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Studies on di-nonyl phenyl phosphoric acid (DNPPA): a potential extractant for uranium recovery from merchant grade phosphoric acid (MGA)

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ABSTRACT

Methods of purification of di-nonyl phenyl phosphoric acid (DNPPA), its solubility in different aqueous solutions and its recovery from acidic as well as alkaline solutions employing various diluents have been described. Liquid-solid separation method based on Nd-DNPPA salt precipitation route as well as by liquid-liquid separation based on mono ethylene glycol treatment has been studied for the purification of DNPPA. While the purity obtained in the two methods was >94%, the recovery in Nd-DNPPA salt method was only 50% as compared to 90% in mono ethylene glycol method. The solubility of DNPPA in aqueous streams like WPA (5.6 M), MGA (12 M), sulphuric acid (5.4 M), phosphoric acid (5.5 M), oxalic acid (0.95 M), sodium carbonate (1.13 M), water etc. has been determined. Recovery of DNPPA from aqueous phase was investigated employing various diluents such as petrofin, benzene, toluene, MIBK, iso-decanol, 1-octanol, etc. The effects of process variables such as phase ratio (O/A), pH, DNPPA concentration in aqueous solution on its recovery have also been studied. Solubility and recovery of TOPO has also been examined under comparable experimental conditions. A four-stage counter current diluent extraction operation at an internal reflux ratio of 20 yielded ~92% recovery for both DNPPA and TOPO from MGA employing petrofin as diluent.

Keywords: Solubility; Recovery; DNPPA; TOPO; MGA; Counter current diluents extraction; Petrofin

1. Introduction

Di-nonyl phenyl phosphoric acid (DNPPA) is a liquid cation exchanger and a close analogue of di-2-ethyl hexyl phosphoric acid (D2EHPA). Its extraction behavior is similar to D2EHPA. However, its higher acidic strength due to the presence of two phenyl groups attached to phosphoryl group (>P=O) makes it a better extractant compared to D2EHPA for the extraction of metal ions from highly acidic solutions. TOPO (tri-n-octyl phosphine oxide) is a neutral extractant and extracts metal ions by solvation mechanism. Use of TOPO for the extraction and separation of metal ions is reported from various aqueous media [1,2]. Recent innovative R & D work by our group led to the development of a solvent extraction process based on the use of synergistic mixture of DNPPA and TOPO for the recovery of uranium from merchant grade phosphoric acid (MGA), which was not reported earlier [3,4]. Previously cited literature on uranium recovery processes are mainly from wet process phosphoric acid (WPA) using synergistic mixture of D2EHPA and TOPO and combination of other organophosphorus compounds [5–8]. Synergistic mixtures of DNPPA with TBP (tri-n-butyl

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phosphate) and DBBP (di butyl butyl phosphonate) have also been explored for the recovery of uranium from WPA [9,10]. It has been reported that the extraction of U(VI) largely depends on the di-ester content of DNPPA [11]. Higher the di-ester content, better will be the extraction of U(VI). The synthesis of DNPPA consists of esterification, hydrolysis and purification [3]. Esterification involves reaction of $POCl_3$ with two moles of p-nonyl phenol in the presence of pyridine at controlled temperature. The mole ratio of nonyl phenol, $POCl_3$ and pyridine was 2:1:2 respectively. The product obtained was found to contain unreacted nonyl phenol and by-product mono nonyl phenyl phosphoric acid as major impurities. The product also contained mono ester, tri ester and neutral fractions. It has been observed that the presence of impurities such as unreacted nonyl phenol (neutral) and mono nonyl phenyl phosphoric acid (MNPPA) adversely affects the extraction of uranium (VI) from phosphoric acid medium [11]. The presence of mono ester not only decreased the extraction efficiency of uranium but also posed problems in phase separation and led to difficulties in stripping and stability of the extractant. It is therefore desirable to purify DNPPA from its impurities prior to its use in solvent extraction circuit. Hence one of the aims of present work was to purify DNPPA in order to increase the di-ester content to >95% with mono ester content ~1.0% using neodymium (Nd) -DNPPA salt precipitation (liquid-solid) and mono ethylene glycol (liquid-liquid) separation methods. The purity and yield of DNPPA obtained by two methods have been compared.

