



Ultrasonic analysis of acoustic properties of binary mixture for extraction of Cerium Oxide (CeO_2)

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ABSTRACT

The ultrasonic velocity, density and viscosity in the pure as well as in the binary mixture of Tributyl Phosphate (TBP) and Carbon tetrachloride (CCl_4) were measured. The variation of ultrasonic velocity and the other calculated acoustic parameters at temperature 30°C for different frequencies shows significant information about the intermolecular interactions present in the binary mixture. The shifting of λ_{max} in UV-visible spectra in the binary mixture agrees with the results of ultrasonic investigation of the binary mixture. The recovery of REE material like CeO_2 with the help of this ultrasonic technique can be explained in terms of intermolecular interactions present in the binary mixture. Again the result provides an optimum value of the binary mixture for recovery of CeO_2 which is well supported by other chemical treatments.

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Introduction

With the current renewed interest in nuclear energy and waste management, there is interest in better understanding of the molecular processes of extraction and determining the thermo physical properties of the phases involved which can be done by a systematic study on the acoustic properties of solvent mixture used for extraction process as well as for fuel reprocessing. The reprocessing of spent nuclear fuels is one of the key processes in the nuclear fuel cycle. Liquid-Liquid extraction was one of the most promising methods of separating REE's material. The repeated use of different organic solvents for the same corrodes the equipment severely and use of lots of volatile organic solvents may results in severe environmental pollution. Again the real picture of the role of extractant-diluent pair (EDP) is not clear as revealed from the work done by many workers. [1-15]. Thus an optimal concentration or range of concentration of extractants with particular diluents is a serious concern in the solvent extraction or purex process. The arbitrary selection of extractants and diluents for extraction process of REE's materials or nuclear fuel with different chemicals may originates serious environmental problem. Thus the present work is one of the ongoing research to find optimum concentration of extractants and diluents pair (EDP) used for extraction process. The accurate concentration of EDP and their variation with different physical factors can be studied well by the propagation of ultrasonic wave in the concerned medium & studying different acoustical parameter along with some derived parameters on the basis of fundamental characteristic property of the EDP.

There are many methods/processes to study such property or behavior of EDP like Surfactant enhanced [16], Microwave irradiation [17], Electro kinetic method [18] etc. But in almost all methods, some catalyst or accelerating chemical are added to understand and accelerate the complex process of extraction. To understand the basic process with the help of some fundamental parameter in a more easy way, another method called ultrasonic irradiation is more effective and more efficient. Ultrasonic wave, being a high frequency and short wave length wave, can interact

with the atoms and materials of the concerned medium without any destruction of the medium or individuality of component. But when this wave propagates through the EDP mixture, many physio -chemical properties may undergo change due to interaction of ultrasonic wave with EDP mixture. Moreover, when ultrasonic wave propagates in the medium, it generates compressions and rarefactions. The compression cycle exerts a positive pressure on the medium by pushing molecules together. The rarefaction cycle exerts a negative pressure by pulling molecules from each other, thereby, micro bubbles can be generated. When these microbubbles grow to an unstable dimension, they can collapse violently and generate shock waves, resulting in very high temperature and pressure in a few seconds [19]. These phenomena can increase the temperature of the EDP system and decrease its viscosity, increase the mass transfer of liquid phase and thus lead to destabilization EDP system [20]. Under the influence of ultrasonic irradiation, smaller droplets in EDP can move faster than the larger ones, and this can increase their collision frequency to form aggregates and coalescence of droplets which can help in extraction processes [21-22].

