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Uranium from phosphoric acid: Kinetic studies of the solvent extraction processes for uranium extraction

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ABSTRACT

Kinetics of the mass transfer processes involved in uranium recovery from wet process phosphoric acid (WPA) by solvent extraction employing synergistic extractants has been studied. In the present investigation results on the kinetics of separation of entrained solvent by diluent washing and uranium mass transfer behaviour have been discussed. Kinetic studies for the entrained solvent separation by diluent (petrofin) wash for D2EHPA/WPA system showed significant dependence of the rate constant value on the variables such as phase ratio, temperature and agitator speed. Kinetic studies on the mass transfer of U(VI) from phosphoric acid with 1.5 M D2EHPA+ 0.2 M TBP have been carried out using a constant interfacial area cell (Lewis cell). The effect of stirring speed, interfacial area, acidity of aqueous phase, extractant concentration in organic phase and temperature on the extraction rate constant indicate that both chemical reaction and diffusion, control the rate of uranium extraction from phosphoric acid to extractant phase. The activation energy for uranium mass transfer is found to be 18.1 kJ/mole. Experimental results showed that the rate of extraction has an inverse first order dependence on phosphoric acid concentration whereas the dependence of the rate constant on D2EHPA+TBP concentration was found to be greater than first order (1.5).

Keywords: Uranium; Kinetics; Lewis cell; Phosphoric acid

1. Introduction

Wet process phosphoric acid (WPA) derived from the dissolution of rock phosphate is an important secondary source of uranium. Exhaustive work in the field of solvent extraction has been carried out for the recovery of uranium from various industrial grades of phosphoric acid employing different synergistic extractant mixtures [1]. Based on the detailed experimental work carried out, a two cycle solvent extraction process for uranium separation from phosphoric acid has been developed at REDS and patented [2,3]. During the sequence of hydrometallurgical operations, organo phosphorus extractants such as di 2 ethyl hexyl phosphoric acid (D2EHPA), di nonyl phenyl phosphoric acid (DNPPA), tri butyl phosphate (TBP) and tri octyl phosphine oxide (TOPO), get entrained or dissolved in the aqueous streams such as WPA, Merchant Grade Acid (MGA), sulphuric acid and ammonium carbonate solution. While the equilibrium extraction behaviour and reaction mechanisms have been reported previously, only limited studies on the kinetic aspects of entrained solvent separation and uranium extraction from phosphoric acid have been reported [4,5]. Kinetic study of mass transfer and entrained solvent separation helps in optimal designing of the separation equipment.

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Several experimental techniques are available for studying the kinetics of solvent extraction [6]. Among the different techniques used, Lewis cell is the one preferred by many investigators [7]. Daoud et al. [8] employed Lewis cell to study U(IV) extraction kinetics from phosphoric acid medium by D2EHPA–kerosene solution and reported that the extraction is controlled by chemical reaction in the bulk phase. While for U(VI) extraction by D2EHPA–cyclohexane solution, Jia et al. [9] reported that the extraction process was controlled by chemical reaction at the interface, whereas in the case of U (VI) extraction by 0.5 M D2EHPA + 0.125 M TOPO from phosphoric acid. Hurst et al. reported it to be diffusion controlled [10].

In the present work kinetics of entrained solvent separation for D2EHPA/WPA system has been described. The mass transfer kinetics for uranium extraction from phosphoric acid with 1.5 M D2EHPA + 0.5 M TBP system employing Lewis cell has been studied.

2. Experimental

2.1. Reagents and solutions

WPA was obtained from fertilizer companies. The acids were treated with activated charcoal to separate humic matter before extraction tests. D2EHPA, DNPPA and TBP were obtained from indigenous sources, whereas TOPO was procured from Cytec Industries. The diester content of D2EHPA was 95% and that of DNPPA 90%. Petrofin (an aliphatic fraction of refined kerosene) was used as diluent to obtain the desired concentrations of mixed extractants. The stock solution of uranyl chloride (0.1 M) was prepared by dissolving an appropriate quantity of nuclear grade uranium metal in hydrochloric acid. After evaporating the excess acid the solution was made up to 250 ml with phosphoric acid (6 M). The stock solution was diluted to the desired concentration as and when necessary. All other chemicals were of AR or GR grade.

