Extraction Study on Uranyl nitrate for Energy Applications

R.Giri[1,a)] and G.Nath[2,b)]

Department of Physics

Veer Surendra Sai University of Technology, Sambalpur -768018, Odisha

Email: [a)]physics.leena@gmail.com, [b)]ganesh_nath99@yahoo.co.in

Abstract

Due to the ever-growing demand of energy nuclear reactor materials and the nuclear energy are now considered to be the most critical materials and source of energy for future era. Deposition of nuclear wastes in different industry, nuclear power sector are very much toxic in open environment which are hazardous to living being. There are different methods for extraction and reprocessing of these materials which are cost effective and tedious process. Ultrasonic assisted solvent extraction process is a most efficient and economical way for extraction of such type materials. The presence of third phase in mixing of extractants-diluent pair with aqueous phase imposes the problems in extraction of nuclear reactor materials. The appropriate solvent mixture in proper concentration is an important step in the solvent extraction process. Study of thermo-physical properties helps in selecting an optimum blend for extraction process. In the present work, the extraction of uranium with the binary mixture of Methyl Ethyl Ketone (MEK) and Kerosene was investigated and discussed with the variation of ultrasonic frequency for different temperatures. The result shows that the low frequency and low temperature is suitable environment for extraction. The extraction of uranium by this method is found to be a better result for extraction study in laboratory scale as well as industrial sector.

Keywords: Rare earth element, acoustic parameter, ultrasonic velocity, organo- aqueous phase, intermolecular interaction

INTRODUCTION

Uranium plays a significant role in the production of nuclear energy but has confined resources. To meet the future challenges, efforts are being made worldwide to explore the newer sources of uranium. It is an essential element used in nuclear energy list and is moreover toxic in nature [1]. Usually uranium locates in association with rare earth materials; therefore separation of this nuclear material has concerned interest of researchers for all time. There are different methods which are adopted for extraction of such type of materials such as solvent extraction, ion exchange, filtration, chemical absorption, membrane separation etc [2-3]. In this regard, solvent extraction technique is more convenient and reasonable method for extraction.

Based on the standard theory of transportation of anions and cations, in solvent extraction the ionic metals are separated due to the variation of chemical potentials among two immiscible phases: organic and aqueous phases. Choice of appropriate solvent is a challenge for the researcher by determining several factors like price, solvating power, chemical strength and selectivity for extraction [3-5]. The familiar extractants tri-n-butyl phosphate (TBP), methyl isobutyl ketone (MIBK), methyl isopropyl ketone (MIPK), methyl ethyl ketone (MEK) and di isobutyl ketone (DIBK) are mainly used for separation and purification of rare earth and nuclear reactor materials. But the major problem occurs during the extraction process is formation of the third phase. Addition of diluents to the solvent gives an improved dispersion and speedier phase disengagement. [6-7]. It is already established that ultrasonic technique is more prominent method to investigate the different molecular interactions take place within the liquid mixture to find out the compatible blend of solvents and diluents [8].

Due to the cavitation phenomena ultrasonic wave with different frequency produces high acoustical energy when transmits through the liquid medium and this acoustical power can be used to split chemical bonds to instigate new reactions. Extraction power of the liquid mixture increases because of these strong acoustical forces occurs during the cavitation process. In the present paper the fundamental concept of ultrasonic wave is applied to study the different kind of intermolecular interactions present in a liquid medium due to which the extraction of nuclear material like uranium is well defined by variation of different sound properties [9].

For present study, a basic mechanism for the extraction process was designed where the binary mixture of methyl ethyl ketone (MEK) and kerosene was taken as extracting agent. The optimum percentage of the liquid mixture was evaluated by using sound wave theory in terms of molecular interaction present in the liquid mixture.

MATERIALS AND METHODS

Reagents

Commercially obtainable products like methyl ethyl ketone (MEK) (AR,> 99%), kerosene (AR,> 98 %), nitric acid (HNO_3, AR, 15. 5mol/L) and uranyl nitrate (AR,> 99 %) are received from CDH Chemicals. These are very much pure and analytical grade samples. All the chemicals were applied as received with no additional purification.

