Desalination and Water Treatment
www.deswater.com

25 (2011) 216–225
January

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doi: 10.5004/dwt.2011.1848

Third phase formation in the extraction of nitric acid and metal ions by octyl(phenyl)-*N*,*N*-diisobutyl carbamoyl methyl phosphine oxide (OΦCMPO) based solvents

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Received 10 February 2010; Accepted in revised form 10 May 2010

ABSTRACT

Formation of a third phase in the extraction of nitric acid and metal ions such as Th(IV), U(VI), La(III), Ce(III), and Gd(III) by OΦCMPO based solvents has been investigated under various conditions. The limiting organic concentrations (LOC) and critical aqueous concentrations (CAC) for third phase formation in the extraction of nitric acid by 0.2 M OΦCMPO + 1.2 M TBP in *n*-tetradecane and 0.2 M OΦCMPO + 1.2 M TBP in *n*-hexadecane were measured as a function of temperature. Extraction of nitric acid by these solvents as a function of equilibrium aqueous phase acidity at 303 K has been studied. Distribution of nitric acid between diluent-rich phase (DP) and third phase (TP) in the extraction of nitric acid by these solvents has also been studied as a function of equilibrium aqueous phase acidity at 303 K. Densities of diluent-rich phase, third phase, and aqueous phase have been measured as a function of equilibrium aqueous phase acidity at 303 K. Third phase formation in the extraction of Th(IV), U(VI), La(III), Ce(III), and Gd(III) by OΦCMPO modified with tri-*n*-butyl phosphate (TBP) or tri-*n*-amyl phosphate (TAP) in various hydrocarbon diluents has also been studied as a function of temperature. Metal loading capacity of some of these solvents has also been studied as a function of equilibrium aqueous phase acidity at 303 K. Results obtained from these studies are presented in this paper.

Keywords: Third phase formation; OΦCMPO; Nitric acid; Lanthanides; Uranium

1. Introduction

High metal and/or mineral acid loading in the organic phase under suitable experimental conditions, leads to “third phase formation”. Earlier this phenomenon has been investigated for a number of solvent extraction systems [1–5]. Since solvent extraction plants are designed to operate only with two phases, formation of a new phase (third phase) can complicate the operations. It creates several problems related to density and viscosity effects in a solvent extraction plant. Hydrodynamic problems like flooding in which organic streams following aqueous and vice versa may arise during the operation of a liquid–liquid extraction equipment. Criticality problems are also associated with this phenomenon in the extraction of plutonium. Third phase formation can also lead to phase inversion due to the formation of organic phases with densities higher than that of aqueous phases.

Earlier, this phenomenon was not considered to be a serious issue. One of the reasons for this is that most of

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the solvent extraction studies have been performed under the conditions of low concentrations of metal ions, which do not promote third phase formation. Apart from this, earlier studies are mainly related to the extraction of U(VI) by TBP or related compounds and third phase formation is unlikely to take place in these systems under normal extraction conditions. However, the development of several highly polar extractants such as octyl(phenyl)-N,N-diisobutyl carbamoyl methyl phosphine oxide (OΦCMPO), N,N′-dimethyl-N,N′-dibutyl-2-tetradecylmalonamide (DMDBTDMA), N,N,N′,N′-tetraoctyl diglycolamide (TODGA), etc., for the recovery of minor actinides and some fission products from waste solutions [6–9] changed the scenario. Tendency of TBP to form a third phase in the extraction of tetravalent metal ions such as Th(IV), Pu(IV), Zr(IV), etc. has also led researchers to study third phase formation in the extraction of these metal ions by TBP [10–16]. The number of publications on third phase formation is currently increasing [17–32] and this is an indication that this subject has gained a lot of importance in recent years.

Most of the reagents developed for the recovery of minor actinides and lanthanides from waste solutions have a tendency to form a third phase in the extraction of nitric acid and metal ions. In order to improve the metal loading capacity without phase splitting, extractant/hydrocarbon mixture is always combined with a suitable phase modifier. In the case of OΦCMPO, TBP is used as the phase modifier and 0.2 M OΦCMPO/1.2 M TBP/n-dodecane is the solvent proposed for the processing of waste solutions by TRUEX process [6].

Concentrations of lanthanides and minor actinides in HAW (raffinate) solutions generated after the processing of thermal reactor fuels are low. However, these concentrations are expected to be high in the case of fast reactor fuels. Concentrations (in g/l) of some of the rare earths such as La, Ce, Pr, Nd, Sm, and Gd are around 0.26, 0.53, 0.24, 0.86, 0.16, and 0.016, respectively, in a typical waste solution of 6500 MWD/Te PHWR fuel and concentrations in the case of waste solutions of 80,000 MWD/Te FBR fuels are around 0.34, 0.68, 0.34, 1.13, 0.31, and 0.066, respectively [33]. Though the extraction behaviour of various trivalent lanthanides in the extraction by OΦCMPO is known, it is important to have a fundamental knowledge of third phase formation in the extraction of lanthanides with OΦCMPO.