Further, it has been noticed that the organic solvents get dissolved and/or entrained in various type of aqueous streams in hydrometallurgical operations. The recovery of dissolved organic solvent from aqueous streams is generally accomplished by diluent extraction or by charcoal adsorption [12,13]. For plant operations parallel plate separators or froth floatation cells are employed for separation of entrained solvents. For DNPPA-TOPO-MGA system there is no information available in literature. Therefore, it is desirable to generate data on its solubility and recovery. Separation of entrained/dissolved solvents yields a two-fold benefit. Firstly it recovers expensive extractants and hence improves process economy. Secondly, it prevents detrimental action on the rubber lining when acid is processed in down stream plant equipment in fertilizer industry. Accordingly, another objective of the present work is to determine solubility of the solvents in different types of aqueous solutions relevant to solvent extraction process and also its recovery from acidic as well as alkaline solution employing different diluents. The solubility of DNPPA in different aqueous solutions (MGA, WPA, 5.4 M H_2SO_4, 5.5 M H_3PO_4, 0.95 M oxalic acid, 1.13 M Na_2CO_3 etc.) has been evaluated. Its recovery from acidic and alkaline solutions has been carried out. Since TOPO has been used as synergistic reagent in the DNPPA-TOPO-MGA process [4], its solubility behaviour in various aqueous streams under comparable experimental conditions and also its recovery has been evaluated. A four stage counter-current diluent extraction set-up using petrofin as diluent has been operated to recover DNPPA and TOPO from MGA. Further, in order to determine the concentrations of DNPPA and TOPO in aqueous media, analytical methods based on potentiometry, HPLC and spectrophotometry have been standardized. The decomposition method for converting organic phosphorus to inorganic phosphate and its subsequent estimation based on spectrophotometry employing the use of sodium molybdate in colour development under reducing conditions have been optimized.

2. Experimental

2.1. Reagents and solution

DNPPA (~88% di-ester) used in the present work was obtained from indigenous sources. TOPO (>95% purity) was obtained from Cytec, Canada and used with out any further purification. WPA (~25–30% P_2O_5; 5.6 M) and MGA (~55% P_2O_5; 12 M) were obtained from local fertilizer plants. Nd_2O_3 used during the course of purification of DNPPA by liquid–solid separation method was of ~95% purity (IRE Ltd. Alwaye, India). Organic solvents like mono ethylene glycol (MEG), benzene, toluene, methyl iso butyl ketone (MIBK), iso decanol, 1-octanol etc. were of AR grade. Petrofin (an aliphatic fraction of refined kerosene) with flash point 102°C was used. All other chemicals including H_2SO_4, HCl, H_3PO_4, oxalic acid, Na_2CO_3 etc. were of analytical reagent grade.

2.2. Procedure

Experiments on solubility of DNPPA in various type of aqueous solutions were carried out in two different ways. In the first set of experiments known quantity of DNPPA was added to the known volume of aqueous solution and it was shaken for 10 min. The aqueous solution was then filtered and known volume of filtered aqueous was equilibrated with required volume of benzene to transfer the dissolved DNPPA in benzene phase. After phase separation, the benzene phase was washed with 10% Na_2SO_4 and water prior to estimation of DNPPA by potentiometric titration/HPLC/spectrophotometry. In the second set of experiments in place of direct addition of DNPPA to the aqueous solution, 0.6 M DNPPA solution prepared in petrofin was equilibrated with different types of aqueous solutions under experimental condition and after phase separation the rest of the procedure was same as above. Recovery experiment on DNPPA and TOPO from the aqueous medium has been carried by contacting the aqueous phase containing known concentration of DNPPA and TOPO with the respective organic solvent at a particular phase ratio. Solubility and recovery experiments were performed in glass separating funnels. The counter current diluent extraction test runs for the recovery of DNPPA and TOPO were performed in a series of separating funnels mounted on a specially designed stand for easy transfer of the phases, each being provided with motor driven perspex stirrer for mixing. All these experiments were performed at ambient temperature (30 ± 1°C).

