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RESEARCH ARTICLE

Analysis of factors affecting uranium stripping from DEHPA/dodecane using FTIR and other analytical methods

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Abstract

Uranium(VI) is stripped from 0.1 mol.l^{-1} DEHPA/dodecane using different concentration of phosphoric acid. This study investigates the main operating variables, mainly phosphoric acid concentration used as a strip solution, and temperature. Infrared spectra of the stripped organic were investigated in region of P=O stretching vibration to represent the effect of the previous variables on uranium stripping and compared with other conventional analytical methods. Results showed that concentration of the strip solution is effective in the range of 5-18 wt% P_2O_5 at fixed temperature, and the temperature effect is less than the strip solution concentration effect by the factor of 1/6. Results obtained enable us to choose the suitable temperature and wt% $P_2O_5$of the strip solution to evaluate the demanded stripping distribution ratio.

Keywords

uranium · infrared · DEHPA · stripping

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1 Introduction

Surfactants are profitably used in the extraction technology of metal ions from aqueous solutions. Of these, di (2-ethyl hexyl) phosphoric acid, DEHPA constitutes an important surfactant, which can react with positively charged metal ions through its functional group (the head group), P=O namely the phosphoryl moiety. In addition to this, it posses long hydrophobic chains, which render the metal complex soluble in the apolar phase (Vandegrift et al [1]).

At a relatively high concentration of DEHPA extractant, the molecules undergo a self-association process. Predominantly, it takes place through a dipole-dipole interaction. This modifies the extraction system, which is manifested in terms of the change in the trend of distribution values. (Das et al [2]).

The infrared spectra of DEHPA showed that the absorption band at 1235 cm^{-1}was assigned to the P=O stretching frequency, where the band at 1665 cm^{-1} was assigned to the O-H bending band (Kiwan et al [3]). The infrared spectra of DEHPA in kerosene, show the P=O frequency at 1230 cm^{-1}, O-H stretching bands at 2680 and 2350 cm^{-1} were attributed to the formation of dimer and the O-H bending band was found at 1690 cm^{-1}. (Sato et al [4]).

The stripping efficiency of uranium from DEHPA can be significantly increased by the use of higher concentration of phosphoric acid in the aqueous strip solution and to ensure that a sufficient fraction of U(VI) will be transferred into the stripping aqueous solution. The phase ratio aqueous to organic was modified to about 2 at 45- 50 °C, (Hurst et al. [5]). Moreover the stripping improvement lies in the use of more concentrated acid, possibly up to 10 mol/dm^3 H_3PO_4 instead of H_3PO_4concentration in the range of only 5 to 5.5 mol.l^{-1}. Hurst et al [6]. A mathematical model was developed to represent the effect of temperature and wt % P_2O_5 on uranium stripping from DEHPA/TOPO. (Dahdouh et al. [7]).

This present work, investigates the intensity variation of P=O group in association with UO_2^{2+}ion stretching band (P-O-U) in DEHPA/dodecane, during uranium stripping, using phosphoric acid as a stripping agent and evaluate the optimum temperature and wt % P_2O_5 of the phosphoric acid in order to achieve the demanded uranium stripping distribution ratio from the organic phase.

2 Experimental

2.1 Reagents

Di-(2-ethyl hexyl) phosphoric acid, DEHPA obtained from Sigma with purity 97%. Dodecane with purity 99% obtained from Merck was used as diluent without further purification. All other reagents were obtained from Merck with Analytical Grade.

2.2 Procedures

The solution of $UO_2(NO_3)_2$. 2DEHPA complex which contains 1995 mg.l^{-1} uranium was obtained by shaking 0.1 mol.l^{-1} DEHPA in dodecane for 5 hours with appropriate quantities of solid $UO_2(NO_3)_2.6H_2O$ (GR). Solvent layer was separated by centrifugation. Uranium concentration of solvent layer was determined after back extraction by colorimetry using the absorption of H_2O_2complex at 420nm. Uranium organic solution of 1500 mg/l and 1000 mg.l^{-1} were prepared by dilution of the above organic solution.

Three aqueous solutions of pure phosphoric acid 5% wt P_2O_5, 15% wt $P_2O_5$and 25% wt P_2O_5, were prepared, and each contained 500 mg/l uranium to simulate the counter-current process, where the recycled stripping agent loaded by uranium after few stripping stages.

25 ml of each of the above three aqueous solutions was mixed individually with 25 ml of organic solutions containing 1995 mg/l uranium, under the following conditions: temperatures:(20, 35, 50) ^{o}C and fixed mixing and settling time 10 minutes to reach the equilibrium. The infrared spectra of the separated and stripped organic phase have been recorded to determine the intensity of P-O-U stretching band.

2.3 Infrared Measurements

The infrared spectra were recorded on a Fourier Transform Infrared spectrophotometer (JASCO-300E FTIR) with a resolution of 4 cm^{-1} using KBr windows. The cell path length of KBr windows of the sample and the reference were 0.55mm.