2.2. Procedure and apparatus

Kinetic studies on entrained solvent separation were carried out by contacting WPA containing known amount of D2EHPA with petrofin for varying time periods, using an agitator where speed can be preset. Analysis of the aqueous phase was carried out by contacting known volume of aqueous containing entrained solvent with benzene twice. The combined benzene phase was washed with 10% sodium sulphate to separate traces of inorganic acids and titrated potentiometrically using an autotitrator. The petrofin phase after washing was directly titrated for its D2EHPA content.

Kinetics studies for the extraction of uranium from phosphoric acid employing different extractants such as D2EHPA + TBP and D2EHPA + TOPO were carried out employing two types of set-up. In the first case mixing of organic and aqueous phase was carried out in a glass beaker employing a motorized stirrer with adjustable speed. In the second case experiments were carried out in a constant interfacial area stirred cell (Lewis cell) in which each phase was stirred by a central paddle. The two halves of the cell were made geometrically similar. The cell design is shown in Fig. 1. Glass beakers (500 or 1000 ml) of 8.3/10.5 cm diameter were used. The cylinder was partitioned in two sections by a circumferential wall baffle and this together with the central baffle divided the cell into two identical halves each of 220/250 ml volume, the annular gap area being about 41.8/85.8 cm^2. The stirrer rod was driven by 1 hp DC motor controlled by electronic speed controller which enables the stirrer speed to be varied from 0 to 500 rpm. For carrying out the experiment, the aqueous phase containing 500 mg/L U_3O_8 was added first into the cell and then the organic phase was very carefully poured into the cell avoiding mixing of the phases. The agitation was started at a pre-set speed and periodically 2 ml samples of aqueous were taken out from the portion just below the interface using syringes. The experiment was carried out for 90 min. The analysis of uranium in the samples was carried out by ICP–AES (ULTIMA 2 JY Model).

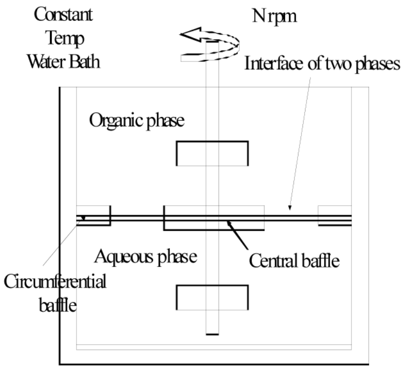

Fig. 1. Constant interfacial area stirred cell (Lewis cell).

2.3. Mathematical equation

The rate constants were calculated for uranium extraction, near time equal zero, using the equation developed by Horner and Mailen [11].

$$k = -(VD/at)\ln\left(1 - C/(C_0 D)\right) \tag{1}$$

k = forward rate constant; C_0 = initial concentration of U in the aqueous phase; C = concentration of U in the organic phase after time t; V = volume of organic phase; D = distribution coefficient; a = interfacial area; t = time.

3. Results and discussion

3.1. Kinetics of entrained solvent separation by diluent washing

A semi-log plot for $Z = 1 - Ct/C\omega$, (where Ct is the concentration of D2EHPA at time t in organic phase

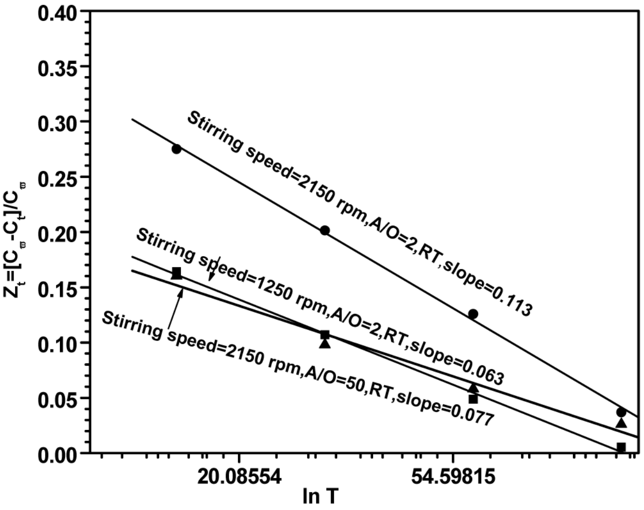

Fig. 2. Plot of *Z* vs. ln (*T*).