Potentiometric titration and HPLC methods were used for the estimation of DNPPA content [14,15]. HPLC of Jasco make employing C-18 column of 30 cm length and 0.5 mm id was used, while Autotitrator of Metrohm make was used for potentiometric titrations for DNPPA determination. Analysis of DNPPA and TOPO mixture was standardized by total 'P' estimation followed by titrimetry for estimating the DNPPA component. The difference between total 'P' and the 'P' component due to DNPPA gave the concentration of 'P' due to TOPO component in the mixture, from which the equivalent TOPO concentration was evaluated. Spectrophotometric measurements were made using Shimadzu UV visible spectrophotometer. Experiments were carried out in triplicate.

Different methods of decomposition of organic phosphorus 'P' for the conversion to inorganic 'P' (H_3PO_4) by means of different reagent solutions such as mixture of (a) $H_2SO_4 + H_2O_2$ (b) $HNO_3 + HClO_4$ and (c) $K_2S_2O_8$+ H_3BO_3 were evaluated for the determination of organic 'P' by spectrophotometric method [16]. For the present work combination of (a) and (b) was found to be the most suitable one with an average error in estimation of ± 5% (Table 1).

A spectrophotometric method based on the formation of a blue colour complex between phosphate (obtained from the digestion of organic 'P') and sodium molybdate in the presence of ascorbic acid as the reducing agent was slightly modified and adopted [17]. The blue color of the complex $[(M{\cdot}O_2.4M{\cdot}O_3)_2{\cdot}H_3PO_4]$ was directly proportional to the amount of P. The optical density (OD) measurement was taken at a wavelength of 823 nm against reagent blank. The OD was found to be constant over a long period of time (5–6 h) with a sharp peak at 823 nm. The conversion of organic 'P' to orthophosphoric acid required for blue colour formation was achieved by digestion of DNPPA/TOPO containing solution with the method (a) + (b). The method was found to be suitable in the range of 10–60 ppm of 'P' (0.01 to 0.06 mg 'P'/ml). In the present method, the ashing step following treatment of the sample with ZnO and KOH followed by HCl addition reported in Ref. [17] has been replaced by direct digestion of samples using the combination of (a) + (b) prior to the colour development by single reagent solution (2.5% sodium molybdate and 5% ascorbic acid). Standards were made with potassium hydrogen phosphate (KH_2PO_4).

Table 1
Decomposition methods for 'P' estimation Concentration of 'P' taken = 27 mg/l

Oxidising agents	Concentration of 'P' obtained
(a)	20.6
(b)	34.0
(a) + (b)	27.2
(c)	47.0
(a) + (c)	42.7

3. Results and discussion

3.1. Purification of DNPPA

Fig. 1 represents the effect of percentage of neutral component nonyl phenol present in DNPPA on the extraction of uranium (VI) from MGA at phase ratio (O/A) = 1. From the plot it is evident that with increase in nonyl phenol concentration the distribution ratio of uranium decreases significantly which may presumably due to association between DNPPA and nonyl phenol. Hence for better extraction of U(VI) from MGA, the nonyl phenol fraction has to be brought down. Table 2 represents the stripping characteristic of DNPPA containing different concentration of mono-ester. From the data it is evident that stripping of uranium from DNPPA is

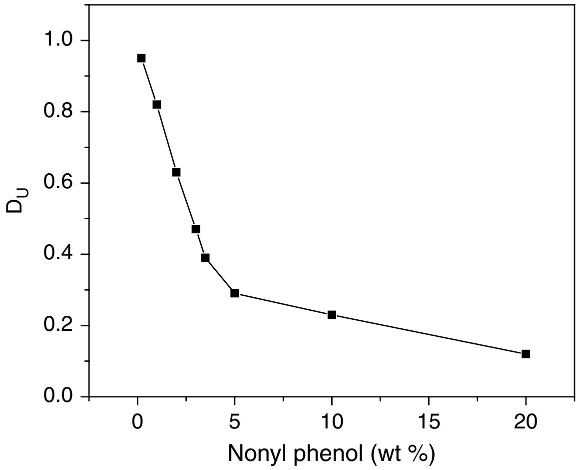

Fig. 1. Effect of nonyl phenol in DNPPA on uranium extraction Feed: MGA containing 250 mg/l U_3O_8, emf > 700 mV, O/A: 1 Organic: 0.6 M DNPPA + 0.3 M TOPO.