Nagasaki et al. [34] have studied third phase formation in the extraction of nitric acid by OΦCMPO modified with TBP in *n*-dodecane as a function of OΦCMPO and TBP concentrations and temperature. Influence of parameters such as nature of modifier, diluent chain length, temperature, and equilibrium aqueous phase acidity on third phase formation in the extraction of Ce(III), Nd(III), Th(IV), U(VI), and Pu(IV) by OΦCMPO has been reported by Kolarik and Horwitz [35]. Earlier, we have also studied this phenomenon in the extraction of Nd(III) by 0.2 M OΦCMPO in *n*-dodecane with TBP and TAP as modifiers as a function of modifier concentration [36].

In the present study, we investigated third phase formation in the extraction of nitric acid by 0.2 M OΦCMPO + 1.2 M TBP in *n*-tetradecane and 0.2 M OΦCMPO + 1.2 M TBP in *n*-hexadecane under various conditions. Studies on third phase formation in the extraction of La(III), Ce(III), Gd(III), Th(IV), and U(VI) by 0.2 M OΦCMPO modified with TBP and TAP as a function of various parameters such as temperature, diluent chain length, equilibrium aqueous phase acidity, etc. have been carried out. Though Th(IV) is not expected to be present in waste solutions, it is included in the present study to understand the third phase formation behaviour of OΦCMPO in the extraction of tetravalent metal ions.

2. Experimental

2.1. Materials

OΦCMPO was purified by column chromatography using neutral alumina as stationary phase and *n*-hexane as mobile phase. To confirm the absence of acidic impurities in purified OΦCMPO, distribution ratio for the extraction of Am(III) by 0.2 M OΦCMPO + 1.2 M TBP/*n*-dodecane was determined and found to be very low (0.01). Lower $D_{\mathrm{Am(III)}}$ values for the extraction by a neutral extractant from 0.01 M HNO_3 indicate the absence of acidic impurities. Details about the synthesis, purification, and characterization of TAP are described elsewhere [30]. TBP (Fluka make), hydrocarbon diluents (supplied by M/s. Lancaster Synthesis Ltd., England and M/s. Tokyo Kasei, Kogyo, Japan) were used for the experiments. All other chemicals used in the present study were of GR or AR grade.

2.2. Third phase formation experiments

The experimental set-up for third phase formation studies consisted of a flat bottom equilibration tube kept in a double walled thermostat vessel which was kept on a magnetic stirrer. Water from a refrigerated and heating circulator (JULABO make, F33-HE) with a temperature controlling accuracy of ±0.01°C was circulated through the double walled vessel. In the experiments carried out without the dissolution of third phase, equal volumes of respective organic and nitric acid solutions were equilibrated using a PTFE coated magnetic stirring bar at 303 K for about 20 min. Subsequently, the phases were allowed to settle by gravity. In the experiments, where third phase formation does not take place, organic and aqueous phases were analysed and the distribution of nitric acid was determined as a function of equilibrium aqueous phase acidity up to the point of organic phase splitting. In the experiments, where phase splitting takes place, equilibrium concentrations of nitric acid in diluent-rich phase, third phase, and the aqueous phase were measured.

In the experiments involving the dissolution of third phase, initially third phase was formed and subsequently, dissolved by the dropwise addition of organic solution of same composition with intermittent stirring. The organic and aqueous phases at the point of dissolution of the third phase were analysed for nitric acid and metal ions. If there is no third phase formation, the concentrations of organic phase in equilibrium with the saturated aqueous phase and the aqueous phase are called maximum organic concentration (MOC) and saturated aqueous concentration (SAC), respectively. Experiments for third phase formation in the extraction of nitric acid and various metal ions from solutions with near-zero free acidity were carried out as a function of temperature. Third phase formation in the extraction of metal ions from nitric acid media as a function of aqueous phase acidity was also carried out as described above.

2.3. Analytical procedures

For the experiments carried out on third phase formation in the extraction of nitric acid (without metal nitrate), acidity of organic and aqueous samples was estimated by acid-base titration with standardised NaOH solution using phenolphthalein as indicator. In the case of solutions of metal nitrates in nitric acid media, acidity was estimated after complexing metal ions with saturated pre-neutralised potassium oxalate solution. Thorium in organic and aqueous samples was estimated by complexometry using diethylenetriaminepentaacetic acid (DTPA) as titrant and xylenol orange as indicator at pH 1 [37]. Concentration of uranium in organic and aqueous solutions was determined by complexometry using 2,6-pyridinedicarboxylic acid (PDCA) as titrant and Arsenazo I as indicator at pH 3.7 [38]. Lanthanum, cerium, and gadolinium in the samples (organic as well as aqueous) were estimated by complexometry with ethylenediaminetetraacetic acid (EDTA) as titrant and methyl thymol blue as indicator at pH 6 [37,39]. In general the complexometric estimation had a precision of better than ±1%.

2.4. Measurement of density

Density of various organic and aqueous solutions was measured by taking the weight of the sample by using a previously weighed Class A, glass micropipette of volume 500 μL (BOROSIL®, India) in an analytical balance of ±0.1 mg sensitivity.

