermodynamic parameter effect on the thermodynamic equilibrium [15,16].

Effect of Surfactant Volume

In this case, prepare two sets of aqueous solutions of 10mL in volume that contains 100µg La^{3+} ion, 0.8M KNO_3, 1×10^{-4}M 2,4-DMP and 0.5mL of Tween-20 for the first set of solution and 0.5mL of Tween-80 for the second set of solutions. Then, heat all the solution at 90^0C for 15min. and complete the working as detailed in comprehensive method. The results were as in Figures -10 and 11:
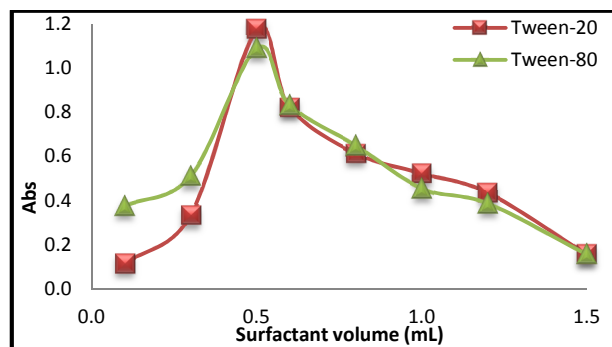

Fig.-10: Effect of surfactant volume on cloud point layer formation with better properties
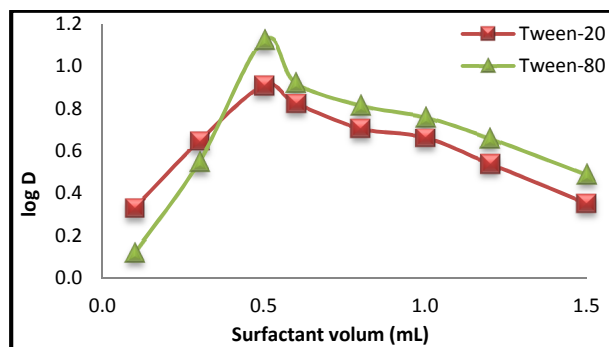

Fig.-11: Effect of surfactant volume on extraction efficiency of solvation species

The results show that 0.5mL of Tween-20 and Tween-80 were the optimum volume giving higher extraction efficiency for solvation species of La^{3+} ion. Any volume less than optimum value will give declination in the extraction efficiency because the optimum volume of surfactant and thermodynamic equilibrium of aggregation micelles allow the critical micelles to reach to concentration CMC in the formation of CPL with smaller volume and higher density. On the other hand, any volume less than optimum will not allow reaching to CMC state and CPL is not suitable for extraction. Also, increasing volume more than optimum value as a consequence to increase diffusion of micelles by the effect of electrostatic interaction [17].

Thermodynamic

According to the comprehensive method, extracted 100µg La^{3+} ion from 10mL aqueous solution at optimum conditions and at different temperatures for 15min has been conducted. The results were as in Figures -12 and 13:
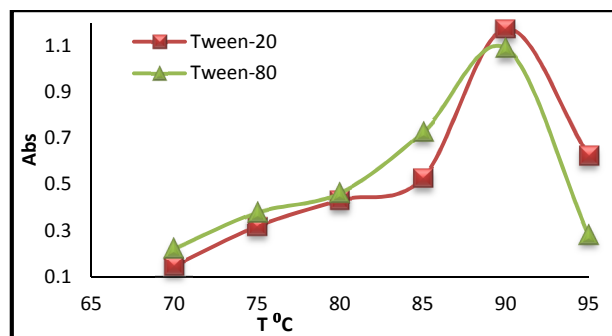

Fig.-12: Effect of temperature on cloud point layer formation and stability and quantitatively transformation of solation species
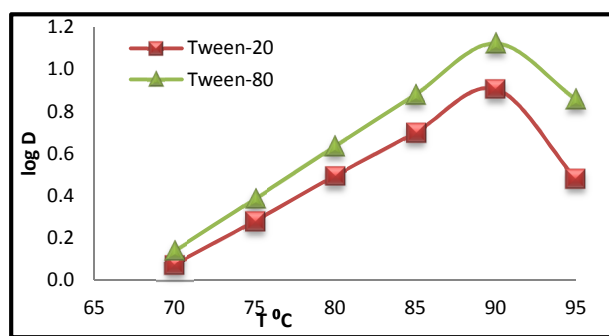

Fig.-13: Effect of temperature on extraction efficiency of solvation species for La^{3+} ion and D value

After calculated extraction constant K_{ex} at a different temperature, the results were as in Figure-14:
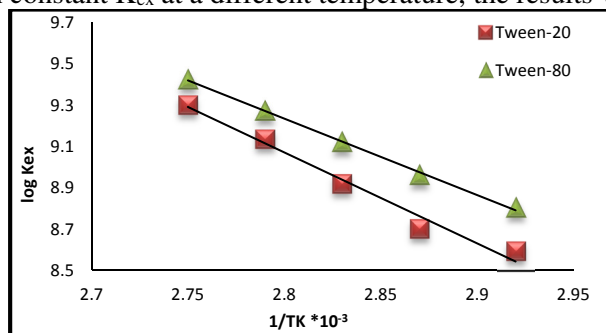

