RJC

RASĀYAN *J. Chem.*
Vol. 14 | No. 1 |433-438| January - March | 2021
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

4-METHYL-N-n-OCTYLANILINE AS AN EMERGING EXTRACTANT FOR THE LIQUID-LIQUID EXTRACTION OF TOXIC METAL LIKE LEAD(II) TO REDUCE ITS HEALTH HAZARDS

L. V. Gavali[1], V. S. Shivankar[1] and P. S. More[2,✉]

[1]Department of Chemistry, Karmaveer Bhaurao Patil College, Vashi, Navi Mumbai-400 703, (Maharashtra) India

[2*]Department of Chemistry, Smt. Chandibai Himathmal Mansukhani College, Ulhasnagar – 421 003 (Maharashtra) India

✉Corresponding Author: prajaktasandeep@gmail.com

ABSTRACT

4-Methyl-N-n-octylaniline has been studied as an emerging extractant for the solvent extraction of Lead(II) from the aqueous iodide phase. 4 % 4-Methyl-N-n-octylaniline dissolved in xylene is used as anion exchanger to extract Lead(II) from the same volume of the aqueous phase. Acetate buffer is used for stripping of lead(II) from the organic phase. Anion exchange mechanism had been proposed based on a study of the effect of acidity and extractant concentration. Effect of other parameters like the effect of diluent, time of equilibration, aqueous to organic phase volume ratio, foreign ions on the quantitative extractive separation of Lead(II) were studied using 0.1 M KI and 1.0 M H_2SO_4 as the concentration of the medium. The method was further studied for the separation of Lead(II) from synthetic mixtures and commercial cosmetic samples like lipstick and face powder.

Keywords: Xylene, Aqueous Iodide Phase, Acetate Buffer, Stripping, Synthetic Mixtures.

RASĀYAN *J. Chem.*, Vol. 14, No.1, 2021

INTRODUCTION

Lead is known since ancient times and ranks about 36th for its natural abundance. It has wide industrial applications. It does not have any confirmed role in biological systems, but it is well known for toxic effects[1,2]. The tremendous usage of lead is not allowing its complete give-up also. Significant treatments are required to reduce environmental hazards associated with the usage of lead[3-7]. Amongst these, solvent extraction provides an economically feasible process for the preconcentration and extractive recovery of lead(II). Various higher amines such as N-n-octyl cyclohexylamine[8], 2-octylamino pyridine[9], Alamine 336, Aliquat 336S[10], N-n-octylaniline[11], N-n-hexylaniline[12] had been investigated as a basic extractant for liquid-liquid extraction of lead(II) and other heavy metals. These higher amines are also called liquid anion exchangers[13]. Comparatively very few solvent extraction systems have been addressed for the extractive separation of lead which involves large molar mass amines as an extractant. We have synthesized, 4-Methyl-N-n-octylaniline in our laboratory and we are assessing its utility as an extractant for various metals[14-16]. Consideration of vast applications of lead and at the same time concern about poisoning effects of this heavy metal on living things, seek our attention to study its liquid-liquid extraction using 4-Methyl-N-n-octylaniline.

EXPERIMENTAL

Chemicals and Instruments

The reagent 4-Methyl-N-n-octylaniline was prepared in the wet laboratory by refluxing 1:2 mixture of 1-Bromo octane and 4-Methyl aniline. Both these chemicals were bought from S. D. Fine Chemicals Ltd., Mumbai, India. The synthesized reagent was used after its purification by recrystallization. Various solutions (% w/v) of 4-Methyl-N-n-octylaniline were prepared by using xylene as a diluent. Stock solution of 1000 µg/ml of lead(II) was prepared by using its nitrate salt (AR grade) and standardized

complexometrically.[17] Bromopyrogallol red solution was prepared by dissolution of 0.039 g of it in 50% ethanol and final dilution to 100 mL.
Equiptronics model number EQ-824 dual-beam UV-Visible spectrophotometer with 1cm quartz cuvette was used for optical density measurement. Equiptronics digital pH meter of EQ-614A was used for pH measurement. All the chemicals used were of AR grade. Distilled water was used throughout. Cosmetic samples were bought from the local market in Ulhasnagar, Mumbai, Maharashtra, India.