Extraction power of solvent depends upon the physical properties of the system. TBP has been extensively used as a solvent in nuclear chemistry for fuel reprocessing due to its excellent chemical resistance and physical properties which results in better separation than other solvents. The extracting power of TBP is mainly due to presence of phosphoryl group which form adducts or solvates with the metal ions. The physical properties like viscosity, density, and surface tension play a very important role in solvent extraction studies. TBP is generally used in conjunction with a hydrocarbon diluent which is inert in nature. The diluent like carbon tetrachloride, n-dodecane, liquid paraffin, kerosene etc. improves the physical properties of TBP by lowering the density and viscosity for better phase separation. Hence, it is important to study various physical properties of TBP in presence of diluent. In applications of liquid-liquid extraction processes for recycling of used nuclear fuel, the aqueous phase co-exists with an organic extracting phase which

consists of a mixture of an extracting agent and a diluent. A commonly used agent is the tri-n-butyl-phosphate (TBP) molecule which has been used to extract Cerium, Uranium, Plutonium, Zirconium and other metal cations. Cerium is a member of the lanthanide series of metals and is the most abundant of the rare-earth elements in the earth's crust. When present in compounds, cerium exists in both the trivalent state (Ce^{3+} , cerous) and the tetravalent state (Ce^{4+} , ceric). Cerium is found in nature along with other lanthanide elements in the minerals alanite, bastanite, monazite, cerite, and samarskite; however, only bastanite and monazite are important sources commercially. Because of its unique stability in the tetravalent state, cerium can be separated out from the other rare-earth elements through oxidation (forming CeO_2) followed by variable solubility filtration. Cerium salts can be prepared by liquid liquid extraction from rare-earth cerium-containing solutions. As a deep insight to the acoustic properties, it is necessary to study the different inter molecular interaction of the solvent mixture which is related to many experimental measurements of fundamental properties of TBP and related systems in the liquid. In the present paper, the exact or approximate concentration of TBP- CCl_4 for extraction of Ce from CeO_2 was taken with HNO_3 at room temperature. The result is discussed in terms of intermolecular interaction present in the E-D system. The study points out that, the main parameters affecting the extraction process are mainly concentration of organic extractants and type of diluents.

The acoustical properties like isentropic compressibility (β_s), intermolecular free length (L_f), acoustic impedance (Z) and their deviated values are evaluated using measured value of velocity, viscosity and density. In addition, UV-visible studies were also carried out to observe the intermolecular interaction in E-D system.

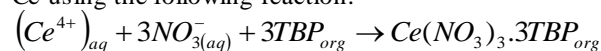
Materials and Instruments

High purity and analytical grade samples of TBP(AR,>98%), CCl_4 (AR,>99%), HNO_3 (AR,15.5mol/L) and CeO_2 (AR,>99%) were procured from CDH chemicals,Pvt.Ltd.The binary mixture was prepared on percentage basis (w/w) by mixing known mass of CCl_4 in appropriate masses of TBP and measuring their masses with the help of a high precision electronic balance of WENSAR,PGB 100.The densities of mixture as well as pure liquid were measured by a bicapillary pycnometer calibrated with deionized double distilled water of density $0.9960 \times 10^3 \text{ kg/m}^3$ at 303K.The precision of density measurement was within $\pm 0.0001 \text{ kg/m}^3$.The ultrasonic velocity in the mixtures as well as in the component liquids were measured at 303K by a single crystal variable path multi-frequency ultrasonic interferometer operating at different frequencies 1MHz-4MHz(Mittal Enterprises, New Delhi,Model-M-81S).The temperature of the mixture was maintained constant within $\pm 0.01\text{K}$ by circulation of water via a thermostatically regulated constant temperature water bath (B-206)through the water jacketed cell. The velocity measurement was precise up to $\pm 0.01\text{m/s}$. Viscosities of the mixtures were measured by Redwood apparatus and the time of flow was determined. The values of viscosities obtained were precise up to $\pm 0.0001 \text{ Ns.m}^{-2}$.UV-visible spectroscopic studies were carried out using U-3010 HITACHI double beam spectrophotometer using quartz cells and suitable reference solutions. The excited wavelength of TBP- CCl_4 was found to vary from 278nm - 284nm.