Table 2
Effect of mono ester concentration on stripping of uranium Loaded organic: 0.6 M DNPPA containing 0.5 g/l U_3O_8

Mono-ester (%)	% Stripping	Observation
8	–	Third phase formation
4	79	Aqueous slightly turbid and slow phase separation
2	95	Clear and fast phase separation
1	97	Clear and fast phase separation
0.65	98	Clear and fast phase separation

quantitative when the mono-ester concentration is ≤1%. It is therefore essential to purify DNPPA for better extraction and stripping efficiencies of uranium from MGA.

3.2. Purification by Nd-salt method

Weighed quantity of impure DNPPA was dissolved in benzene and treated with 70% methanol 3–4 times at a phase ratio (O/A) = 1. Due to hydrophilic nature, the mono ester fraction present in DNPPA gets dissolved in methanol phase and was separated out. The resulting DNPPA/benzene phase obtained after methanol wash was then loaded with Nd by equilibrating it with 30–40 g/l $NdCl_3$ (pH = 2.0) at O/A = 1. The Nd loaded DNPPA was poured into excess of acetone solution to precipitate out DNPPA-Nd-salt. After washing the resulting precipitate with acetone, it was re-dissolved in benzene. This treatment further removes mono-ester as only di-ester forms complex with Nd. The Nd loaded DNPPA benzene solution was equilibrated with 10% oxalic acid/6.0M HCl 2–3 times at O/A = 1 to strip out Nd. Finally, the DNPPA phase was washed with water and 10% sodium sulphate solution prior to evaporation of benzene. After evaporation of benzene the purity of DNPPA (di-ester) was found to be ~95%, but the recovery was poor (50–60%).

3.3. Purification by mono ethylene glycol (MEG) treatment

DNPPA fraction obtained after hydrolysis contains major impurities like mono-nonyl phenyl phosphoric acid and nonyl phenol. These impurities were separated by successive washing of the organic phase with NaOH solution and mono ethylene glycol. Nonyl phenol was separated from the organic phase during NaOH wash in the form of insoluble third phase. The process of alkali washing was repeated till the formation of third phase was negligible. After alkali wash the resulting DNPPA solution was subjected to mono ethylene glycol wash. This step selectively separates mono nonyl phenyl phosphoric acid from the organic phase. The organic phase obtained after the washing steps was finally distilled using centrifugal molecular distillation unit at 100°C and 0.01 mm Hg pressure to yield high purity DNPPA of the order of 95% diester and less than 0.5% monoester. Table 3 gives the yield and purity obtained from different batches of DNPPA employing the two methods.

Purification of DNPPA by mono ethylene glycol wash resulted in high yield and purity of the product. This method was found to be more suitable over Nd-salt precipitation method for preparation of pure DNPPA. The purified DNPPA was analyzed by potentiometric titration and HPLC method to establish the purity.

3.4. Solubility of DNPPA and TOPO in aqueous medium

Experiments on solubility determination of DNPPA and TOPO in various aqueous solutions were carried out as per the procedure described in experimental section. After transferring the DNPPA and TOPO from aqueous phase to organic phase, the concentration of DNPPA was analysed by potentiometry and HPLC method, while the TOPO content was determined using spectrophometery after prior digestion of samples. The solubility values obtained by both the experimental procedures were found to be comparable and the average values, within the analytical error of ±5%, are shown in Table 4. From the solubility data it is evident that the solubility of DNPPA and TOPO in various aqueous solutions followed the order: MGA > WPA ≈ sodium carbonate > phosphoric acid > oxalic acid > sulphuric

Table 3
Purity and yield obtained from different batches of DNPPA Crude DNPPA composition: Diester (88.0%), mono-ester (2.5%) and neutral (9.5%)