3. Results and discussion

3.1. Third phase formation in the extraction of nitric acid

Fig. 1 and Fig. 2 are the simplified phase diagrams for the extraction of nitric acid by 0.2 M OΦCMPO + 1.2 M TBP in *n*-tetradecane and *n*-hexadecane, respectively, at 303 K. The point of intersection of the three curves describing the nitric acid concentrations in the organic phases in biphasic and triphasic regions of the simplified phase diagram represents the CAC and LOC values. As shown in Figs. 1 and 2, nitric acid distributes asymmetrically between the light and heavy organic phases. Concentration of nitric acid in the heavy organic phase (third phase) is always higher than that in the corresponding light organic phase (diluent-rich phase). Though the concentrations of CMPO, TBP, and water in diluent-rich and third phases are not measured in the present study, these species are also expected to be distributed asymmetrically between the light and the heavy organic phases as in the case of nitric acid. Work reported by Nagasaki et al. [34] has revealed that both CMPO and TBP are enriched in the third phase after the phase splitting.

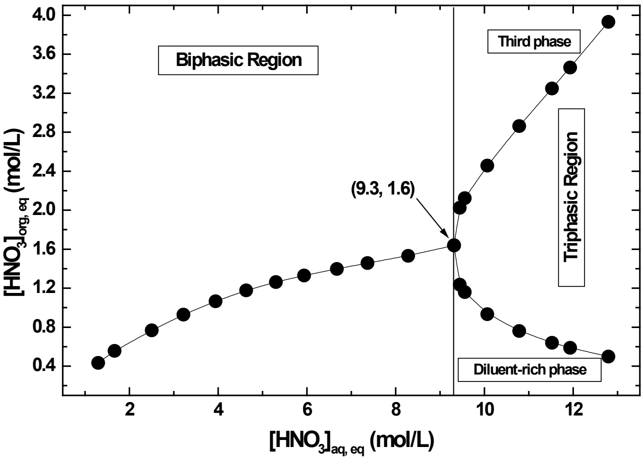

Fig. 1. Simplified phase diagram for the extraction of nitric acid by 0.2 M CMPO + 1.2 M TBP/*n*-tetradecane at 303 K.

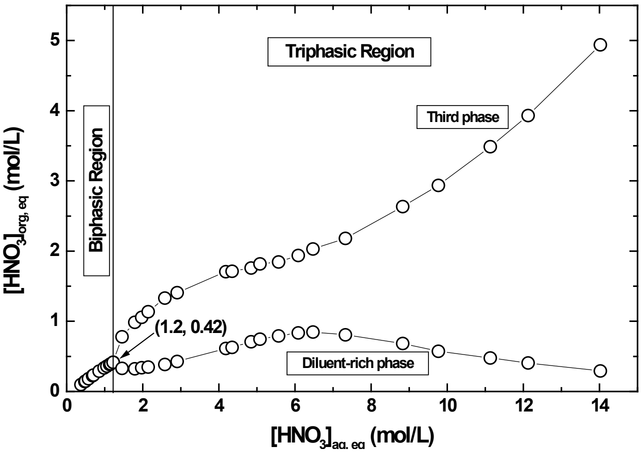

Fig. 2. Simplified phase diagram for the extraction of nitric acid by 0.2 M CMPO + 1.2 M TBP/*n*-hexadecane at 303 K.

The effect of temperature on third phase formation in the extraction of nitric acid by 0.2 M OΦCMPO + 1.2 M TBP in *n*-tetradecane and *n*-hexadecane is shown in Fig. 3. CAC values for these systems as a function of temperature are shown in Fig. 4. In both cases, LOC and CAC values increase with the increase in temperature in a nonlinear fashion. Interestingly, there is a sharp change in LOC and CAC values in a particular temperature band (20–25 K for *n*-tetradecane and 30–35 for *n*-hexadecane) and the reason for this is not very clear. The data on LOC also indicate that at higher temperature, nitric acid loadings in both the systems are higher than the total amount of TBP and CMPO available (1.4 M) as compared to that at lower temperatures (less than 0.52 M). This can be explained based on the possible formation of disolvate complexes of the type TBP.2HNO_3 and CMPO.2HNO_3.

Earlier, Nagasaki et al.[34] have determined the boundary of third phase formation for OΦCMPO – TBP – *n*-dodecane – HNO_3 as a function of concentrations of CMPO, TBP, and temperature. They have observed that phase splitting does not take place at higher temperature even if TBP/CMPO concentration ratio is below 1.0. They reported that the effect of TBP as a phase modifier is predominant at higher temperatures as compared to lower temperatures. Kolarik and Horwitz [35] also reported an increasing trend of LOC with the increase in temperature in the extraction of Nd(III) by 0.2 M OΦCMPO + 1.2 M TBP/*n*-dodecane as a function of equilibrium aqueous phase acidity. An increasing trend of LOC with temperature in other solvent extraction systems has also been reported by various authors [3,5]. Fig. 3 and Fig. 4 also show that LOC and CAC values, respectively, in the case of *n*-tetradecane are higher than those values of *n*-hexadecane system at a particular temperature. However, the difference between *n*-tetradecane and *n*-hexadecane systems decreases with increase in temperature at higher temperature range. Earlier, we have reported that 0.2 M OΦCMPO + 1.2 M TBP in *n*-dodecane does not form third phase with nitric acid up to an equilibrium aqueous phase acidity of 9.3 M with an organic phase nitric acid loading of around 1.7 M at 303 K [36].