Experimental procedure

Different concentrations of extractant were prepared by dissolving various amounts of TBP in CCl_4 .All samples were

stored in ground-glass stopper bottles to prevent the evaporation. The concentrations of extractant was studied and optimized by ultrasonic method in terms of existence of different intermolecular interaction explaining the various acoustic parameters with their deviated values. The ultrasonic velocity of the pure liquids and their freshly prepared mixtures of (TBP- CCl_4) were measured using multi-frequency ultrasonic interferometer operating at different frequencies like 1MHz-4MHz. The working principle used in the measurement of velocity of ultrasonic wave through medium was based on the accurate determination of the wave length of ultrasonic waves of known frequency produced by quartz crystal in the measuring cell. The temperature of the solution was controlled by circulating water at a desired temperature through the jacket of double walled cell. The necessary volumes of both aqueous and organic phases were put into a separating funnel, which was dipped in water bath. After the temperature had reached equilibrium shaking of about one minute was repeated at interval of fifteen or twenty minutes. Both phases were separated rapidly after equilibrium time of about three or four hours. The prepared solution of TBP- CCl_4 of different concentration was treated to complexes of CeO_2 for extraction of Ce using the following reaction:



Theory

The experimental values of ultrasonic velocity, density and viscosity are used to determine different acoustic parameters such as isentropic compressibility (β), intermolecular free length (L_f), acoustic impedance (Z) and molar volume, surface tension and their excess values. The above acoustic parameters were computed with the help of the following relationship.

$$\beta_s = \frac{1}{\rho C^2}$$

Isentropic compressibility: (1)

$$L_f = k\beta^{1/2}$$

Intermolecular free length: (2)

Acoustic impedance : $Z = \rho C$ (3)

$$V_m = \frac{M}{\rho}$$

Molar volume: (4)

and their excess values were calculated as

$$(Y^E) = Y_{mix} - (X_A Y_A + X_B Y_B) \quad (5)$$

where X_A , X_B , Y_A , Y_B and Y_{mix} are mole fraction, isentropic compressibility, inter molecular free length ,acoustic impedance, molar volume, surface tension of CCl_4 ,TBP and mixture respectively. The constant k is temperature dependent which is given as $[93.875 + (0.375T)] \times 10^{-8}$ as per literature [23] and T being the absolute temperature. The extraction efficiency of TBP- CCl_4 can be calculated using the formula

$$E(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (6)$$

Where C_i and C_f represents the initial and ultimate concentration of Cerium ion in the aqueous phase respectively.

Result and discussion

The measured values of ultrasonic velocity(C), density (ρ) viscosity (η) and computed values of β_s , L_f , Z, V_m , S and their deviated values have been graphically plotted in Figs.1to 10. The ultrasonic velocity and intermolecular free length decrease up to 0.3-0.4mole fraction of TBP and then increases linearly with increasing concentration of TBP which is governed by the combined effect of intermolecular free length and density. Since the difference between density of CCl_4 and TBP is maximum,

the ultrasonic velocity in the TBP-CCl₄ mixture is expected to undergo a very large range of variation which is supported from the experimental findings. TBP contains P=O functional group which is polar and hence it can interact with non polar molecules like CCl₄ through polar-induced dipolar interaction. In pure TBP there is dipole-dipole as well as the dispersive interaction. The effect of adding non polar second component is primarily to disrupt the dipolar interaction of the first component.

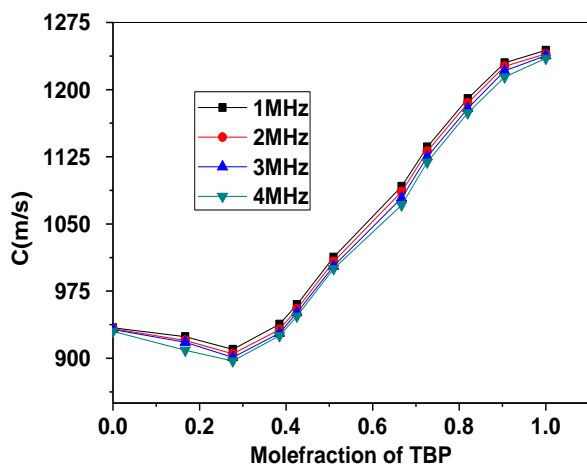


Fig 1. Variation of ultrasonic velocity with TBP

From the Fig-1 it is clear that the ultrasonic velocity decreases with decrease of mole fraction of CCl₄ up to 0.3-0.4 mole fraction then increases linearly with mole fraction of TBP. This may be due to self dissociation of the molecules and a very strong dipole-induced dipole interaction between the component molecules which is concentration dependant. Further, in this binary system the interaction becomes weak with increase of frequency causing thermal agitation in the system due to which molecules of the mixture move randomly leading to decrease of velocity very slowly with frequency, but almost same trends noticed for all four frequencies.