Method of purification	Sample	Diester (%)	Monoester (%)	Neutrals (%)	Yield (%)
Nd-salt method	Batch 1	94.2	1.5	4.3	55.0
	Batch 2	94.6	1.6	3.8	52.0
Mono ethylene glycol method	Batch 1	95.0	0.5	4.5	92.0
	Batch 2	95.5	0.5	4.0	90.0

Table 4
Solubility of DNPPA and TOPO in various aqueous medium

Aqueous stream	DNPPA conc. (mg/l)	TOPO conc. (mg/l)
MGA (12 M)	37	23
WPA (5.6 M)	28	18
Sulphuric acid (5.4 M)	15	10
Oxalic acid (0.95 M)	11	9
Sodium carbonate (1.13 M)	27	19
Phosphoric acid (5.5 M)	21	17

acid for DNPPA and MGA > WPA > sodium carbonate ≈ sulphuric acid > oxalic acid for TOPO respectively.

It may be noted that the solubility of DNPPA is higher than TOPO in any aqueous solution under experimental conditions. TOPO being a neutral extractant has lower solubility in aqueous solution compared to DNPPA, which is polar in nature. Additional experiments were carried out to study the effect of variables like quantity of DNPPA, temperature and equilibration time on solubility of DNPPA in MGA and WPA. The quantity of DNPPA was varied in the range of 0.2 g to 5.0 g in 100 ml of MGA and WPA respectively. The resulting mixtures were equilibrated separately for 30 min at ambient temperature 28 ± 1°C. The solutions were then allowed to settle and filtered to remove the entrained DNPPA. There after, the soluble contents of DNPPA in MGA and WPA were transferred from aqueous phase to organic phase (benzene) prior to washing of organic phase by 10% solution of sodium sulphate. The DNPPA concentrations for both MGA and WPA experiments were estimated by potentiometer as well as by HPLC. The readings were found to be within the error limit of 5%, i.e., (37 ± 1.18 mg/l) and (28 ± 1.12 mg/l) for MGA and WPA respectively. These studies indicated that the solubility of DNPPA in aqueous phases like MGA and WPA is independent of amount of DNPPA. This behaviour may probably be due to (a) high concentration of phosphate ion present in MGA and WPA and/or (b) the aqueous phase is saturated with DNPPA.

The effect of equilibrium time in the range of 5 min to 5 h on the solubility of DNPPA in MGA and WPA (both 100 ml each) containing 0.2 g DNPPA were separately investigated. Equilibration time of 5 min was found to be more than adequate to attain equilibrium for mass transfer from aqueous to organic phase. Results indicated that within the limits of experimental error, the solubility of DNPPA in MGA and WPA was independent of equilibrium time and the values obtained were consistent with those reported in Table 4. Additional experiments were carried out to study the effect of temperature in the range of 30 to 65°C on DNPPA solubility. It was found that there was no significant effect of temperature on solubility of DNPPA in both MGA and WPA under present experimental conditions. The solubility values were found to be (37 ± 2.0 mg/l) and (28 ± 1.5 mg/l) for MGA and WPA respectively.

3.5. *Effect of diluents on recovery from various aqueous media*

The effect of different types of organic diluents namely benzene, toluene, petrofin, isodecanol, octanol and MIBK has been examined to recover the DNPPA from aqueous solutions such as WPA, MGA, 5.4 M H_2SO_4, 0.95 M oxalic acid and 5.5 M H_3PO_4. The concentration of DNPPA was kept constant at 250 mg/l in these solutions. The recovery experiments were performed by equilibrating the two phases at a phase ratio (O/A) = 1: 5 for 30 min at temperature 28°C. The estimation of DNPPA was done as per the procedure mentioned in experimental section. The data obtained with different diluents are presented in Table 5. It is observed that the recovery of DNPPA with the diluents studied is in the range 75 and 99%. It may be noted that in the case of MIBK and MGA a single phase was formed and hence experiment could not be carried out. In the case

Table 5
Effect of diluents on DNPPA recovery from various aqueous media initial DNPPA: 250 (mg/l), O/A: 1/5