3 Results and Discussion

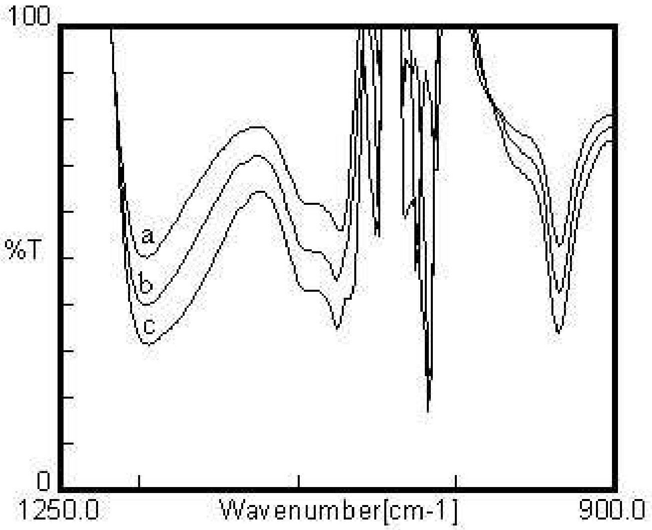

Fig. 1. Infrared spectra of P=O band in association with different uranium concentration (a: 1000, b: 1500, c: 1995) mg/l in the organic phase (0.1mol.l^{-1} DEHPA/dodecane).

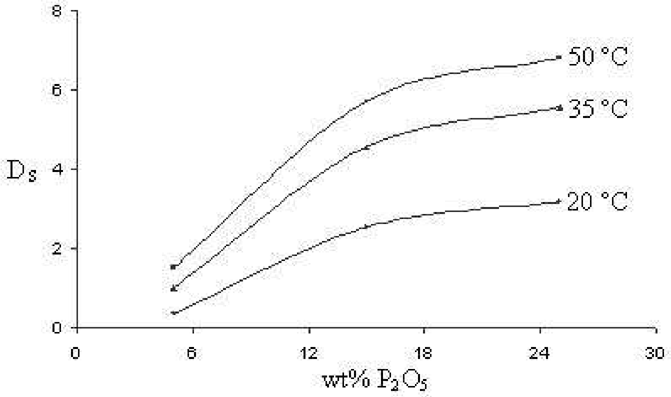

Fig. 2. Uranium stripping distribution ratio D_S as a function of wt% P_2O_5at different temperatures.

The P=O stretching frequency in DEHPA is observed at 1235 cm^{-1}by Kiwan et al [3]. The infrared spectra of 0.1 mol.l^{-1} DEHPA/dodecane solutions containing 1000, 1500, 1995 mg/l uranium, were recorded, Fig. 1 shows their corresponding infrared spectra, a, b and c respectively. The P=O band was shifted from 1235 cm^{-1} to lower frequency 1197 cm^{-1}, which was assigned to the P=O group in association with UO_2^{2+} ions stretching band (P-O-U), and the P-O-U stretching band intensity was strongly decreased when uranium concentration was increased. It's also well considered that the intensity of the band at 940 cm^{-1} which assigned to the uranyl group in DEHPA was decreased along with the increasing of uranium concentration in the aqueous phase (Ohwada et al [8]). Uranium stripping from the organic phase solution of 0.1 mol.l^{-1} DEHPA/dodecane containing 1995 mg/l uranium was carried out using aqueous solutions of 5%wt, 15%wt and 25%wt P_2O_5, under the above mentioned conditions. The effect of wt% P_2O_5 of the strip solution on uranium stripping distribution ratio D_s at different temperatures is represented in Fig. 2, where, uranium stripping distribution ratio represents the ratio of uranium concentration in the aqueous phase/ uranium concentration in organic phase. Uranium in the stripped organic phase was determined using direct gamma spectrometry of the gamma emission peaks of ^{235}U (Addam and Dams[9]) and UV-VIS spectrophotometer, and in the aqueous phase by mass balance. Results obtained showed that D_s values were agreeing well with the P-O-U band absorption. Fig. 3 shows that the P-O-U stretching band absorption of the stripped organic phase decreased as temperature increased from 20 to 50^{o}C, therefore uranium stripping distribution ratio also increased. This means that uranium stripping is less efficient at low temperatures.

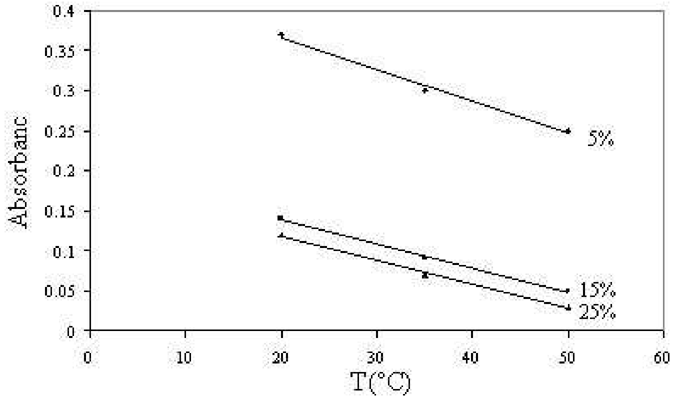

Fig. 3. Absorption of the remained P=O stretching band in the association with UO_2^{2+} of the organic phase as a function of temperature, using phosphoric acid containing 5% wt, 15% wt and 25% wt P_2O_5 as a strip solution.