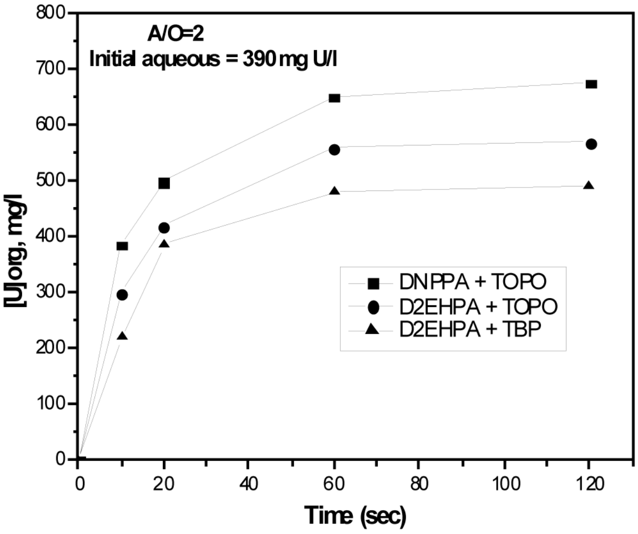

Fig. 3. Plot of U extraction from 6 M phosphoric acid using various solvent systems.

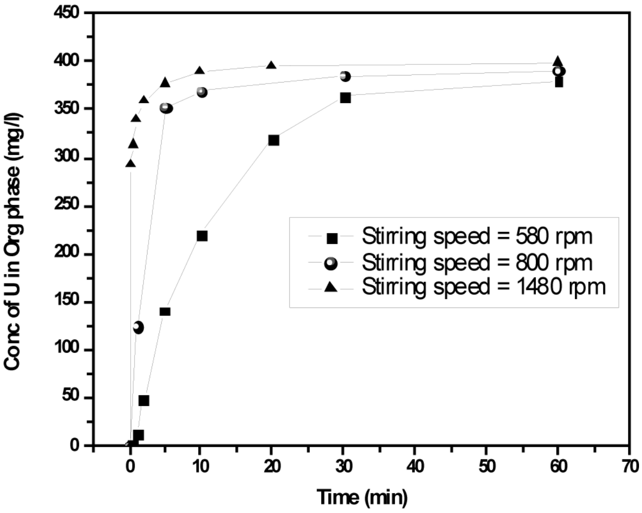

Fig. 4. Effect of stirring speed on U extraction from 6 M phosphoric acid.

and Cω is the equilibrium concentration of D2EHPA in organic phase) versus time is shown in Fig. 2. The slopes of the lines represent rate constants (s^{-1}) for separation of entrained D2EHPA. The effect of three variables namely phase ratio, stirring speed and temperature on entrained solvent separation was studied and the rate constant values were calculated using semi-log plot (Fig. 2). The rate constant values were statistically analyzed by Student's *t* test. When the phase ratio changes from A/O = 50 to A/O = 2, the rate constant changes from 0.11 to 0.05 s^{-1}, an effect which is statistically significant at 99.5% level. Similarly when the speed increases from 1225 to 2150 rpm, there is a 50% change in the rate constant (from 0.066 to 0.113 s^{-1}), which is again significant at 99.5% level. The effect of increasing temperature from RT (30°C) to 45°C showed an increase in the rate constant from 0.12 to 0.18 s^{-1}, an effect which is statistically important at 99% level of significance.

3.2. Mass transfer studies of uranium employing bulk mixing

Uranium mass transfer studies from 6 M phosphoric acid employing three solvent systems, namely D2EHPA (1.5 M) + TBP (0.2 M), D2EHPA (0.5 M) + TOPO (0.125 M) and DNPPA (0.6 M) + TOPO (0.3 M), showed that the rate of extraction takes place in the following order DNPPA + TOPO > D2EHPA + TOPO > D2EHPA + TBP. The distribution ratio (*D*) values in the three systems were found to be 14.2, 5.18 and 2.1 respectively. Due to the bulk mixing of the two phases, equilibrium was attained in a very short time. Fig. 3 gives a comparative plot of the different solvent systems.

3.3. Effect of stirring speed on the uranium mass transfer

The effect of stirring speed on U mass transfer from 6 M phosphoric acid containing 390 mg/l U_3O_8 using D2EHPA (1.5 M) + TBP (0.2 M) was studied. At stirring speeds of 580, 800 and 1480 rpm, equilibrium was attained in 60, 30 and 10 min, respectively. This showed that at lower speed the equilibration time increases. The plot is shown in Fig. 4.