Diluent	Solubility in water*	% Recovery of DNPPA				
		WPA (5.6 M)	MGA (12 M)	H_2SO_4 (5.4 M)	Oxalic acid (0.95 M)	H_3PO_4 (5.5 M)
Benzene	1.8 g/l	97.4	79.0	99.0	92.0	93.6
Toluene	0.47 g/l	99.0	93.7	87.0	85.8	66.9
Petrofin	Insoluble	95.6	96.5	85.6	78.0	80.3
Isodecanol	0.1 g/l	95.0	86.2	88.8	93.5	66.9
1 – Octanol	0. 3 mg/l	97.0	93.7	81.8	89.6	73.5
MIBK	19.1 g/l	99.0	One phase	99.0	97.4	76.9

* The solubility data reported is at temperature (20–25°C).

Source: en.wikipedia.org; www.sciencelab.com; www.kyowachemical.co.jp.

of MGA, except for benzene and isodecanol the recovery was >93%. However, the recovery of DNPPA from WPA was >95% with all the diluents. Industrially benzene, toluene, MIBK, isodecanol etc. are not preferred due to low flash point and toxicity, hence petrofin is a preferred diluent for recovery purposes. The solubility of petrofin in the aqueous phase was found to be below detection limit.

3.6. Effect of phase ratio (O/A)

The effect of phase ratio (O/A) on the recovery of DNPPA from MGA with benzene was studied for two different concentrations of DNPPA namely 500 mg/l and 1000 mg/l in MGA at two different phase ratios (O/A) = 1: 5 and 1:10. Following the similar procedure of equilibration/phase separation/washing with 10% solution of sodium sulphate, the concentration of DNPPA was estimated for all the experimental samples shown in Table 6. The recovery of DNPPA was higher at O/A = 1:5 than O/A = 1:10. However, the recovery of DNPPA at any phase ratio was found to be independent of concentration of DNPPA present in MGA. This showed that for efficient recovery of DNPPA, the phase ratio should be maintained at 1:5 or the number of contacts have to be increased when O/A is 1:10. Higher recovery at O/A = 1:5 may be due to the presence of more diluent available for the recovery of DNPPA from aqueous MGA.

3.7. Effect of DNPPA concentration

The recovery of DNPPA by organic diluents such as benzene, toluene, octanol and petrofin from MGA containing varying concentration of DNPPA in the range of 250 mg/l to 1000 mg/l has been carried out at a phase ratio (O/A) = 1:10. After transferring the DNPPA into diluent followed by washing, the DNPPA contents were analyzed. The recovery data are presented in Table 7. It is observed that with increase in DNPPA concentration from 250 mg/l to 1000 mg/l in MGA, the percentage recovery of DNPPA decreased irrespective of diluents. Also, their separation behaviour for DNPPA were comparable. However, petrofin was selected as diluent for further experiments since it is industrially preferred.

Table 6
Effect of phase ratio (O/A) Aqueous Phase: MGA containing DNPPA, O/A: 1:10

O/A	DNPPA taken (mg/l)	DNPPA recovered (mg/l)	% Recovery
1:10	500	385	77.0
1:5	500	498	98.5
1:10	1000	775	77.4
1:5	1000	964	97.0

Table 7
Effect of DNPPA concentration on percentage recovery using different diluents Aqueous phase: MGA containing DNPPA, O/A: 1:10

% Recovery of DNPPA				
DNPPA taken (mg/l)	Benzene	Octanol	Toluene	Petrofin
250	96.3	96.4	96.0	96.5
500	86.7	77.1	86.8	77.1
1000	77.1	67.4	74.3	74.7

3.8. Effect of pH on DNPPA recovery

The recovery of DNPPA from 1.13 M Na_2CO_3 solution containing different concentration of DNPPA in the range of 100 mg/l to 1000 mg/l has been studied. The pH of the 1.13 M sodium carbonate solution was varied by addition of acid (HCl) and DNPPA from aqueous phase was transferred in to the petrofin phase (O/A = 1:5). The DNPPA concentration was analyzed by potentiometric method. Fig. 2 represents the recovery of DNPPA as function of pH starting with a solution of 1.13 M Na_2CO_3 and subsequent pH variation by the addition of acid. It is evident from the plot that the recovery of DNPPA increased with decrease in pH irrespective of DNPPA concentration in the alkaline solution. Further,