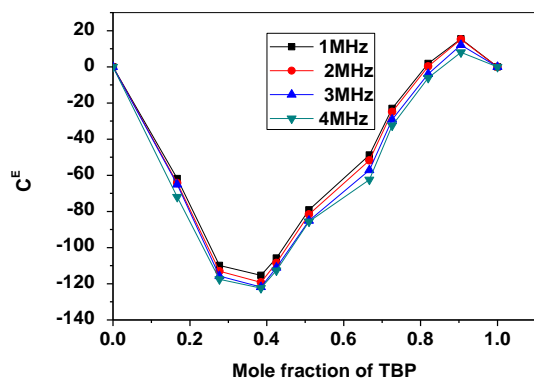


Fig 2. Variation of deviated ultrasonic velocity with TBP

In order to understand the nature of molecular interactions between the components of the liquid mixture, it is interesting to discuss the acoustical properties in terms of excess parameter rather than actual values. Non-ideal liquid mixture show considerable deviation from linearity in their physical behavior with respect to concentration which have been interpreted as arising from the presence of strong or weak interaction. The effect of deviation depends upon the nature of the constituents and composition of the mixture. The excess velocity shows a negative deviation suggesting the presence of weak dipole-induced dipole interactions in the system as shown in Fig.2. With increase of frequency the deviation increases relatively

suggesting the interaction becomes weaker and weaker due to loss of energy of the agitating molecules. The sharp peak is at about 0.4 mole fraction of TBP, the negative deviated value decreases indicating the interaction between TBP-TBP is dominant throughout and no significant change in cluster formation involving dissimilar molecules.

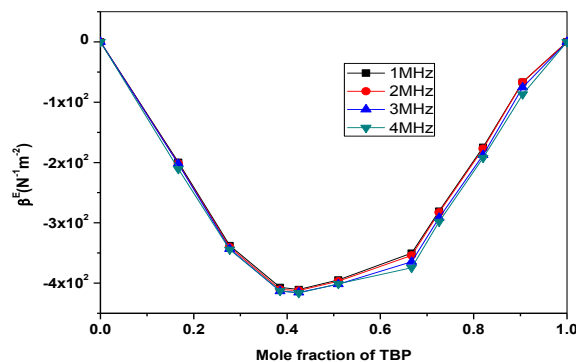


Fig 3. Variation of deviated isentropic compressibility with TBP

The values of β^E changes from positive to negative in TBP-CCl₄ as shown in Fig.3. Mixing of TBP with CCl₄ will induce the breaking up of the associated clusters of TBP releasing several dipoles which in turn can induce a dipole moment in CCl₄ molecules, resulting dipole-induced dipole interactions. Thus, CCl₄ acts as a structure breaker of TBP. The breaking up of associated O^{δ+} of TBP leads to an expansion in volume, hence an increase in β^E and the dipole-induced dipole interaction is responsible for contraction in volume, hence a decrease in β^E . With the increase of frequency the interaction becomes weak and the breaking of associated structure of TBP dominates, increase in β^E .

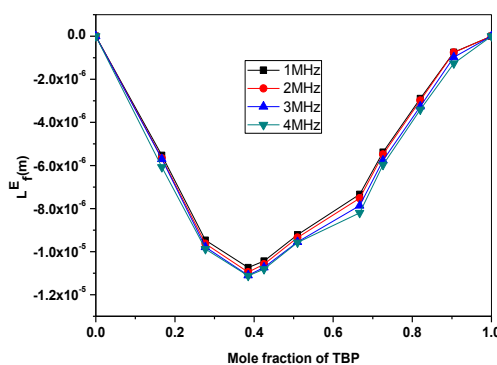


Fig 4. Variation of deviated intermolecular free length with TBP

The positive values of L_f^E are attributed to loose packaging of the component molecule up to 0.4 mole fraction of TBP and then increases relatively attributing to close packing of the component molecules which in fact supports the hetero molecular association between the TBP and CCl₄, which results the decrease in free length between the component molecules indicates that the system is more resistant to the sound propagation as shown in Fig.4. The variation of β^E and L_f^E is

again supported by the positive variation of Z^E as shown in Fig.5.