Extraction Procedure

The aqueous phase of volume 10 mL, containing 100 µg Lead(II) in iodide medium was transferred to the separating funnel and manual shaking was done with the organic phase. The organic phase was consisting xylene with the extractant i.e. 4-Methyl-N-n-octylaniline embedded in it. The concentration of the extractant was varied from 1- 4 % using xylene as a diluent and the minimum but constant shaking time chosen was 3 minutes. The two distinct phases were allowed to set in a separating funnel. Lead(II) was extracted back into the aqueous phase from the organic phase by stripping with 12 mL acetate buffer pH 4.56. The stripped solution was evaporated carefully to remove traces of xylene. The amount of lead(II) in the stripped solution was determined spectrophotometrically using bromopyrogallol red after adjustment of pH 5.5. Absorbance measurement was done at λmax =630 nm.[17] The amount of lead(II) extracted was determined in terms of percentage extraction (%E). This percentage extraction was further related to the distribution ratio by the following equation:

$$D = \frac{\%E}{100-\%E} \times \frac{Vaq}{Vorg}$$

Here, D stands for Distribution ratio. Vaq and Vorg stand for volume of aqueous and organic phase respectively.

RESULTS AND DISCUSSION

Effect of Acidity and Extractant Concentration

Lead (II) was extracted by varying concentration of H_2SO_4 from 0.1 M - 2.0 M keeping the concentration of KI constant i.e. 0.1 M and by varying concentration of KI from 0.02 M -1.0 M keeping the concentration of H_2SO_4 constant i.e. 1.0 M. The concentration of the extractant in xylene was varied from 1 % to 4 %. Quantitative extractive separation of Lead(II) was observed from 0.1 M to 1.0 M KI and 0.2 M - 2.0 M H_2SO_4 with 4 % reagent solution in xylene when equal volumes of organic and aqueous phases were taken. To study other parameters, 0.1 M KI and 1.0 M H_2SO_4 were chosen as the concentration of the medium and 4 % as the concentration of the reagent (Fig.-1, Fig.-2).

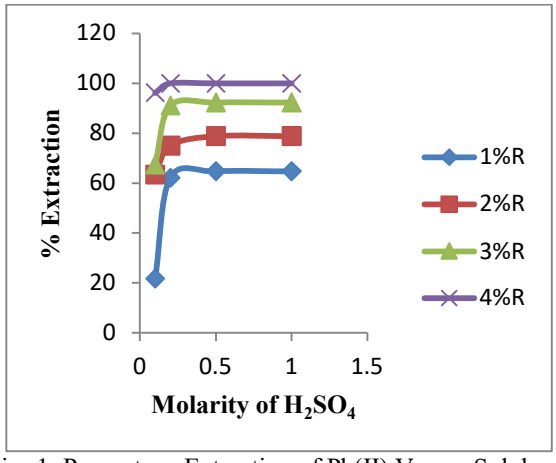

Fig.-1: Percentage Extraction of Pb(II) Versus Sulphuric Acid Concentration at Fixed Concentration of KI (0.1 M) with 1 %, 2 %, 3% and 4% R i.e. 4-Methyl-N-n-octylaniline in Xylene

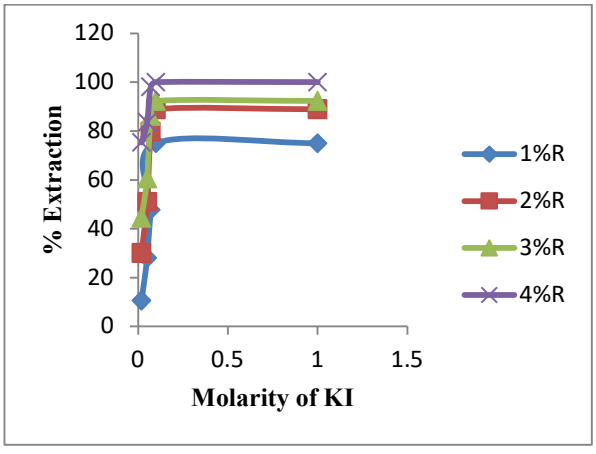

Fig.-2: Percentage Extraction of Pb(II) Versus Potassium Iodide Concentration at Fixed Concentration of H_2SO_4 (1.0 M) with 1 %, 2 %, 3% and 4% R i.e. 4-Methyl-N-n-octylaniline in Xylene

Nature of Extracted Species and Extraction Mechanism

The log-log plot at a concentration of KI 0.05 M and 0.07 M keeping the concentration of sulphuric acid as 1 M (Fig.-3) and at a low concentration of sulphuric acid i.e. 0.1 M keeping the concentration of KI as 0.1 M (Fig.-4) gave slopes 1.24, 1.74 and 2.0 respectively. It indicated the metal (Lead) to ligand (amine) ratio in the extracted species is 1:1 at a low concentration of KI and 1:2 at a high concentration of KI. Using this data probable formula of extracted species was explained through probable extraction mechanism as follows:

$Pb^{+2}_{aq} + 4I^{-}_{aq} \rightarrow Pb\ I_4^{-2}{}_{aq}$

$[RR'NH]_{org} + HI \rightarrow [RR'NH_2^{+}\ I^{-}]_{org}$

$[RR'NH_2^{+}\ I^{-}]_{org} + Pb\ I_4^{-2} \rightarrow [RR'NH_2^{+}\ Pb\ I_4^{-2}]_{org} + I^{-}$ (at low concentration of KI)

$2[RR'NH_2^{+}\ I^{-}]_{org} + Pb\ I_4^{-2} \rightarrow [(RR'NH_2^{+})_2\ Pb\ I_4^{-2}]_{org} + 2I^{-}$ (at high concentration of KI)

$R = -C_6H_4-CH_3$ $R' = -C_8H_{17}$

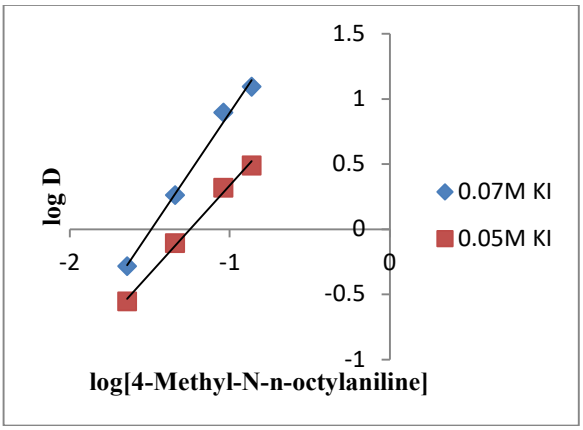

Fig.-3: Log-log Plot of Distribution Ratio of Pb(II) vs 4-Methyl-N-n-octylaniline Concentration at 0.07 M KI and 0.05 M KI with 1.0 M H_2SO_4

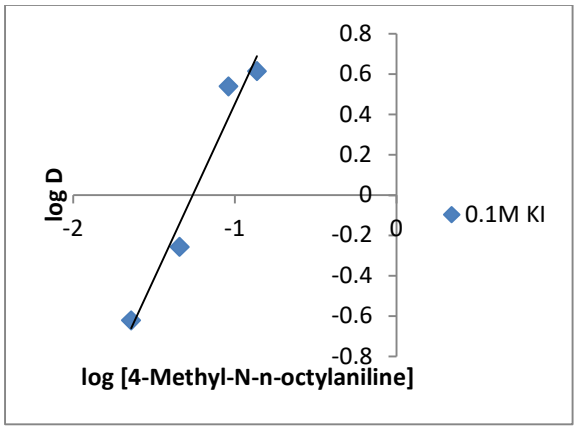

Fig.-4: Log-log Plot of Distribution Ratio of Pb(II) vs 4-Methyl-N-n-octylaniline Concentration at 0.1M KI with 0.1M H_2SO_4

Effect of Diluent, Time of Equilibration and Aqueous to Organic Phase Volume Ratio

Several other solvents were also tried as a diluent for preparing organic phase encompassing 4-Methyl N-n-octylaniline. The extraction was quantitative with hydrocarbon diluents such as xylene, benzene, toluene i.e. 99.9%, 99.9% and 98.9% while with other solvents such as CCl_4, $CHCl_3$, isoamyl acetate, isoamyl alcohol and cyclohexanol it was 80.2%, 40.3%, 99.9%, 59.6% and 58.5% respectively. Xylene was selected as solvent as it gave distinct separation of the phases without the formation of an emulsion. Also, it is non-volatile, easily available, comparatively less carcinogenic and gives high distribution ratio for ion-pair complex.

Variation of shaking time from 1-4 minutes showed that a minimum of 2-minute shaking was essential for quantitative extraction of lead(II). To ensure complete extraction 3 minute shaking time is recommended in the general procedure. Long time shaking found no adverse effect on the extraction of lead(II)

Extraction of Lead(II) was carried out from aqueous phase of volume 10ml to 50ml containing 0.1M KI and 1M H_2SO_4 with 10mL of 4% 4-Methyl-N-octylaniline in xylene. The study showed that extraction of lead(II) was quantitative i.e. 99.9%, when aqueous to organic phase volume ratio was changed from 1:1 to 5:1. The ion pair formed may have high stability up to a wide volume ratio of aqueous: organic phase.

Effect of Foreign Ions

An interference study was carried out by adding foreign ions to the 10mL solution of 100 µg lead(II) in 0.1 M KI and 1 M H_2SO_4. Error of ±2 % in the recovery of lead(II) was accepted. Interference due to some cations was removed by the use of a suitable masking agent. Table-1 shows the tolerance limit set after the study of the effect of foreign ions on the extraction of Pb(II).