Fig.-14: Effect of temperature on extraction constant of La^{3+} ion as solvation species

Based on the slope value of straight line in Figure-14 and the thermodynamic relations, the thermodynamic details of extraction La^{3+} ion as solvation species are illustrated in Table-1:

Table-1: Thermodynamic data for extraction La^{3+} ion as solvation species [17]

	Δ Hex kJ.mol^{-1}	Δ Gex kJ.mol^{-1}	ΔSex J.mol^{-1}.K^{-1}
Tween-20	0.0914	-61.53	169.76
Tween-80	0.109	-62.99	173.83

The results show that 90^0C was the optimum temperature for extraction solvation species of La^{3+} ion by joined solvation method with cloud point extraction method. At this temperature, the formation of CPL can be complete to give the best extraction for solvation species of La^{3+} ion.

Effect of Heating Time

By Extracting 100µg La^{3+} ion from a 10mL aqueous solution according to the comprehensive method at optimum conditions except heating the solution at 90^0C for different times, the results were as in Figures-15 and 16:
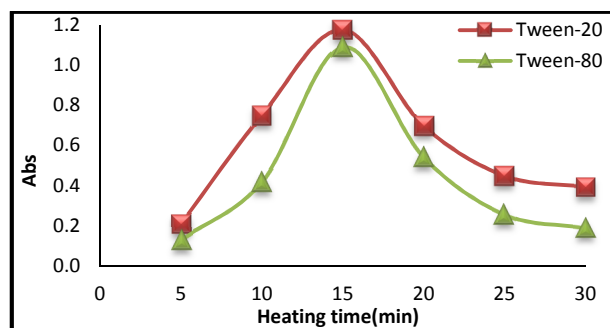

Fig.-15: Effect of heating time on formation and stability of CPL and quantitatively transferred of solvation species
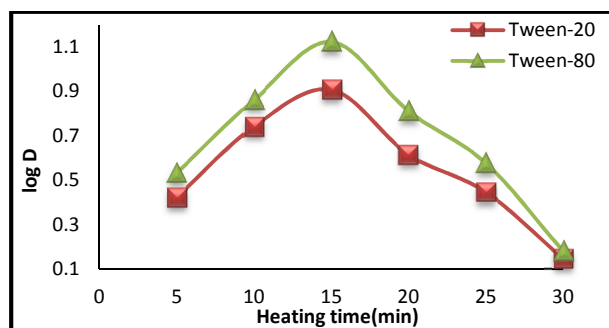
Fig.-16: Effect of heating time on extraction efficiency of La^{3+} ion as solvation species and D value

The results show that 15min was the optimum time of heating for extraction La^{3+} ion by joining solvation and cloud point extraction methods, whereas time of heating deals with the kinetic side of extraction for CPE methodology. It is important to note that heating time helps the micelles to be approached together with dehydration to form CPL at CMC state. However, the heating time less than optimum value will not allow reaching good aggregation for micelles as well as not completely dehydration. So, heating time more than optimum value and by the effect of higher kinetic energy causes an increase in the diffusion of micelles with a decrease in extraction efficiency [18, 19].

Effect of Salting Out Kind

According to the comprehensive method, extracted 100µg La^{3+} ion from 10mL aqueous solution at optimum conditions by using Tween-20 and Tween-80 and rising concentrations of different salting out cases have been investigated. The results were as in Figures-17 to 20:
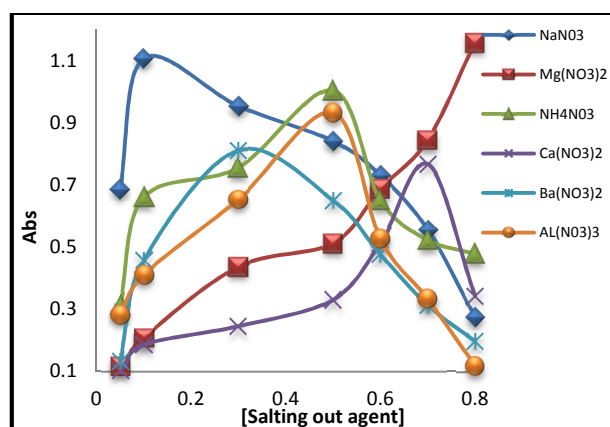