3.4. Studies using Lewis cell

3.4.1. Dependence of rate constant on stirring speed

The influence of the stirring speed on the extraction rate of uranium (VI) with 1.5 M D2EHPA + 0.2 M TBP dissolved in petrofin is shown in Fig. 5. An initial linear

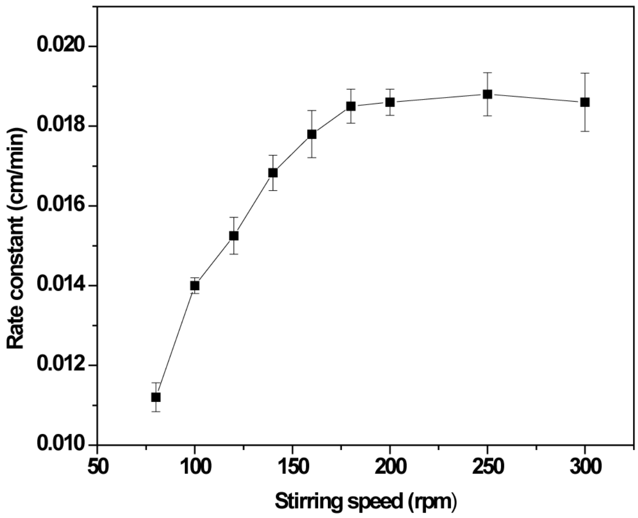

Fig. 5. Influence of the stirring speed on the extraction rate.

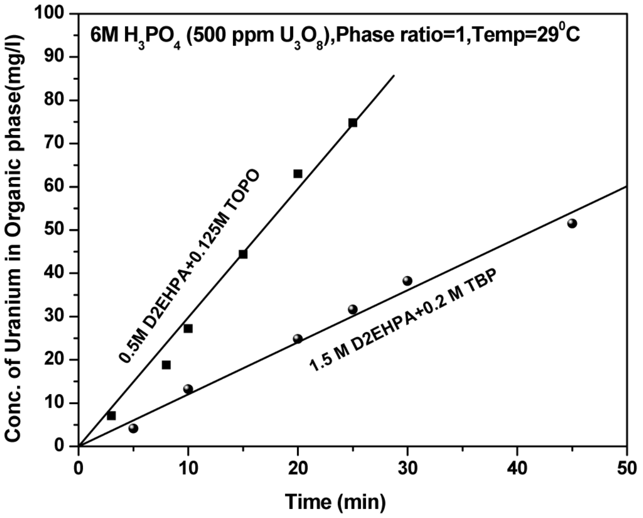

Fig. 6. Extraction of uranium vs. time in a LEWIS cell.

dependence was found when the stirring speed was less than 200 rpm. A plateau region was present with an increase of the stirring speed (200–350 rpm). Above 400 rpm, the rate constant value again increased due to the disturbance observed at the interface. The above observation was due to the fact that in a constant interfacial area stirring cell, the thickness of the stationary interfacial film is more at a lower stirring speed and the diffusion limits the rate for an extraction with a relatively fast chemical reaction. With an increase in the stirring speed, the stationary diffusion film becomes thinner and the diffusion resistance smaller. Above a certain stirring speed, the extraction rate is independent on the stirring rate. It is an indication that the extraction rate may be kinetically controlled in that (200–350 rpm) zone because the stationary diffusion film becomes thinner as slow chemical reaction starts to become competitive with diffusion process.

All kinetic experiments were carried out at 250 rpm in order to maintain the same hydrodynamic conditions.

