Publications

Available Online

J. Sci. Res. **9** (2), 255-266 (2017)

JOURNAL OF SCIENTIFIC RESEARCH

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Kinetics of Forward Extraction of V(V) in V(V)-NO_3^- (H^+, Na^+)-TOA-Kerosene System using Single Drop Technique

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Received 13 January 2017, accepted in final revised form 14 March 2017

Abstract

The titled system has been investigated using a single drop technique and flux (F) method of data treatment. In calculating fluxes, the time for drop formation and coalescence ($\Delta t = 0.75$ s) is considered. At lower concentration region of vanadium, V(V), the rate of V(V) transfer is directly proportional to its concentration. With the increase in [V(V)], slowly extractable V(V) species are formed gradually resulting in decrease in rate. Rate is directly proportional to the square root of [TOA]. It is reported that the most favorable extractable V(V) species exists in maximum amount at pH 2, and so, log F vs pH plots show a maximum at pH~2. The flux of V(V) transfer in most cases is found to be decreased with increasing [NO_3^-]. Reaction orders with respect to [V(V)], pH and [NO_3^-] have been attempted to be estimated, but in vein due to non-linearity of plots in most cases. Activation energies for the present system is ~ -12 kJ/mol. This is unexpected but explained. Due to irregular variation of the composition of extractable species with [V(V)], [H^+]; as well as temperature; it is not possible to elucidate the value of rate constant (k) and mechanism in simple way.

Keywords: Vanadium(V); TOPO; Kinetic; NO_3^- medium; Single drop technique.

doi: http://dx.doi.org/10.3329/jsr.v9i2.31113 J. Sci. Res. **9** (2), 255-266 (2017)

1. Introduction

In a previous paper, the solvent extraction of vanadium, e.g. V(V)) from nitrate medium by tri-n-octylamine (TOA) has been reported from the equilibrium point of view [1]. It is seen that the extraction ratio is increased significantly with increasing initial V(V) concentration in the aqueous phase pointing out the enhanced polymerization at higher [V(V)]. Moreover, the distribution ratio in logarithmic scale (log D) passes through a maximum at equilibrium pH of ~ 2.3, indicating that most favorable extractable species exists in maximum amount around this pH. The extractant dependence varies within 0.50-2.50 depending on pH. The suggested extraction equilibrium reaction is:

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$V_{10}O_{26}(OH)_2^{4-}$ + 4 H^+ + n TOA→ $H_2V_{10}O_{26}$.nTOA + 2 H_2O. The extractable product is a solvated ion pair. It may also be presented as ($HTOA^+$).($HV_{10}O_{26}$.(n-1)TOA^-). However, the non-linearity of dependence curves does not permit to evaluate the value of the extraction equilibrium constant [2,3] for reaction suggested above. This work discusses on the kinetics of the process cited.

In sixties and seventies of the last century, the solvent extraction chemists used the Shake Out [4,5] or Stirred Tank (AKUFVE) [6,7] methods for investigating the solvent extraction kinetics. They used to report the kinetic data on demanding that the measurements had been carried out at maximum interfacial area without incorporating its value in rate calculations. Being a heterogeneous system, the kinetics of a solvent extraction process is now-a-days studied using either the Lewis Cell [8,9], Rotating Diffusion Cell [10,11] or Single Drop Technique [12,13]. All these techniques permit the inclusion of interfacial area in rate calculations which is essential for a heterogeneous system. In this work, the single falling drop method has been used.

It has been established that the pseudo first - order rate constant (q) [5,8,14,15] and the flux (F) [8,10,12] are the two methods available for kinetic data treatment in solvent extraction of a metal ion by an extractant. In both methods, identical reaction orders with respect to reactant concentrations are obtained but the values of rate constant (k_f) differ due to the fact that the (q) method ignores the basics (surface area) of heterogeneous kinetics [8]. The F-method of data treatment has been applied to find out the reaction orders with respect to various concentration terms and activation energy to provide mechanism of the extraction system under consideration.

2. Experimental

2.1. *Materials*

Tri-n-octylamine (TOA) was collected from Tokyo Kaie Ind. (90%) and was used without further purification. It was diluted with distilled colorless kerosene to constitute the organic phase. All other chemicals were of reagent grade and used without further purifications. Kerosene was bought from the local market and distilled to collect colorless fraction distilling over 200-260°C. Stock solution of V(V) containing 5.00 g/L V(V) and 1.92 mol/L HNO_3 was prepared by dissolving NH_4VO_3 in dilute HNO_3 solution. In most cases, this solution was 5 times diluted to obtain test solutions containing 1.00 g/L V(V) and 0.38 mol/L HNO_3 or NO_3^- for kinetic study.