Experimental procedure

A series of solvent mixture was prepared by taking methyl ethyl ketone (MEK) and kerosene on proportion basis (w/w) by determining their masses using a high accuracy electronic balance of WENSAR, PGB 100(±0.001gm) for various concentration ranges of MEK. These samples were kept in ground-glass stopper bottles to avoid the contamination and evaporation. By ultrasonic interferometer (Mittal Enterprises, New Delhi, Model-M-81S) ultrasonic velocity for the mixture and pure liquid were determined and required concentration of the mixture for extraction was found out by studying different acoustical parameters evaluated using the data of ultrasonic velocity, viscosity and density. The velocity measurement of the liquid was precise up to ± 0.01m/s. Density and viscosity of the liquids was calculated using bicapillary Pyknometer and Redwood viscometer respectively. Organic phase was equilibrated by putting suitable amount of MEK with kerosene of various mole percentage of MEK and aqueous phase was produced by adding uranyl nitrate in diluted nitric acid (1 mol/dm^3) with increasing concentration of uranium (15, 20, 25, 30, 35, 40, 50)g/dm^3 for different temperature range varying from 25°C to 50°C . Both the phases were subjected to a magnetic stirrer individually for 10 minutes to make sure that the two phases were completely mixed. Distribution studies were carried out by equilibrating equal volumes of aqueous phase with organic phase (phase ratio=1:1) in a beaker. Again the whole biphasic medium was placed within the ultrasonicator bath (125 KHz frequency) for dispersion. Then the mixture was put in a separatory funnel and allowed it to rest for 15 minute at normal room temperature for phase settle. By using Whatman filter paper No. 42, the extract was filtered from the aqueous and organic phase. Total experimental procedure is presented by a schematic diagram in FIGURE 1.

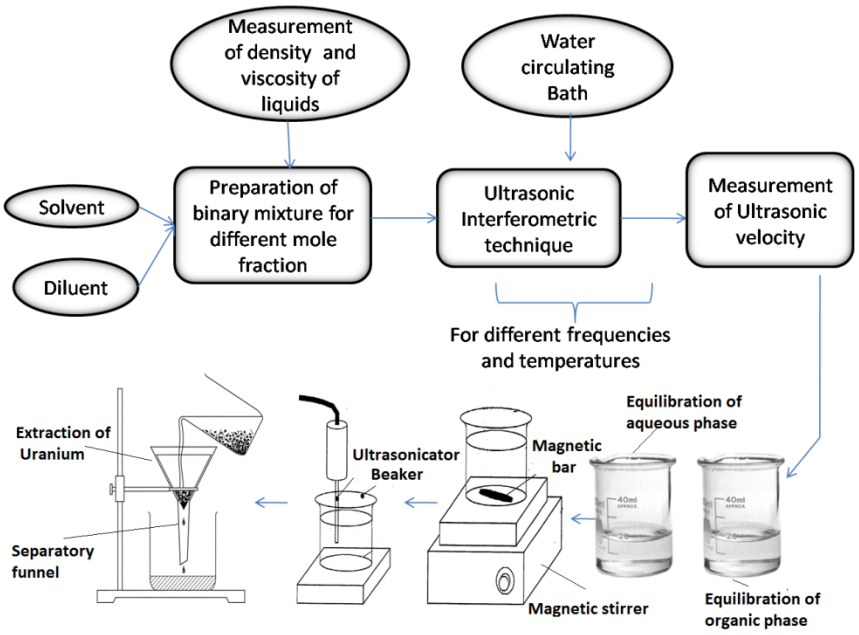


FIGURE 1 Schematic diagram of extraction of uranium from uranyl nitrate using binary mixture of MEK and kerosene [Ref: 10]

The mechanism of the uranium extraction by MEK is given by the equation below:

$$UO_2^{2+}(aq.) + 2NO_3^-(aq.) + 2MEK(org.) \leftrightarrow UO_2(NO_3)_2(MEK)_2(orq.) \quad (1)$$

Uranium concentration was evaluated from the organic phase $[U]_{org}$ by volumetric process and mass balance analysis was carried out to determine the concentration of uranium in the aqueous phase $[U]_{aq}$ .The measured distribution ratios in both organic and aqueous phase was verified by comparing the theory of chemical equilibrium as per Nernst distribution law:

$$K_D = \frac{[U]_{org}}{[U]_{aqu}} \quad (2)$$

The equilibrium constant of Eq. (1) can be expressed as:

$$K_U = \frac{[UO_2(NO_3)_2.2MEK]}{[UO_2^{2+}][NO_3^-]^2[MEK]^2} \quad (3)$$

RESULTS AND DISCUSSION

Effect of ultrasonic technique to investigate various intermolecular interactions