Table-1: Effect of Foreign Ions on the Extraction of Pb(II)

Foreign Ion added	Tolerance Limit mg
Acetate, Succinate, Ascorbate, Citrate, Tartarate, HPO_4^{-2}	40
Oxalate, Thiocyanate, Thiourea, Ba(II), Mg(II)	10
Ca(II), Ce(IV), Cr(III), Mn(II), Zr(IV), Ga(III), Al(III), U(VI), Ge(IV)[a], Hg(II)[a]	4
As(III), Ni(II)[b], Co(II)[c], Zn(II)[c], Cu(II)[d], Tl(III), Fe(III)[e]	1
Bi(III), In(III)	0.5
Sb(III)	Interfere

a-masking with acetate; b-masking with EDTA; c-masking with tartarate;
d-masking with thiourea; e-masking with ascorbate

Separation and Determination of Lead(II) in Synthetic Binary Mixtures

It was found that Lead(II) was selectively extracted in organic phase consisting of 10 ml 4 % 4-Methyl-N-n-octylaniline in xylene from the binary mixtures containing Zr(IV), Al(III), Ga(III),U(VI),Cd(II). The raffinate containing unextracted metal ion was estimated by standard procedures given in the literature.[17-18] Table-2 shows the percentage recovery of Lead(II) and associated metal ions by the proposed method.

Table-2: Separation and Determination of Lead(II) in a Synthetic Binary Mixture

Metal ion	Amount Taken µg	% Recovery	Estimation Procedure for Associated Metal Ion
Pb(II)	100	99.8	Alizarine Red S
Zr(IV)	100	98.8	Spectrophotometry[18]
Pb(II)	100	99.8	EDTA Complexometry[17]
Al(III)	500	96.5	
Pb(II)	100	99.8	Xylenol Orange
Ga(III)	500	99.8	Spectrophotometry[18]
Pb(II)	100	99.8	Bromopyrogallol Red
U(VI)	100	96.6	Spectrophotometry[18]
Pb(II)	100	99.8	Xylenol Orange
Cd(II)	100	95.4	Spectrophotometry[18]

Separation and Determination of Lead(II) in Synthetic Mixtures

Mixtures containing Lead(II) along with various elements were prepared. The composition of the mixtures was prepared considering their tolerance limit during the extraction of Lead(II) by the recommended procedure. Extractive separation of Lead(II) was carried out by using the proposed method. The amount recovered from each composition was in good agreement with the amount taken. From the mixture of lead, aluminium and gallium, lead was selectively extracted from iodide medium whereas aluminium and gallium were not extracted. Similarly from the mixture of lead, germanium and cerium, lead was selectively extracted by the proposed method but germanium and cerium remained in the raffinate. From the mixture of lead, thallium and chromium, thallium was first extracted from 0.6 M HCl using 2 % 4-Methyl-N-n-octylaniline. However, lead and chromium remained in the aqueous phase. Then lead was extracted by the recommended procedure from iodide medium whereas chromium remained in the aqueous phase. From the mixture of lead, indium, cadmium and zirconium, lead was quantitatively extracted in the organic phase by the proposed method whereas indium and cadmium were also weakly extracted. in organic phase by the proposed method. The lead was selectively stripped by using 1 M NaOH. Zirconium remained in the mother aqueous phase since it is not extracted at all. The percentage recovery data of Lead(II) from synthetic mixtures are shown in Table-3.

Table 3: Separation and Determination of Lead(II) in Synthetic Mixtures

Composition of the Synthetic Mixture, µg	Pb(II) Found µg	Percentage Recovery %
Pb(II), 100 ; Al(III), 500 ; Ga(III), 500	99.6	99.6
Pb(II), 100 ; Ge(IV), 100 ; Ce(IV), 500	99.6	99.6

Pb(II), 100 ; Tl(III), 100 ; Cr(III), 500	99.2	99.2
Pb(II), 100 ; In(III), 100 ; Cd(II), 100 ; Zr(IV), 500	98.6	98.6

Separation of Lead From Cosmetic Samples

2.0 g of cosmetic sample was digested twice with 10 ml of aqua regia on a hot plate at 80º C until it is dried. Then 2 ml of concentrated H_2O_2 was added to oxidize organic impurities if any. The residue was then extracted with distilled water, nearly neutralized and diluted to make the final volume 25 mL. Lead(II) content in the sample was found by the standard addition method. Since certified value was not available, lead(II) content in the prepared cosmetic sample solution was confirmed by ICP AES method. Extraction data from the cosmetic sample is showed in Table-4.