Variation of density of organic and aqueous phases as a function of equilibrium aqueous phase acidity is shown in Fig. 5. Differences in nitric acid concentration and density between third phase and diluent-rich phase are shown in Fig. 6 and Fig. 7, respectively. These figures show that, differences in density and nitric acid concentration between third phase and diluent-rich phase increase with increase in equilibrium aqueous phase acidity. However, in the case of *n*-hexadecane diluent, there is a slight decrease in density difference by increasing the aqueous phase acidity from around 3 M to 5 M. It can also be seen in Figs. 6 and 7 that nitric acid concentration difference and density difference between the heavy and light organic phases for *n*-hexadecane

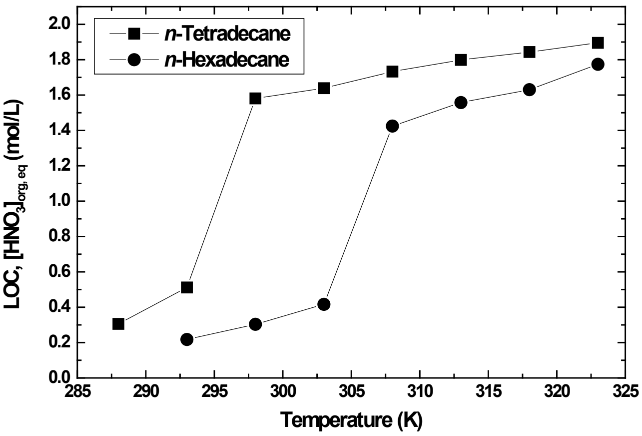

Fig. 3. Variation of LOC with temperature for third phase formation in the extraction of nitric acid by 0.2 M CMPO + 1.2 M TBP/$C_nH_{(2n+2)}$.

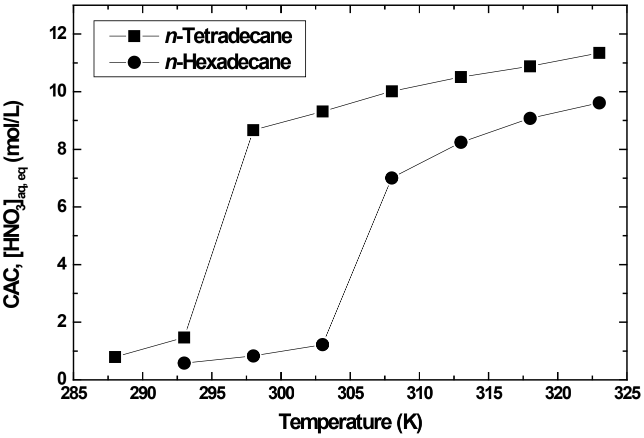

Fig. 4. Variation of CAC with temperature for third phase formation in the extraction of nitric acid by 0.2 M CMPO + 1.2 M TBP/$C_nH_{(2n+2)}$.

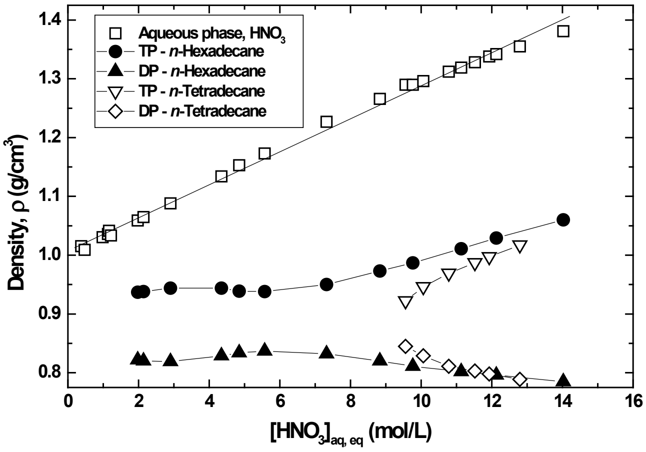

Fig. 5. Variation of density of organic and aqueous phases with equilibrium aqueous phase acidity for the extraction of nitric acid by 0.2 M CMPO + 1.2 M TBP/$C_nH_{(2n+2)}$ at 303 K.