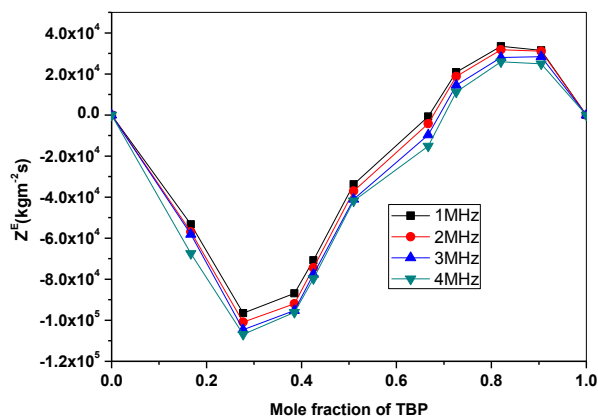


Fig 5. Variation of deviated acoustic impedance with TBP

The Z^E values are found to be negative initially but then become positive. These values indicate weaker interaction which may be due to decreasing proton donating ability of CCl_4 to TBP. This trend occurs up to 0.3-0.4 mole fraction of TBP. When concentration of TBP increases, the Z^E value decreases negatively and becomes positive as shown in Fig.5. This is attributed due to interaction between component molecules and formation of closer molecular aggregates which leads to decrease in the intermolecular free space. This behavior is supposed to be caused by structural arrangement of phosphoryl group of TBP and $Cl^{\delta-}$ of CCl_4 .

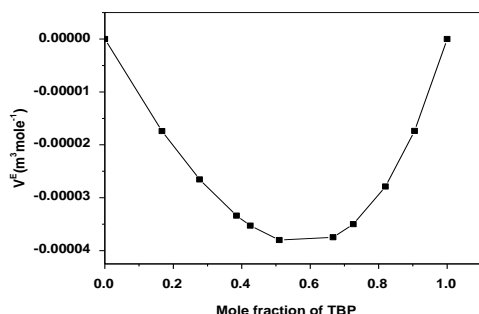


Fig 6. Variation of deviated molar volume with TBP

The deviated molar volume V^E also exhibits a negative trend as shown in Fig.6 with composition that can be attributed due to increase in molecular interaction between the component mixtures up to 0.3-0.4 mole fraction of TBP then increases positively. This also indicates that this mole fraction of liquid mixture is optimum value of TBP for extraction process. The deviated volume is influenced by i) the mutual dispersion of associated present in the pure liquid ii) dipole-dipole/dipole-induced dipole interaction between unlike molecules and iii) internal accommodation of small molecules in to void created dissociation. Negative V^E (Fig.6) are mainly ascribed to the latter two factors. It also points out that the negative values of V^E may to some extent due to difference in molecular size of the component molecules. The deviated viscosity is positive over the entire composition range.