3.4.2. Uranium extraction kinetics in 1.5 M D2EHPA + 0.2 M TBP/ 0.5 M D2EHPA + 0.125 M TOPO from 6 M PA

Mass transfer kinetics for U(VI) extracted from 6 M phosphoric acid was studied by two different extractant systems namely 0.5 M D2EHPA + 0.125 M TOPO and 1.5M D2EHPA + 0.2 M TBP. Phosphoric acid (6 M) containing known amount of U (500 mg/L) was stirred with equal volumes of 0.5 M D2EHPA + 0.125 M TOPO and 1.5 M D2EHPA + 0.2 M TBP in separate experimental runs. Fig. 6 shows the change in concentration of U in organic phase with increase in time. The rate of extraction of uranium was more in case of 0.5 M D2EHPA + 0.125 M TOPO than for 1.5 M D2EHPA + 0.2 M TBP. The linearity of the plot over 60 min showed that up to 30 min less than 20% of the equilibrium distribution has reached. The uranium mass transfer rate constant values for each data point were calculated applying Eq. (1) and were plotted against time. To obtain the rate constant for the chemical reaction in the extraction process, rate constant data points were extrapolated back to time zero as illustrated in Fig. 7. At time $t = 0$ when very little or no U has been transferred, the rate is not diffusion controlled, because little or no diffusion exists at initial contact. Hence extrapolation back to initial time yields rate constant for the chemical reaction. The rate constant (k) for the extraction of U from 6 M H_3PO_4 using 0.5 M D2EHPA + 0.125 M TOPO as an extractant was found to be 2.7×10^{-2} cm/min whereas, k value for 1.5 M D2EHPA + 0.2 M TBP was found to be 1.79×10^{-2} cm/min. The lower k value of U extraction by D2EHPA + TBP may be attributed to higher viscosity of

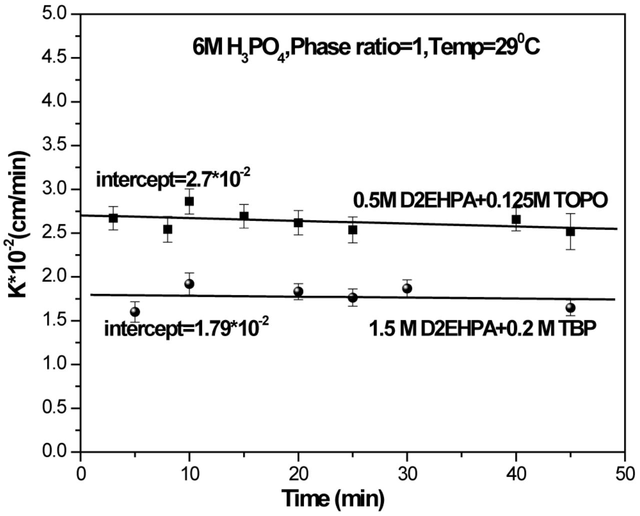

Fig. 7. Plot of rate constant vs. time.

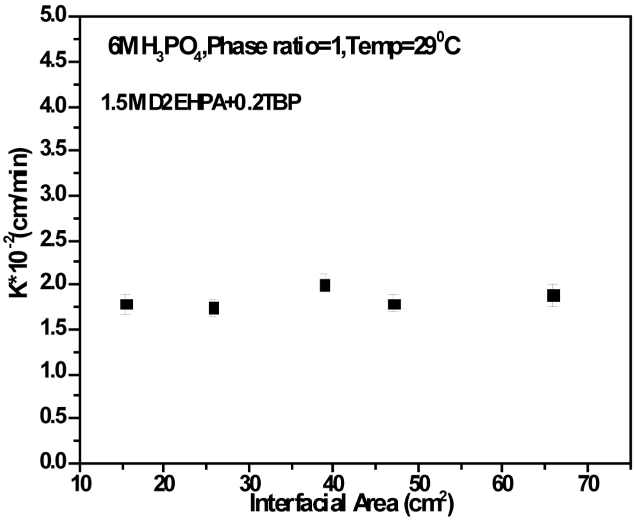

Fig. 8. Influence of the interfacial area on the extraction rate.

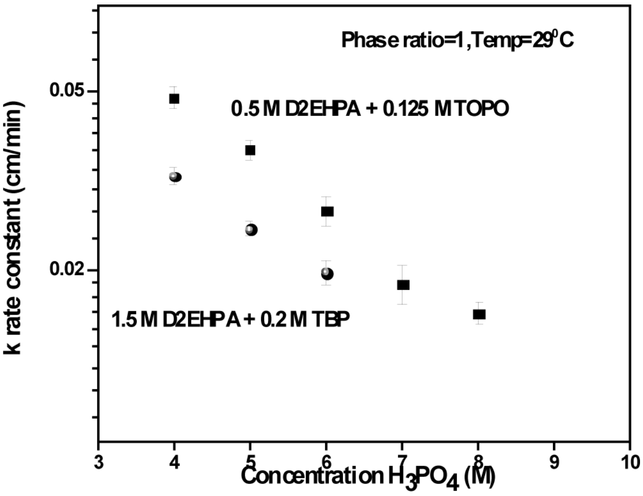

Fig. 9. Effect of phosphoric acid concentration on the transfer rate of uranium.

the extractant 1.5 M D2EHPA + 0.2 M TBP in comparison to 0.5 M D2EHPA+ 0.125 M TOPO.