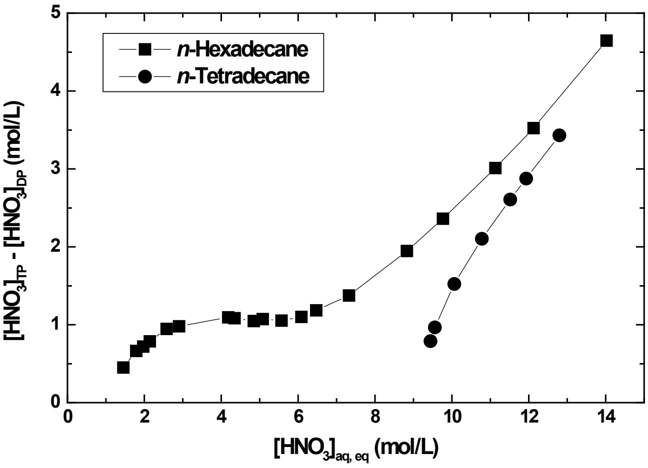

Fig. 6. Variation of difference in nitric acid concentration between TP and DP with equilibrium aqueous phase acidity for the extraction of nitric acid by 0.2 M CMPO + 1.2 M TBP/$C_nH_{(2n+2)}$ at 303 K.

system are higher than that of *n*-tetradecane system at a given equilibrium aqueous phase acidity.

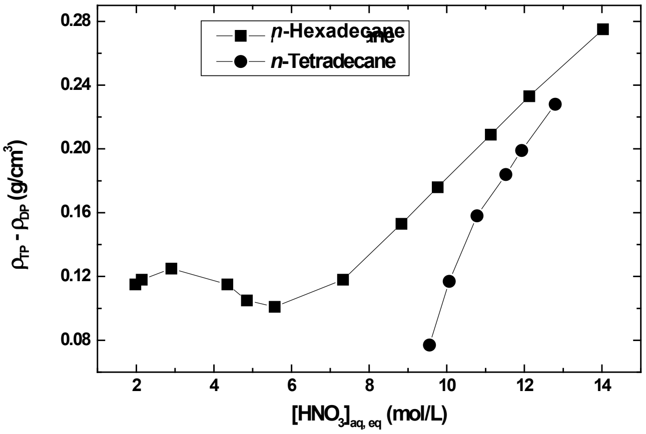

Fig. 7. Variation of difference in density between TP and DP with equilibrium aqueous phase acidity for the extraction of nitric acid by 0.2 M CMPO + 1.2 M TBP/$C_nH_{(2n+2)}$ at 303 K.

3.2. Third phase formation in the extraction of metal nitrates

The data on LOC for third phase formation in the extraction of Th(IV), U(VI), and La(III) by CMPO based solvents as a function of equilibrium aqueous phase acidity at 303 K are shown in Fig. 8. LOC data for third phase formation in the extraction of Nd(III) reported earlier [36] is also shown in Fig. 8 for comparison. It can be seen from Fig. 8 that in all the cases there is an initial sharp decrease in LOC, which gets flattened at higher aqueous phase acidity. Fig. 8 shows that LOC values for the extraction of La(III) and U(VI) by 0.2 M OΦCMPO + 1.2 M TBP/*n*-dodecane from 3 to 4 M nitric acid solutions are low and range from 0.074 to 0.069 mol/L (10.3–9.6 g La/L) and 0.045–0.038 mol/L (10.7–9.04 g U/L), respectively. Hence in CMPO based extraction processes, care has to be taken to ensure that the concentration of lanthanides as well as residual uranium in aqueous feed solutions is well below the third phase formation limits, especially in extraction stages where aqueous phase acidity is expected to be high.

Variation of nitric acid loading in the organic phase as a function of equilibrium aqueous phase acidity during the extraction of Th(IV), U(VI), and La(III) by CMPO based solvents is also shown in Fig. 9. It is seen in Fig. 9 that in all the cases nitric acid concentration in the organic phase increases with increase in equilibrium aqueous phase acidity. This indicates that TBP and CMPO molecules are predominantly free at lower acidities, whereas

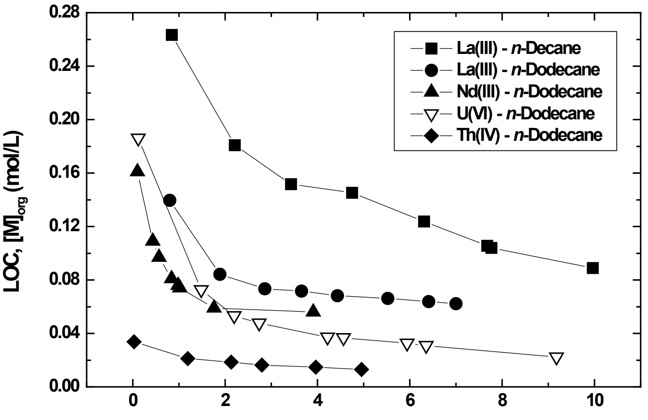

Fig. 8. Variation of LOC with equilibrium aqueous phase acidity for third phase formation in the extraction of La(III), Nd(III), Th(IV) and U(VI) by 0.2 M CMPO + 1.2 M TBP/$C_nH_{(2n+2)}$ at 303 K.