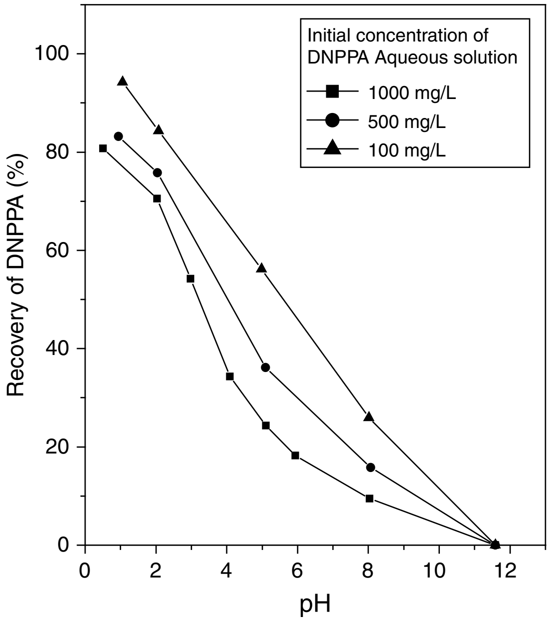

Fig. 2. Effect of pH on recovery of DNPPA from carbonate solution.

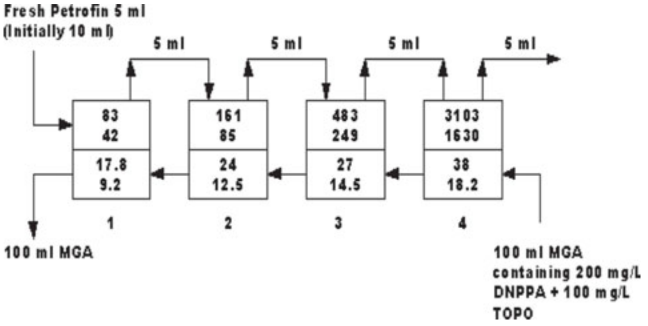

Fig. 3. Counter current diluent wash for DNPPA and TOPO separation from MGA (Figures in the box indicate DNPPA and TOPO concentrations in mg/l).

at any particular pH, the recovery of DNPPA followed the order: 100 mg/l > 500 mg/l > 1000 mg/l DNPPA. Approximately 94% recovery was achieved at pH 1.0 when DNPPA concentration was 100 mg/l. The results indicated that diluent extraction of DNPPA was possible only from solutions having <pH 2.

3.9. Recovery of DNPPA and TOPO by counter-current diluent extraction

Based on the results petrofin was selected for counter current diluent extraction studies. A four stage counter current extraction was carried out in series of glass separating funnels using 100 ml MGA containing 200 mg/l DNPPA and 100 mg/l TOPO and 10 ml petrofin as an extractant with a recycle ratio of 20 as per the scheme given in Fig. 3. A high internal reflux ratio of 20 in each stage was maintained by partial transfer of petrofin from one stage to another. After phase separation 5 ml of petrofin was taken out from stage no. 4 followed by the subsequent transfer of 5 ml of petrofin from stage 3 to 4 then from 2 to 3 and finally from 1 to 2. Fresh 5 ml petrofin was added to stage no. 1 to maintain the ratio. Similarly aqueous phase of each stage was moved in a counter current manner with the addition of 100 ml fresh MGA containing DNPPA and TOPO to the stage no. 4. The raffinate was taken out after each contact at stage no. 1 and was periodically analysed by extracting DNPPA into Petrofin phase. The outgoing 5 ml portion of petrofin was analysed each time for DNPPA and TOPO content. Equilibrium was attained after 25 contacts (Fig. 4). At equilibrium the concentrations of DNPPA and TOPO in the outgoing petrofin phase were found to be 3.1 g/l and 1.63 g/l while in the raffinate it was 0.017 g/l and 0.0092 g/l respectively indicating ~92% recovery. Fig. 5 shows the equilibrium isotherm plot for DNPPA extraction with petrofin. The overall material balance was found to be within an error limit of 13%.