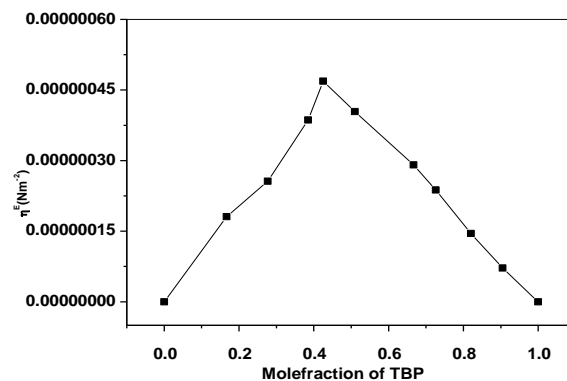


Fig 7. Variation of deviated viscosity with TBP

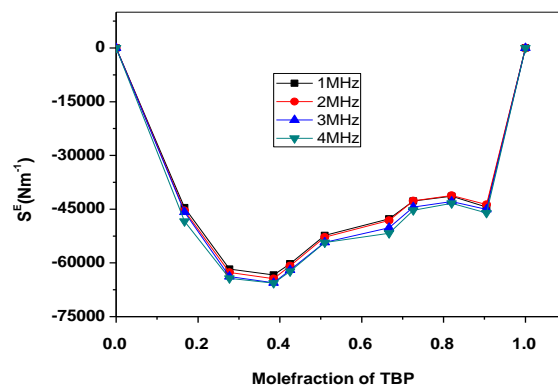


Fig 8. Variation of deviated surface tension with TBP

The positive values of deviated viscosity suggests that specific interaction like formation of charge complexes, transfer of complexes, dipole-dipole interaction are predominant in the system as shown in Fig.7. Similarly, the deviated surface tension is also negative throughout the system. The maximum deviation at 0.4 to 0.5 mole fraction of TBP. The negative deviated S^E of mixture indicates the weak interaction between the components as shown in Fig.8.

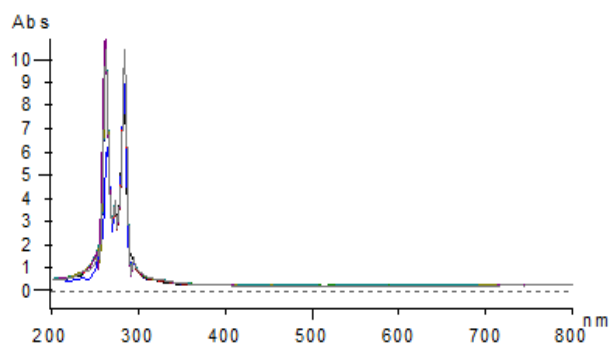


Fig 9. Variation of absorbance in EDP solution with wavelength

To understand the nature of EDP, UV-visible spectroscopic studies were carried out (Fig.9). The spectra of the EDP solution were compared with that of the ultrasonic computational value of wave length and velocity suggesting almost similar coordination environment. On the other hand, the spectra of the EDP solution showed enhanced absorbance, though the characteristic spectral features were retained. However, on closer examination one can notice a shift in the bands to higher wavelength suggesting possible changes in the coordination environment.

This suggested change in the nature of EDP solution which is possible due to only the intermolecular interaction between the EDP solutions.

This clearly indicates that the atom/molecules of CCl_4 and TBP only influences each other externally by making themselves partially ionized. TBP is polar liquid having dipole moment $\mu=2.92\text{D}$ and dielectric constant $\epsilon=8.29$. The Kirkwood-Fohlich linear correlation factor $g=1.3$ for TBP, indicates that short range specific interaction between TBP molecules leads to preferential dipolar alignment. Reinforcement of angular correlation among the polar molecules of similar nature results in parallel dipolar alignment leading to the formation of α -multimers for which, the Kirkwood-Fohlich linear correlation factor g is greater than unity whereas anti parallel dipolar alignment results in β -multimers for g less than unity. As TBP is known to be a mild associated polar liquid having $g > 1$, it can remain in head tail arrangement with α -multimerization. With addition of polar liquid like CCl_4 breaking of α -multimers takes place which facilitates the extraction processes.

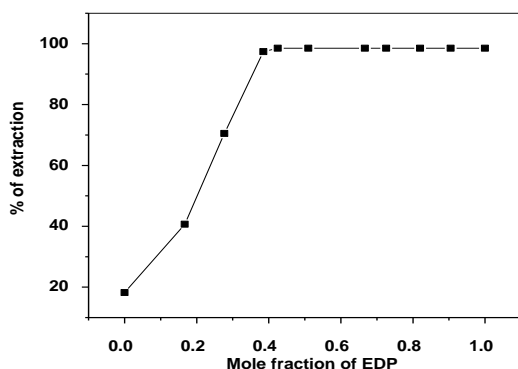


Fig 10. Variation of % extraction of Ce from CeO_2 with EDP solution

When each concentration of EDP was treated with CeO_2 in addition of HNO_3 the calculated amount of $\text{Ce}(\text{NO}_3)_3$ increased up to 0.3 to 0.4 mole fraction of TBP and was unaltered after that mole fraction, even though concentration of TBP was increased as shown in Fig.10. Thus it is clear that the optimized concentration of EDP is suitable for extraction study of Ce from CeO_2