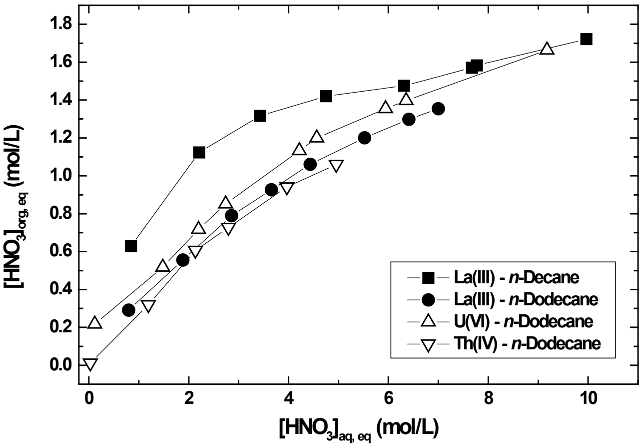

Fig. 9. Isotherms for the extraction of nitric acid by 0.2 M CMPO + 1.2 M TBP/$C_nH_{(2n+2)}$ in the presence of various metal ions at 303 K.

at higher acidities major fraction of TBP and CMPO is associated with nitric acid. This is the reason for the higher organic phase metal loadings at lower acidities and lower organic phase metal loadings at higher acidities. The decreasing trend of LOC with equilibrium aqueous phase acidity is also explainable based on the interacting reverse-micelles model.

The variation of LOC for third phase formation in the extraction of Th(IV), U(VI), La(III), Ce(III), and Gd(III) by OΦCMPO based solvents from corresponding metal nitrate solutions with near-zero free acidity as a function of temperature is shown in Figs. 10–13. It is seen in these figures that LOC increases with increase in temperature in a linear manner. Very recently we have reported a linear relationship between LOC and temperature in the extraction of $Th(NO_3)_4$ by 1.1 M solutions of several tri-alkyl phosphates in different diluents [30]. In contrast to third phase formation in the extraction of nitric acid, in the case of extraction of nitrates of La(III), Ce(III), and Gd(III), the difference between the LOC values of *n*-tetradecane and *n*-hexadecane systems increases with temperature increase at higher temperature range.

Data on third phase formation in the extraction of lanthanides such as La(III), Ce(III), and Gd(III) from solution with near-zero free acidity by 0.2 M OΦCMPO + 1.2 M TBP/$C_nH_{(2n+2)}$ clearly show that at a particular temperature LOC values vary in the order La > Gd > Ce. Since concentration of OΦCMPO in the organic phase is 0.2 M and lanthanide nitrates form trisolvate with OΦMPO, LOC values are not expected to exceed 0.0667 M

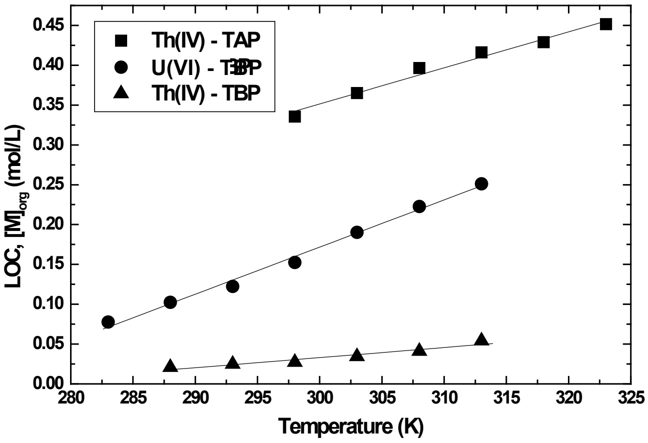

Fig. 10. Variation of LOC with temperature for third phase formation in the extraction of $Th(NO_3)_4$ and $UO_2(NO_3)_2$ from solutions with near-zero free acidity by 0.2 M CMPO + 1.2 M TalP/$C_{12}H_{26}$.

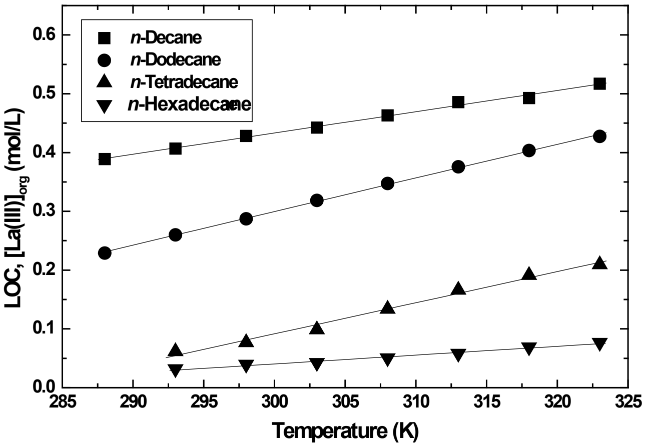

Fig. 11. Variation of LOC with temperature for third phase formation in the extraction of $La(NO_3)_3$ from solutions with near-zero free acidity by 0.2 M CMPO + 1.2 M TBP/$C_nH_{(2n+2)}$.