Table 4: Lead(II) in Cosmetic Sample

Cosmetic Sample	Amount of Lead(II) Found by ICP AES Method, µg/g	Amount of Lead(II) Found by proposed Method*, µg/g
Lipstick	12.362	12.0
Face powder	15.837	15.0

*average of three determinations

CONCLUSION

The important conclusions drawn from the present investigation are enumerated here as follows:

- Laboratory preparation of 4-Methyl-N-n-octylaniline is easy and cost-effective compared to its analog N-n-octylaniline.
- Extraction is remaining quantitative although the aqueous to organic phase volume ratio is changed from 1:1 to 5:1. It is convenient to use acetate buffer for stripping of lead. The method is suitable to separate lead(II) from associated metal ions and cosmetic samples.
- There is no problem with third-phase formation. This method does not require any modifier for clear-cut phase separation.
- The method is simple and does not require a long time for extraction.

ACKNOWLEDGEMENT

We are very grateful to SAIF, IIT Bombay for handling our samples for some instrumental analysis such as ICP-AES and we also acknowledge the Chemistry Research Laboratory of KBP College, Vashi, Navi-Mumbai to facilitate us with the variety of instruments and glassware required for the presented research work.

REFERENCES

1. A. L. Wani , A. Ara and J. A. Usmani , *Interdisciplinary Toxicology*, **8(2)**, 55(2015), **DOI:**10.1515/intox-2015-0009
2. G. Flora, D. Gupta and A. Tiwari, *Interdisciplinary Toxicology*, **5(2)**, 47(2012), **DOI:**10.2478/v10102-012-0009-2
3. A. Kaushal and S. K. Singh, *International Journal of Hydrology*, **1(2)**, 38(2017), **DOI:**10.15406/ijh.2017.01.00008
4. A. K. Wanjari and U. E. Chaudhari, *Rasayan Journal of Chemistry*, **10(1)**, 82(2017), **DOI:**10.7324/RJC.2017.1011556
5. R. Mahalaxmi, K. Preethi, D. Kalaiselvi, M. Manjuladevi, K. Karthik and Ramalatha Marimuthu *Rasayan Journal of Chemistry*, **12(1)**, 245(2019), **DOI:**10.31788/RJC.2019.1215001
6. B. Mandal and U. S. Roy, *Indian Journal of Chemistry*, **47A**, 1497(2008).
7. A. Agrawal and K. K. Sahu, *Journal of Hazardous Materials,* **B133**, 299(2006), **DOI:**10.1016/j.jhazmat.2005.08.029
8. A. Kokare , V. Suryavanshi, S. Zanje, G. Kore and M. Anuse M, *Analytical Methods* , **8(32)**, 6158(2016), **DOI:**10.1039/C6AY00887A
9. C. P. Mane and M. A. Anuse, *Journal of Hazardous Materials*, **152**, 1146(2008), **DOI:**10.1016/j.jhazmat.2007.07.119

10. C. McDonald, M. M. Mahayni and M. Kanjo, *Separation Science and Technology*, **13(5)**, 429(1978), **DOI:**10.1080/01496397808058292
11. S. R. Kuchekar, S. R. Phule , B. H. Zaware and S. H. Han, *Indian Journal of Chemical Technology*, **21**, 205(2014)
12. N. B. Kadam Patil, R. B. Thorat and A. S. Burungale, *Rasayan Journal of Chemistry*, **2(4)**, 953(2009).
13. S. M. Khopkar , Solvent Extraction Separation of Elements with Liquid Ion Exchangers, New Age International Pvt. Ltd., First edition (2007).
14. P. S. More and R. J. Patil, *Rasayan Journal of Chemistry*, **5(2)**, 152(2012).
15. P. S. More, V. S. Shivankar and L. V. Gavali, *Journal of Chemistry and Chemical Sciences*, **8(2)**, 326(2018), **DOI:**10.29055/jccs/589
16. L. V. Gavali, V. S. Shivankar and P. S. More, *International Journal of Chemical and Physical Sciences*, **7(2)**, 52(2018), **DOI:**10.30731/ijcps.7.2.2018.52-61
17. F. J. Welcher, The Analytical Uses of Ethylenediamine Tetraacetic Acid, Van Nostrand Company, Inc. New York London, p. 190, 166 (1958) .
18. F. D. Snell, Photometric and Fluorometric Methods of Analysis, Part I, Part II Wiley Interscience New York, p. 39, 523, 292, 1136,1399. (1978).

[RJC-5936/2020]