3.4.3. Effect of interfacial contact area on rate constant

As reported by Danesi et al. [12], if a slow extraction (chemical reaction/diffusion) occurs in the bulk phase, the initial rate constant for the mass transfer will be independent of interfacial area. On the contrary, a reaction occurring at the interface will exhibit a direct proportionality between the rate and interfacial area. The effect of the interfacial area on the extraction rate was studied. Fig. 8 shows that the change in interfacial area has no effect on extraction rate constant for uranium extraction from phosphoric acid phase to D2EHPA+TBP phase, which is a characteristics of an extraction process having fast interfacial reaction where the mass transfer rate is determined by slow extraction process in the bulk of aqueous phase.

3.4.4. Effect of phosphoric acid concentration in the aqueous phase on the rate constant value

Experiments were performed to explore the effect of H_3PO_4 concentration on the rate constant for U extraction by 0.5 M D2EHPA + 0.125 M TOPO and 1.5 M D2EHPA + 0.2 M TBP. Fig. 9 shows the change in the rate constant with the change in the acid molarity which indicates that the phosphate concentration plays a significant role in extraction kinetics for the mass transfer from aqueous to organic phase. An increase in phosphoric acid concentration from 4 to 8 M resulted in a decrease in *k* value from 0.048 cm/min to 0.0011 cm/min in 0.5 M D2EHPA + 0.125 M TOPO. In the case of 1.5 M D2EHPA + 0.2 M TBP, *k* value decreased from 0.031 cm/min to 0.0181 cm/min with the increase in H_3PO_4 concentration from 4 to 6 M. These observations indicate that the rate constant value has significant dependence on phosphoric acid concentration.

The experimental results are in good agreement with the reported literature data [10] for 0.5 M D2EHPA + 0.125 M TOPO and also support Thamer et al. [13] that the dominating species of uranium are neutral in H_3PO_4 concentration of 6–8 M. Thus, it is very likely that a slow rate of exchange to a charged extractable species is the rate controlling step for chemical regime whereas for diffusional regime the viscosity of the aqueous phase controls the rate constant.

3.4.5. Effect of extractant concentration in organic phase

The rate constant value of uranium mass transfer from 6 M H_3PO_4 (500 mg/l U_3O_8) were evaluated for D2EHPA + TBP extractant system at two fixed mole ratios D2EHPA:TBP of 7.5:1 and 4:1. In these experiments the D2EHPA concentration was varied from 0.5 to 1.5 M and accordingly TBP was added to obtain the desired mole ratio. The rate constant value and *D* value increased in the range of 0.5–1.5 M for both the mole ratios. Fig. 10 represents the variation in the rate constant value for the change in extractant and synergist concentration.

In the case of 4:1 mole ratio of D2EHPA:TBP, when concentration of D2EHPA was increased from 0.5 M to 1.5 M, *k* increased from 0.0051 cm/min to 0.0240 indicating the influence of extractant concentration on rate constant. For 7.5:1 mole ratio of D2EHPA:TBP, the change in the rate constant value follows the same trend. The increase in *k* and *D* was found to be higher in the case of D2EHPA:TBP ratio of 4:1 which shows a high dependence of extractant to synergist mole ratio on the extraction rate constant for uranium.