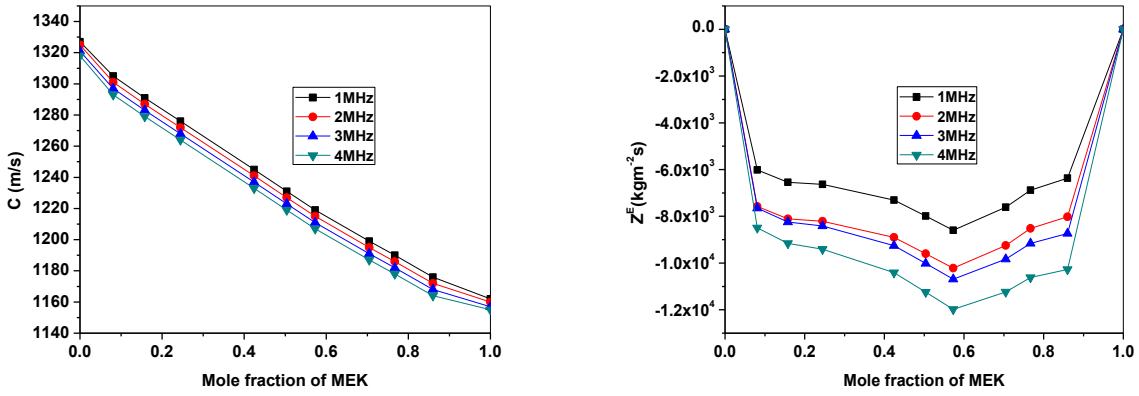
The transmission of ultrasonic wave inside the liquid mixture taken for extraction process changes different properties of the molecules present in the liquid medium. When ultrasonic waves transmit within the treated medium it generates acoustical pressure which in terns increases the temperature of the liquid medium. This

phenomenon is the main reason for the generation of micro bubbles and also bubble coalescences [11]. By studying different acoustical parameters computed using the calculated value of ultrasonic velocity, density and viscosity, we can easily find out the appropriate blend and optimum percentage of solvent mixture. In Table 1, ultrasonic velocity, density and viscosity values are given for pure methyl ethyl ketone (MEK) and kerosene at room temperature.

TABLE 1 Density (ρ) and Viscosity (η) of pure methyl ethyl ketone (MEK) and kerosene at room temperature

Liquids	Ultrasonic velocity (ms^{-1})		Density (ρ) (Kgm^{-3})		Viscosity (η) ($10^{-3}kg\ m^{-1}\ s^{-1}$)	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
MEK	1162	1153.3[a]	832.235	799.900[b]	0.3963	0.3855[c]
Kerosene	1327	1327[d]	775.892	775.892[e]	1.456	1.640[f]

[a,b]Ref. [12] at 298.15 K
[c]Ref. [12] at 303.15 K
[d,e]Ref. [13] at 303.15 K
[f]Ref. [14] at 303.15 K

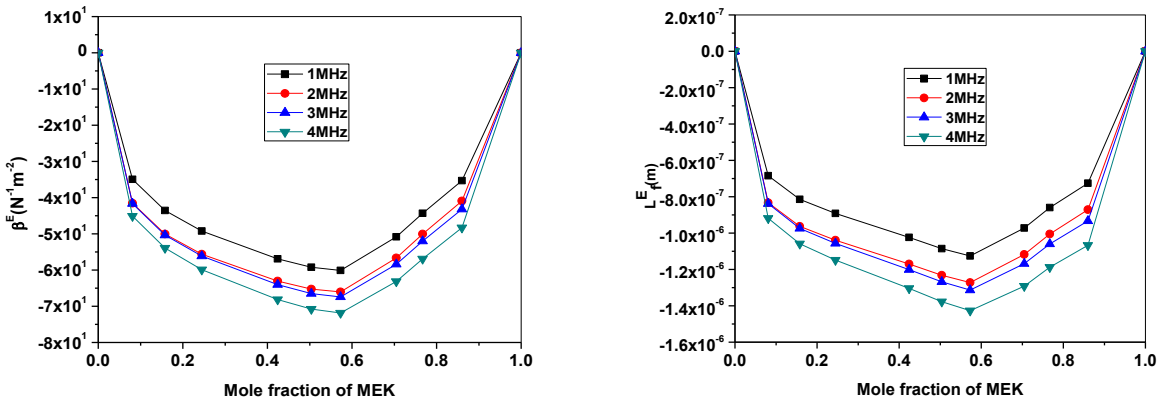


(a) **(b)**

FIGURE 2 Variation of Ultrasonic velocity and deviated acoustic impedance with different mole percentage of MEK with kerosene

In FIGURE 2, variation of ultrasonic velocity with mole percentage of MEK for the medium of MEK with kerosene is linear. It is observed from the variation of diagram that the ultrasonic velocity decreases linearly through the mole fraction of MEK with kerosene in the complete biphasic scheme. The effect of adding a non-polar second component with polar compound is mostly to dislocate the dipolar interactions of the first element. This may be due to self-association of the solvent molecules and a very strong dipole-induced dipole interaction between the constituent molecules, which is concentration dependent. This also indicate the specific interaction exist between the component molecules present in the solvent mixtures which are used for the study of structural variation. The negative excess acoustic impedance (Z^E) value decreases with the increasing mole fraction of MEK and gives maximum deviation at 0.6 mole % for MEK which indicates prominent interactions between the molecules of

solvent. This is attributed due to interaction between constituent molecules and arrangement of closer molecular aggregates which leads to decrease in the intermolecular free space [15].