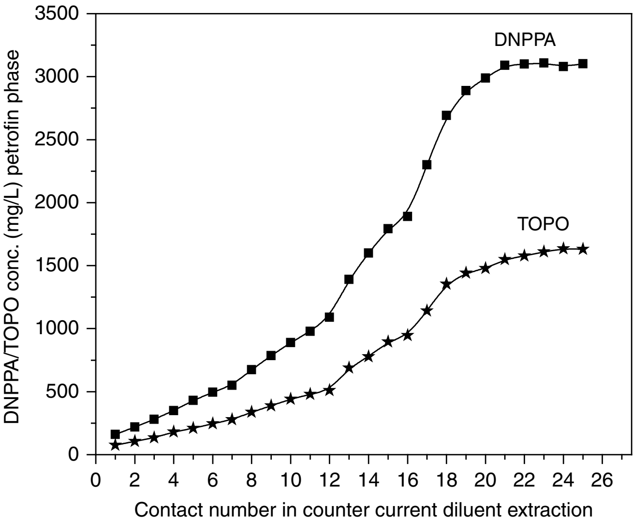

Fig. 4. DNPPA/TOPO concentrations in the loaded Petrofin phase in counter-current experiment.

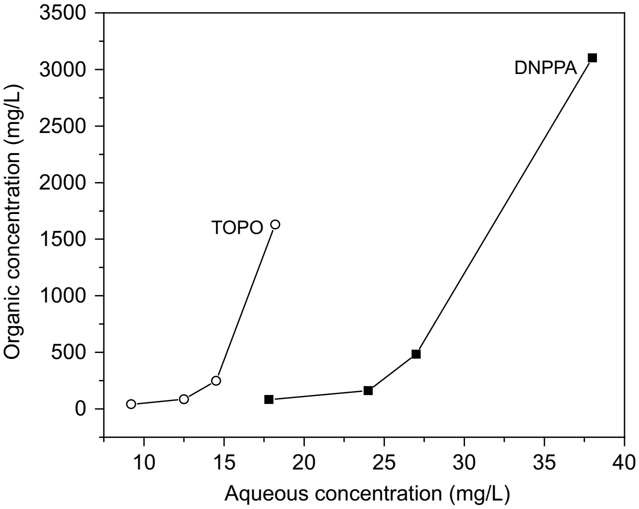

Fig. 5. Equilibrium isotherm for DNPPA and TOPO extraction from MGA with petrofin in a four stage counter current experiment.

4. Conclusions

DNPPA containing 88% diester was purified by two methods namely the Nd-salt method and the mono ethylene glycol wash method. While the purity of DNPPA by both the methods was ~95%, the recovery in the case of Nd-salt method was only 50% as compared to monoethylene glycol method where it was 90%. The procedure of analysis of total phosphorus was modified with respect to decomposition and spectrophotometric analysis. A combination of digestion with conc. H_2SO_4/H_2O_2 mixture followed by addition of $HNO_3/HClO_4$ mixture prior to digestion for 2 h gave near quantitative recovery. The solubility of DNPPA and TOPO in various aqueous solutions namely MGA, WPA, 5.4 M sulphuric acid, 0.95 M oxalic acid, 1.13 M sodium carbonate and 5.5 M phosphoric acid has been determined. Its recovery from acidic as well as alkaline solutions was studied. The recovery of DNPPA from MGA was found to decrease with increase in its concentration irrespective of diluent. In case of alkaline solution, neutralization is essential for DNPPA recovery. Although the various diluents investigated gave comparable recoveries, petrofin is preferred for large scale operations and hence was used for counter current diluent wash experiment. The feasibility of recovery of DNPPA and TOPO from MGA by petrofin has been established using a four stage counter current diluent extraction scheme. The recovery was found to be ~92% for both DNPPA and TOPO.

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