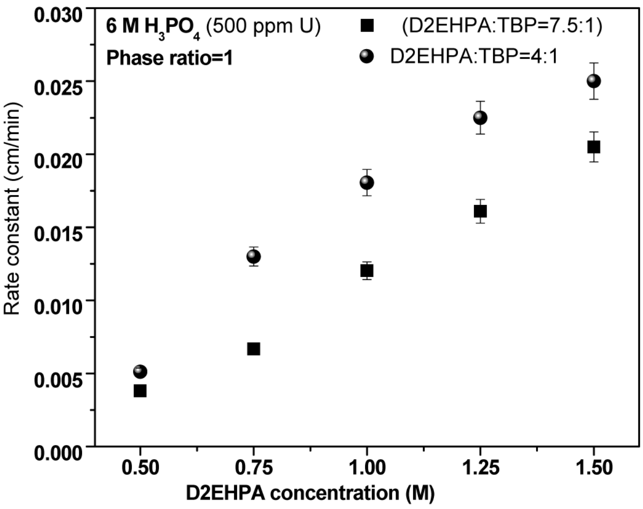

Fig. 10. Plot of rate constant for U extraction vs. D2EHPA concentration.

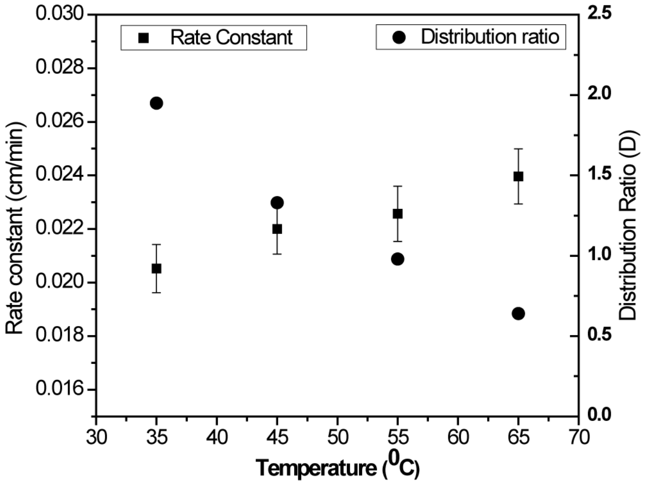

Fig. 11. Dependence of rate constant and distribution ratio on temperature.

3.4.6. Dependence of rate constant on temperature

The effect of temperature on the rate constant and distribution ratio was investigated for U(VI) from 6 M phosphoric acid with 1.5 M D2EHPA + 0.2 M TBP. The results are shown in Fig. 11. The extraction rate increases with increasing temperature and the experimental data follows Arrhenius equation. It was found that with an increase in temperature from 30 to 65°C, the *k* value increased from 0.021 to 0.024 cm/min, however *D* value decreased from 2.0 to 0.6. The decrease in *D* value indicated that the extraction process is exothermic. The activation energy for the extraction reaction was obtained from Arrhenius plot and was found to be 18.1 kJ/mole. Generally, when the activation energy (E_a) of an extraction reaction is more than 42 kJ/mol, the extraction process is controlled by chemical reaction; when E_a is lower than 20 kJ/mol, species diffusion is rate-limiting step [14]. The extraction rate is determined by both chemical reaction and diffusion when E_a is in the range from 20 to 42 kJ/mol. The data obtained in the present system indicates that the extraction rate for U(VI) may be controlled by a mixed regime (both kinetic and diffusion). Interestingly, Hurst et al. have also reported a comparable value of activation energy of 13.5 kJ/mole for 0.5 M D2EHPA + 0.125 M TOPO for U (VI) extraction from 6 M phosphoric acid [10].

4. Conclusions

Kinetic studies for the entrained solvent separation by diluent wash showed significant dependence of the rate constant values on parameters such as phase ratio, temperature and agitator speed.

Uranium mass transfer from aqueous to organic phase in D2EHPA + TBP – phosphoric acid system employing Lewis cell has been investigated. It was observed that the rate constant value (*k*) was directly dependent on phosphoric acid concentration, extractant concentration and temperature, whereas it was independent of interfacial contact area of the phases in the Lewis cell. The *k* values decreased linearly with an increase in phosphoric acid concentration from 4 to 8 M, whereas k increased with an increase in the concentration of D2EHPA (0.5–1.5 M) and TBP (0.06–0.4 M) in the organic phase. It was also observed that with an increase in temperature (30–65°C) the *k* value increased from 0.020 to 0.024 cm/min. However, the distribution ratio decreased from 2.0 to 0.6 with an increase in temperature from 30 to 65°C, which indicates that the extraction process is exothermic. The activation energy calculated by Arrhenius plot for uranium mass transfer was found to be 18.1 kJ/mole.

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