Fig.-17: Effect of different sating out concentration on formation and absorbance value for solvation species with Tween-20
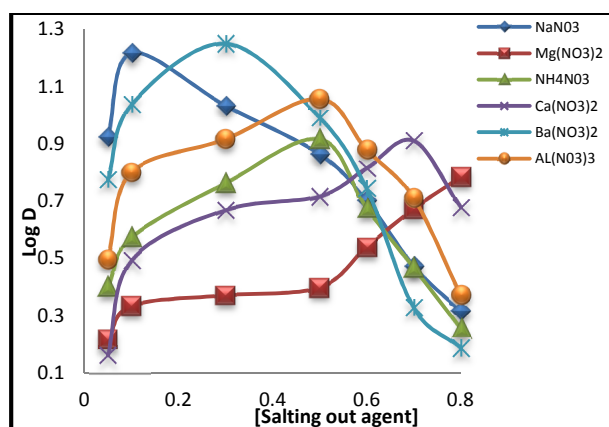
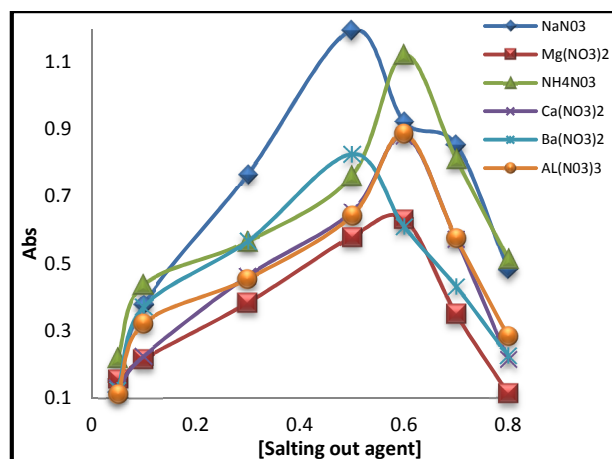Fig.-18: Effect of different sating out concentration on extraction efficiency and D value with Tween-20

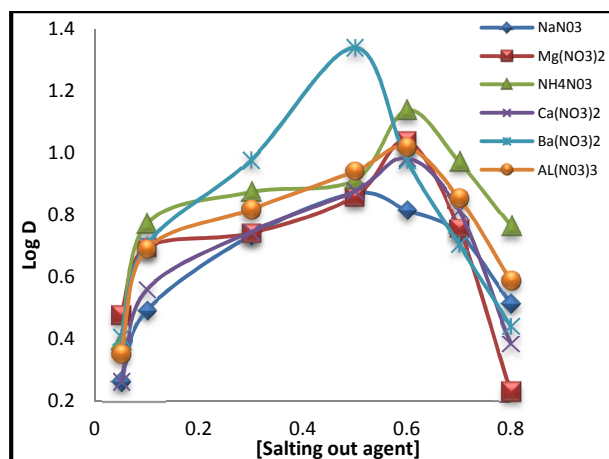Fig.-19: Effect of different sating out concentration on solvation species formation with Tween-80

Fig.-20: Effect of different sating out concentration on extraction efficiency and D value with Tween-80

The results demonstrate that different salting out concentrations have different effects on extraction efficiency, because there are different abilities for formed solvation species. That means the rate of the forward direction of thermodynamic equilibrium differs with salting out change, because each salting out as the electrolyte has a specific behavior in aqueous solution with the specific capability to formed solvation species [20].

Spectrophotometric Determination

By quantitatively determination of La^{3+} ion in different samples, calibration curve by can be performed based on a followed comprehensive method for extraction rising concentration of La^{3+} ion in 10mL aqueous solutions. After measuring the absorbance of alcoholic solutions of separated CPL, the results were shown in Figures-21, 22 and applications in Table-2:
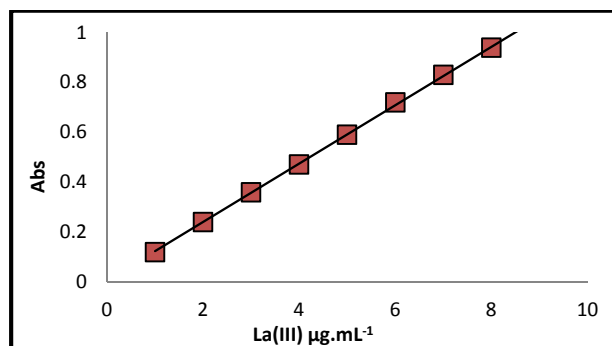

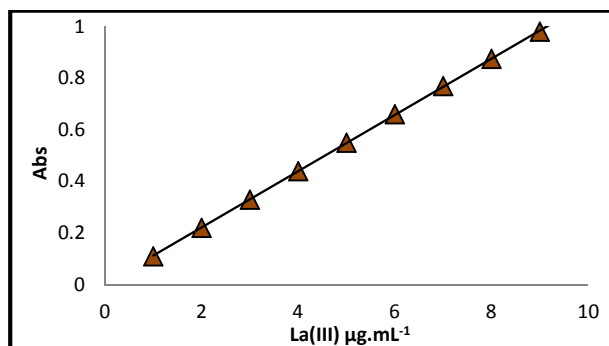Fig.-21: Calibration curve for spectrophotometric determination La(III) by using Tween-20

Fig.-22: Calibration curve for spectrophotometric determination La(III) by using Tween-80

Table-2: Applications

Sample No.	Sample Name	La(III) amount μg.mL^{-1} Tween-20	RSD%	La(III) amount μg.mL^{-1} Tween-80	RSD%
1	Mobile Screen	3.8	0.25	6.3	0.15
2	Laptop Screen	5.2	0.18	7.5	0.32

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