Conclusion

The results confirmed that the TBP in conjunction with CCl_4 provided the significant extraction efficiency of CeO_2 . The variation of all the studied acoustical parameters shows that the EDP mixture is well suitable for extraction of CeO_2 . The nature of interaction present in the EDP provides an optimized value for the extraction process. The propagation of ultrasonic wave

through the EDP makes it possible for selection of suitable EDP for extraction of particular REE material. Finally the present work based on the study of acoustic properties shows that the nature of molecular interaction of TBP with CCl_4 may be non-specific dipole-induced dipole, dispersive and dipole-dipole type. As such CCl_4 with TBP may be used as an effective diluents/modifier in the extraction of REE's material.

Reference

- [1] K T Tran, T Van Luong, D J An W Kang and M J Kim *Hydrometallurgy* **138** 93 (2013)
- [2] Y Z Tan, W Qin *Chem. Eng.* **39** 26 (2011)
- [3] Y H Zhang, L J Li, J F Li, L M Ji, Q R Xu and G.H.Chen, *Inorg. Chem. Ind.* **44** 12 (2012)
- [4] S Y Sun, F Ye, X F Song, Y Z Li, J Wang and J G Yu *Chin. J. Inorg. Chem.* **27** 439 (2011)
- [5] X Q Sun, H M Luo and S Dai *Chem. Rev.* **112** 2100 (2012)
- [6] A V Mudring and S F Tang *Eur. J. Inorg. Chem.* **18** 2569 (2010)
- [7] C Zhang and J Chen *Chem. Commun.* **46** 592 (2010)
- [8] R D Rogers *Nature* **447** 917 (2007)
- [9] A B Lakshmi, A S Balasubramanian Venkatesan *Clean – Soil Air Water* 349 (2013)
- [10] S Panja, P K Mohapatra, S C Tripathi, P M Gandhi and P A Janardan *Sep. Purif. Technol.* **96** 289 (2012)
- [11] M Sun, L Y Yuan, N Tan, Y L Zhao, Z F Chai and W Q Shi *Radiochim. Acta* **102** 87 (2014)
- [12] H Okamura, H Takagi, T Isomura, K H Morita and H. Imura Nagatani *Anal. Sci.* **30** 323 (2014)
- [13] A Rout and K Binnemans *Dalton Trans.* **43** 1862 (2014)
- [14] S Chen, H Sun and Y S Zhong *J. Beijing Univ. Technol.* **39** 98 (2013)
- [15] J Castillo, M T Coll, A Fortuny, P N Donoso, R Sepulveda and A M Sastre *hydrometallurgy* **141** 89 (2014)
- [16] D Grasso, K Subramaniam, J J Pignatello, Y Yang and D. Ratte *Colloids Surf. A* **194** 65 (2001)
- [17] T J Appleton, R I Colder, S W Kingman, I S Lowndes and A G Read *Appl. Energy* **81** 85 (2005)
- [18] C H Kuo and C L Lee *Sep. Purif. Technol.* **74** 288 (2010)
- [19] S Pilli, P Bhunia, S Yan, R J LeBlanc, R D Tyagi and R Y Surampalli *Ultrason. Sonochem* **18** 1 (2011)
- [20] H I Chung and M. Kamon *Eng. Geol.* **77** 233 (2005)
- [21] X Yang, W Tan and X Tan *Petrol. Sci. Technol.* **27** 2010 (2009)
- [22] R C Gholam and M Dariush *Ultrason. Sonochem.* **20** 378 (2013)
- [23] A Ali, A K Nain and M Kamil *Thermochim. Acta* **274** 209 (1996)