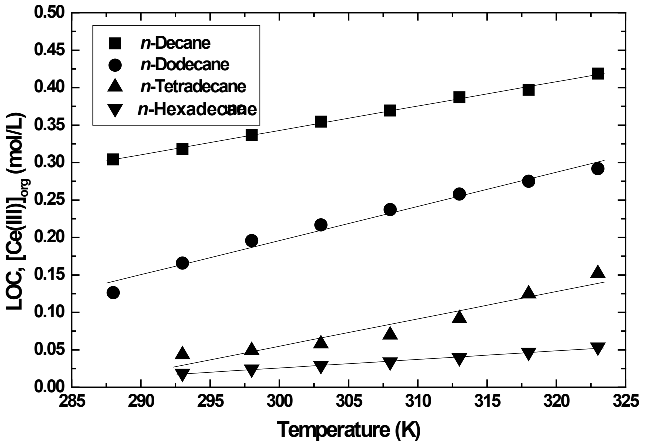

Fig. 12. Variation of LOC with temperature for third phase formation in the extraction of $Ce(NO_3)_3$ from solutions with near-zero free acidity by 0.2 M CMPO + 1.2 M TBP/$C_nH_{(2n+2)}$.

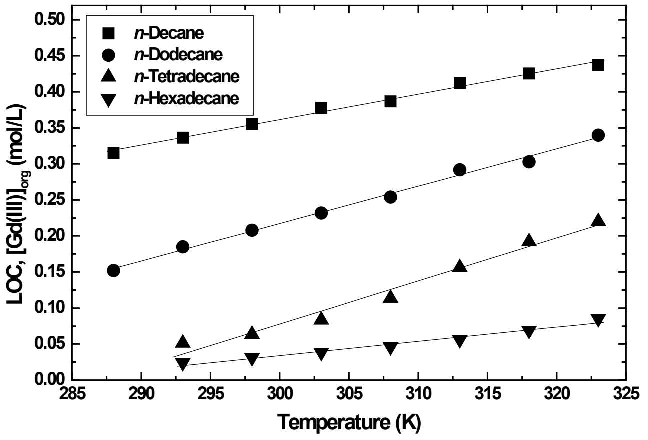

Fig. 13. Variation of LOC with temperature for third phase formation in the extraction of $Gd(NO_3)_3$ from solutions with near-zero free acidity by 0.2 M CMPO + 1.2 M TBP/$C_nH_{(2n+2)}$.

[35]. However, data shown in Figs. 11–13 reveal that LOC values are significantly higher than the theoretical loading at elevated temperatures. Earlier it has been reported that the presence of TBP as a modifier in TRUEX solvent changes the diluent properties as well as the extraction behaviour of extractant system [40]. Possibility of the formation of mixed extractant complexes consisting of TBP and OΦCMPO, particularly at high solvent loading conditions is also reported [35]. Present study also supports the possible formation of mixed OΦCMPO-TBP complexes of the type $Ln(NO_3)_3.2O\Phi CMPO.TBP$.

Figs. 11–13 also reveal that LOC values for third phase formation in the extraction of La(III), Ce(III), and Gd(III) by 0.2 M OΦCMPO + 1.2 M TBP/$C_nH_{(2n+2)}$ from solutions with near-zero free acidity decrease with increase in the chain length of the diluent. Earlier, Kolarik and Horwitz [35] have also reported decrease of LOC with increase in the carbon chain length of diluent for third phase formation in the extraction of Nd(III) by 0.2 M OΦCMPO + 1.2 M TBP in alkane diluents as a function of aqueous phase acidity. Several authors reported similar trend for the variation of LOC with the carbon chain length of diluent for several other systems also [3,10].

The change in LOC with diluent structure can be explained by the energetics of the distribution of the metal-solvate in the diluent medium [10]. It is easier for shorter diluent molecules in the organic phase to rearrange to accommodate the bulky metal-solvate molecules as compared to longer ones during the dissolution of a metal-solvate molecule in a alkane diluent. Recently, Berthon et al. [41] have also explained the effect of diluent chain length on third phase formation based on interacting reverse micelle model. According to the short chain penetration concept, shorter diluent molecules easily penetrate and swell the hydrophobic outer region (apolar layer) of reverse-micelles as compared to longer diluent molecules. Therefore, the attraction between the polar cores decreases and prevents third phase formation, when the carbon chain length of diluent molecule decreases.

Fig. 10 also shows that CMPO modified with TAP has higher loading capacity as compared to TBP system. It has also been observed in the present study that third phase formation does not take place in the extraction of $Gd(NO_3)_3$ by 0.2 M OΦCMPO + 1.2 M TAP/*n*-dodecane even from its saturated solution with near-zero free acidity in the temperature range 293–323 K. Earlier, we reported that third phase formation does not take place in the extraction of Nd(III) with 0.2 M OΦCMPO + 1.2 M TAP/*n*-dodecane from saturated $Nd(NO_3)_3$ solution over a wide range of acidity (0–7 M HNO_3). Kolarik and Horwitz [35] have also reported that metal loading capacity of 0.2 M OΦCMPO + 1.2 M modifier/*n*-dodecane solvent systems can be increased by using trialkyl phosphates with longer alkyl groups such as tri-*n*-octyl phosphate (TOP) and tri-2-ethyl hexyl phosphate (TEHP) as modifiers.