(a) **(b)**

FIGURE 3 Variation of deviated isentropic compressibility and intermolecular free length with different mole percentage of MEK with kerosene

Both isentropic compressibility (β^E_s) and intermolecular free length (L_f^E) (FIGURE 3) value drop off with the increase of mole fraction of MEK and then increases with the increasing concentration of MEK. This specifies the existence of relatively stronger molecular interaction within the molecules of the solvent mixture which is due to occurrence of hydrogen bonding between the constituent molecules. The negative variation of β^E_s and L_f^E value indicates that the solvent mixture is less compressible than the pure liquids forming the complex and in case of the mixture molecules are more strongly bound than in pure liquids. The negative value of excess intermolecular free length indicates that the sound wave covers a larger distance and this is due to dominant nature of interactions between the unlike molecules present in the binary mixture [16]. The negative values of L_f^E are also attributed to close packaging of the component molecule decreases up to 0.6 mole fraction of MEK and then again increase negatively attributing to lose packing of the component molecules which is describe in terms of hetromolecular association between component molecules present in the mixture of MEK and kerosene. The decrease in free length between the connected molecules indicates that the medium is more resistant to the sound wave propagation. Mixing of MEK with kerosene will stimulate the infringement up of the associated clusters of MEK releasing several dipoles which in turn can induce a dipole moment in kerosene molecules, resulting dipole-induced dipole interactions. Thus, kerosene acts as a structure breaker of MEK [17].

Effect of temperature on extraction of uranium

The method of uranium extraction from Uranyl nitrate was performed by using 60 % of MEK in kerosene which was pre-equilibrated with 0.5, 1.0, 1.5, 2.0 and 3mol/dm^3 nitric acid and Uranyl nitrate. To study the effect of temperature in the extraction process, the mixture for extraction was put in to a magnetic stirrer, and then the mixture was stirred for 10 minutes at Uorg./Uaq. = 1 for different temperatures increasing from 25°C-50°C. The variation extraction efficiency is shown in FIGURE 4 for different temperature ranges. For increasing temperature, efficiency of the extractant for extraction of uranium gradually decreases. So in low temperature the extraction process of uranium can be done easily [5].

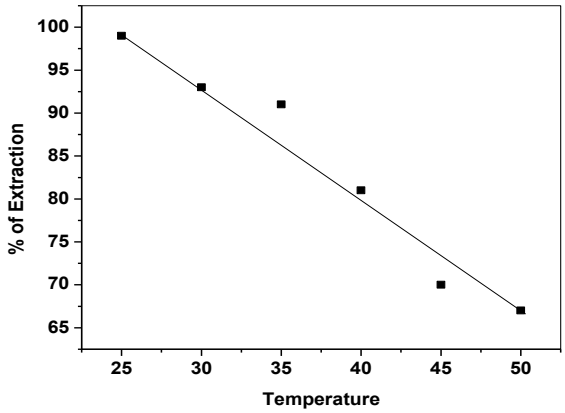


FIGURE 4 % of extraction varying with increasing temperature range from 25°C to 50°C

Effect of sonication time of the equilibrated phases

It was observed from the experiment that in ultrasonic interferometer the high frequency ultrasound (1-4) MHz did not have sufficient influence to cause mixing of organic and aqueous phases. This poor performance of the high frequency ultrasound was responsible for absence of cavitations in the treated medium. Cavitations effects can be created only at low frequencies [9]. For that reason, the extraction of uranium with the extractants was treated with low frequency ultrasonicator of 125 KHz for mixing of the two phases and settlement of the biphasic system. The higher frequency ultrasonic interferometer was used only for physico-chemical study of the liquid mixtures of MEK and kerosene.