3.1 Optimization of Variables Affecting Uranium Stripping

Plots in Fig. 3 represents the variation of P-O-U band absorption at 1197 cm^{-1} versus temperature while, wt% $P_2O_5$was fixed. Plots of 15%wt P_2O_5 and 25%wt P_2O_5 are closed to each other, and their corresponding P-O-U band absorption values are also close at various temperatures.

In contrary, the P-O-U band absorption plots of 5%wt P_2O_5 and 15%wt P_2O_5 are well separated. It can be concluded that the effect of increasing wt % P_2O_5 on uranium stripping from DEHPA/dodecane-uranyl solution is negligible in the range of about 18-25 wt % P_2O_5, but the effect is remarkable in the range of 5-18%wt P_2O_5.

The plots of the P-O-U band absorption at 1197 cm^{-1} versus wt % P_2O_5at the following temperatures: 20 ^oC, 35 ^oC and 50 ^oC are represented in Fig. 4. These plots show that, the P=O band absorption in association with UO_2^{2+} ions is strongly decreased when wt% P_2O_5 increased from 5% up to approximately 18%wt P_2O_5, where, P-O-U absorption remains constant as wt% P_2O_5 increased from 18% to 25%wt, this means that, using stripping solution of 18%wt P_2O_5 is quite efficient to strip uranium from DEHPA/dodecane-uranyl complex.

P-O-U band absorbance values of 0.2 and 0.15 were selected from Fig. 4 of 0.2 and 0.15, where, each represents a certain amount of uranium stripping distribution ratio. Temperatures as a function of wt% P_2O_5were plotted in Fig. 5 forboth ofthe above selected band absorptions. These plots enable us to choose different temperature and wt% P_2O_5 values to get the demanded distribution ratio. Moreover, it can be concluded from Fig. 5, that the proportional coefficient of Δwt% P_2O_5/ ΔT (temperature) is about 1/6, which means that temperature is less effective on uranium stripping distribution ratio if compared with the wt% P_2O_5 effect by the factor of 1/6, which is from the economical point of view a valuable result.

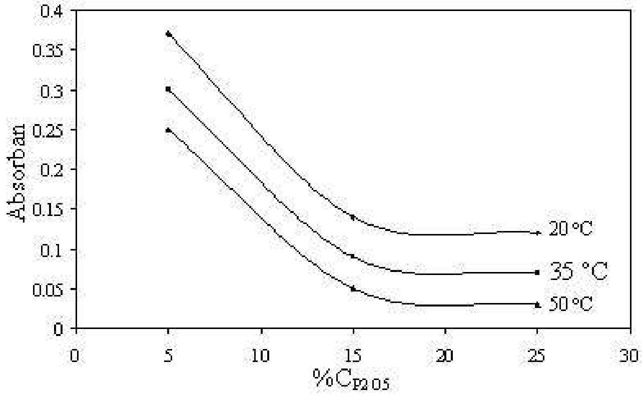

Fig. 4. Absorption of the remained P=O stretching band in the association with UO_2^{2+} of the organic phase as a function of wt% P_2O_5at 20˚C, 35˚C and 50˚C.

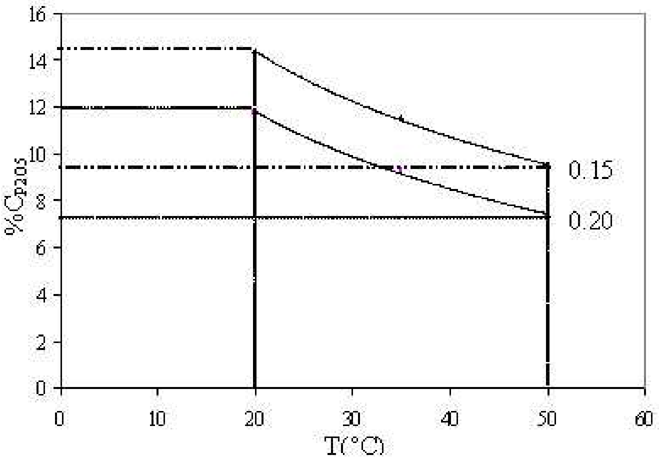

Fig. 5. wt% P_2O_5 of the stripping agent at the selected band absorption of 0.15 and 0.20 as a function of temperature.

4 Conclusion

It can be concluded from the recorded infrared spectra of the DEHPA-uranyl complex in dodecane that uranium stripping was increased, when wt% $P_2O_5$of the stripping agent and temperature increased from 5% to 18%, and from 20 ^oC to 50 ^oC, respectively. Temperature influence on uranium stripping is less by the factor of 1/6 if compared with that of the wt% P_2O_5 of the stripping agent. The influence order of temperature and wt% P_2O_5 on uranium stripping is agreeing well with results obtained by (Dahdouh et al [7]).

Results obtained enable us to select the suitable temperature and wt % $P_2O_5$of the stripping agent to evaluate the demanded uranium stripping distribution ratio.

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