If third phase formation is explained based on the interacting reverse micelles model, higher metal loading capacity of TAP systems as compared to TBP systems, indicates that modifier molecules along with OΦCMPO molecules also participate in reverse micelle formation. Elongation of the alkyl groups of the phosphate molecules, which constitute the reverse-micelles, favours the reverse-micelle formation in nonpolar alkane diluents. Longer alkyl chains weaken the energy of attraction between the polar cores of the interacting reverse micelles, due to longer distance between the cores.

Data on CAC for third-phase formation in the extraction of Th(IV) and U(VI) by solutions of 0.2 M CMPO + 1.2 M TBP/n-dodecane from solutions with near-zero free acidity are shown in Table 1. CAC values for third phase formation in the extraction of nitrates of La(III), Ce(III), and Gd(III) by 0.2 M OΦCMPO + 1.2 M TBP/alkane diluent at 303 K are given in Tables 2 and 3. Data shown in Tables 1, 2 and 3 also illustrate the influence of temperature and carbon chain length of the diluent on third phase formation. It can be seen in these tables that for all the cases, there is a gradual increase in CAC values with an increase in temperature as well as with a decrease in carbon chain length of diluent.

4. Conclusions

Results indicate that 0.2 M OΦCMPO + 1.2 M TBP/*n*-hexadecane is more susceptible for third phase formation in the extraction of HNO_3 and it undergoes phase splitting with a large difference in density and solute concentrations between the heavy and light organic phases as compared to 0.2 M OΦCMPO + 1.2 M TBP/*n*-tetradecane. Hence, difference in density and solute concentrations

Table 1
CAC values for third phase formation in the extraction of Th(IV) and U(VI) from solutions with near-zero free acidity by 0.2 M CMPO + 1.2 M TalP/$C_{12}H_{26}$

Temperature (K)	CAC (mol/L)		
	TBP		TAP
	Th(IV)	U(VI)	Th(IV)
283	—	0.0240	—
288	0.0077	0.0324	—
293	0.0101	0.0506	—
298	0.0108	0.0711	0.4429
303	0.0148	0.0979	0.5607
308	0.0168	0.1372	0.6419
313	0.0344	0.1675	0.7335
318	0.0743	—	0.7766
323	0.1003	—	0.8657

Table 2
CAC values for third phase formation in the extraction of La(III) from solution with near-zero free acidity by 0.2 M CMPO + 1.2 M TBP/$C_nH_{(2n+2)}$

Temperature (K)	CAC (mol/L)			
	$C_{10}H_{22}$	$C_{12}H_{26}$	$C_{14}H_{30}$	$C_{16}H_{34}$
288	1.91	0.672	0.074	-
293	2.15	0.912	0.111	0.054
298	2.45	1.12	0.173	0.071
303	2.71	1.34	0.288	0.096
308	2.95	1.58	0.487	0.129
313	3.21	1.81	0.696	0.171
318	3.47	2.03	0.901	0.220
323	3.75	2.58	1.09	0.297

Table 3
CAC values for third phase formation in the extraction of Ce(III) and Gd(III) from solution with near-zero free acidity by 0.2 M CMPO + 1.2 M TBP/$C_nH_{(2n+2)}$

Temperature (K)	CAC (mol/L)							
	Ce(III)				Gd(III)			
	$C_{10}H_{22}$	$C_{12}H_{26}$	$C_{14}H_{30}$	$C_{16}H_{34}$	$C_{10}H_{22}$	$C_{12}H_{26}$	$C_{14}H_{30}$	$C_{16}H_{34}$
288	1.18	0.312	0.048	—	1.01	0.419	0.073	—
293	1.36	0.504	0.063	0.035	1.14	0.580	0.101	0.055
298	1.56	0.675	0.087	0.047	1.28	0.736	0.150	0.074
303	1.74	0.834	0.125	0.060	1.41	0.748	0.235	0.097
308	1.93	0.979	0.185	0.077	1.55	0.846	0.393	0.127
313	2.13	1.14	0.311	0.100	1.69	1.09	0.601	0.169
318	2.35	1.28	0.506	0.130	1.82	1.22	0.761	0.233
323	2.59	1.46	0.687	0.166	1.99	1.34	0.894	0.322

between third phase and diluent-rich phase can be treated as index of third phase formation tendency.

Temperature, carbon chain length of diluent, and equilibrium aqueous phase acidity influence third phase formation in the extraction of metal ions by OΦCMPO based solvents. OΦCMPO modified with TAP has higher metal loading capacity as compared to OΦCMPO modified with TBP under identical conditions. Hence, OΦCMPO modified with TAP can be employed for the processing of waste solutions, particularly the raffinate solutions generated from fast reactor fuels.

Acknowledgement

One of the authors, Swayam Mallick, is thankful to Dr. P. Sasidhar and Shri S. E. Kannan, SRI, AERB, Kalpakkam, for their keen interest in this work.

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