Extraction efficiency for different concentration of MEK

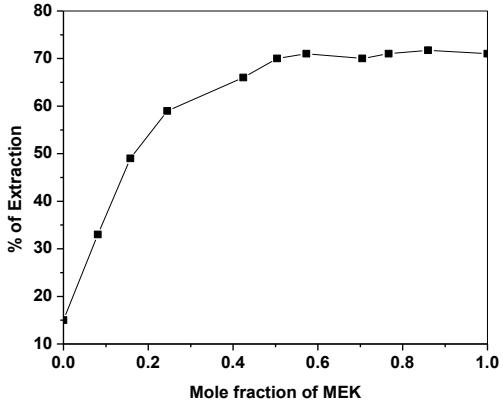


FIGURE 5 % of Extraction of uranium from Uranyl nitrate for different mole percentage of MEK with kerosene

During the extraction process each concentration of MEK /kerosene was treated with uranium in addition of HNO_3 and as per Nernst distribution law the distribution coefficient was recorded. The extraction of uranium increased steadily with a rise in MEK concentration up to 0.6 mole fraction and then plateau as shown in FIGURE 5. Thus

from the analysis of the figure and computed data, it was confirmed that for 60 % concentration range of MEK shows highest effectiveness for uranium extraction [18].

CONCLUSION

Different acoustical forces present within the solvent mixture due to transmission of ultrasonic wave, demonstrate the fundamental mechanism present in the liquid mixtures to estimate the extraction efficiency for extraction of uranium from Uranyl nitrate. These acoustical forces have established their importance in extraction technology in terms of measurement of sound wave parameters. The deviation of different acoustic parameters indicates the presence of different mutual interactions between the molecules of the solvent mixture from which the optimum concentration and suitable parameters for extraction is evaluated. From the above investigation it is confirmed that MEK with kerosene may be used as effective diluents/modifiers and the extraction efficiency of uranium is found to be (65-72) % in presence the optimum blend at 60 % of MEK for low frequency and low temperature. It is also verified that even if diluents are unable to extract metal ion from the aqueous phase, but they significantly have an effect on the extraction behavior of extractants.

ACKNOWLEDGEMENTS

The authors are grateful to Hon'ble Vice chancellor and Dean (PGS & R) for providing the financial support and laboratory facilities to carry out the research work and Dr.R.Paikaray of Ravenshaw University, Cuttack for the precious discussion and suggestion.

REFERENCES

1. M. Karve and R. V. Rajgor, Desalination **232**, 191-197 (2008).
2. A. F. Abdel-Magied and M. I. Amin, Int J Ind Chem **7**, 21-28 (2016).
3. S. N. Joung, S. J. Yoon, S. Y. Kim and K. Yoo, Journal of supercritical fluid **18**, 157-166 (2000).
4. I. Mohanty and V Chakravortty, Indian Journal of chemical technology **3**, 282-284 (1996).
5. A. H. Orabi, Journal of radiation research and applied sciences **6**, 1-10 (2013).
6. X. Fu, H. Xiaopeng, Z. Zuhua, H. Zhengshui and W. Debao, Colloids and surfaces A **152**, 335-343 (1999).
7. H. Zhengshui, H. Xiaopeng, C. Wei, W. Debao and F. Xun, Colloids and surfaces A **155**, 383-393 (1999).
8. V. Kannapan and R. J. Santhi, Indian journal of pure & applied physics **43**, 167-171 (2005).
9. B. Pesic, "Application of Ultrasound in Solvent Extraction of Nickel and Gallium", Idaho National Engineering Laboratory (Published July 1996).
10. R. Giri and G. Nath, Journal of Analytical Science and Technology **7,** 21 (2016).
11. J. Jiao, Y. He, K. Yasui, S. E. Kentish, M. Ashok kumar, R. Manasseh and J. Lee, Ultrasonic sonochemistry **22**, 70-77 (2015).
12. V. K. Syal, P. S. Baljeet and S. Chauhan, Indian journal of pure and applied physics **37**, 366-370 (1999).
13. R. Giri and G. Nath, J. Pure Appl. Ultrason. **37**, 44-47 (2015).
14. The engineering tool box, "Dynamic viscosity of common liquids", link: www.EngineeringToolBox.com.
15. A. N. Kannappan, V. Rajendran, K. Ramalingam and R. Palani Indian J. Phys. **65**, 266 (1991).
16. S. Praveen, M. Yasmin, M. Gupta and J. P. Shukla, Int. J. of Thermodynamics **13**, 59-66 (2010).
17. F. Nabi, C. G. Jesudason, M. A. Malik and S. A. Al-Thabaiti Chem.Engg Comm. **200**, 77 (2013).
18. F. Habashi, "A Text book of hydrometallurgy", *Metallurgie extractive Quebec*, Enr (1993).