2.2. *Analytical*

A double buffer calibrating pH meter (Mettler Toledo 220) was used for pH measurement and to control adjustment of aqueous pH by the addition of anhydrous Na_2CO_3 under constant stirring. Aqueous V(V) concentration was determined by the H_2O_2 colorimetric method [16] at 450 nm using a visible spectrophotometer (WPA S104 Spectrophotometer).

2.3. *Rate measurement procedure by single-drop technique*

The construction of the single-drop apparatus used in this investigation was as described earlier [17]. A schematic diagram of the apparatus used in this study is displayed in Appendix. The continuum (20-100 cm in height) was the organic phase having a definite concentration of TOA, and the drops of the aqueous phase containing definite amount of V(V) at a certain pH were allowed to fall through the continuum and collected continuously from the bottom of the column, leaving a pool of ~2 drops of aqueous phase to avoid entrainment of organic solution in the collected drops. In actual experiments, an uncounted number of almost spherical, internally circulating, and slightly oscillating aqueous drops of diameter (1.70±0.10) mm were allowed to fall and collected in a previously weighed dry beaker and the volume of the collected drops (2.60±0.30 mL) was determined by the density-mass (weight) method. For each set of organic and aqueous solutions, the volume of 100 collected aqueous drops was estimated by the density (measured by a density meter) mass method. An accurate volume determination permitted the calculation of the volume of a single drop. Otherwise, on knowing the volume of a drop, the number of drops in actual / subsequent experiments could be determined. The V(V) content in the collected mass was then estimated. V(V) transferred from the aqueous drop to the organic continuum occurred during drop formation, travel, and coalescence. The time for drop travel was determined by dividing cumulative time for travel of separate 20 drops by the drop number, which obviously depended on the continuum height, drop size, and densities of the aqueous and organic solutions involved.

2.4. *Data treatment method*

If [V(V)], V_t, N and t represent the concentration change of V(V) in the aqueous phase in mg dm^{-3}, volume of the collected drop in cm^3, number of drops collected and the drop fall time in s, respectively, then the flux (F) of V(V)-transfer can be calculated by the following relationship [13]:

$$F\ (\text{kmol m}^{-2}\ \text{s}^{-1}) = \{[V(V)]\ V_t^{1/3}\}/(2.4695\ n^{1/3}\ t)\} \times 10^{-7} \qquad (1)$$

The quantity, F, at a constant temperature is proportional to [V(V)], $[H^+]$, [TOA] and $[NO_3^-]$ as:

$$F = k\ [V(V)]^a\ [H^+]^b\ [TOA]^c\ [NO_3^-]^d \qquad (2)$$

Where, k is the rate constant whose unit depends on the values of the reaction orders a, b, c and d. Equation (2) can be reproduced as:

$$\begin{aligned} \log F &= \log k + a \log [V(V)] + b \log [H^+] + c \log [TOA] + d \log [NO_3^-] \\ &= \log k + a \log [V(V)] - b\ pH + c \log [TOA] + d \log [NO_3^-] \end{aligned} \qquad (3)$$

Equation (3) indicates that if pH (or, $[H^+]$), [TOA] and $[NO_3^-]$ are kept constant at pH (or, $[H^+]$), [TOA] and $[NO_3^-]$, respectively; and the F-values are determined for various initial concentrations of V(V) then the plot of log F vs log [V(V)] should produce a straight line with slope equaling to log k - b pH + c log [TOA] + d log $[NO_3^-]$ from which the value of k could be calculated after obtaining the values of b, c and d. In a similar way, the values of b, c and d together with three sets of k-value can be determined from log F vs. pH, log F vs. log [TOA] and log F vs. log $[NO_3^-]$ plots, respectively. The data of temperature dependence can be treated by Arrhenius equation for determining the value of activation energy (E_a).

3. Results and Discussion

3.1. *Determination of drop formation and coalescence time*

In order to determine the time needed for drop formation and coalescence, the amounts of V(V) transferred at different drop fall times (drop fall time has been varied by varying the column height) were determined for a particular set of aqueous and organic phases. It is seen that metal ion transferred from a drop ($a_{V(V)}$) is increased with increasing drop fall time or column height, however, the related straight lines do not pass through the origin (Fig. 1). The lines intersect the drop fall time axis at -0.75 s. This time (0.75 s) is attributed to time for drop formation and coalescence. In calculating fluxes, the time for drop formation and coalescence (Δt = 0.75 s) must be added to the drop fall time, otherwise, errors in flux calculation will be appeared.

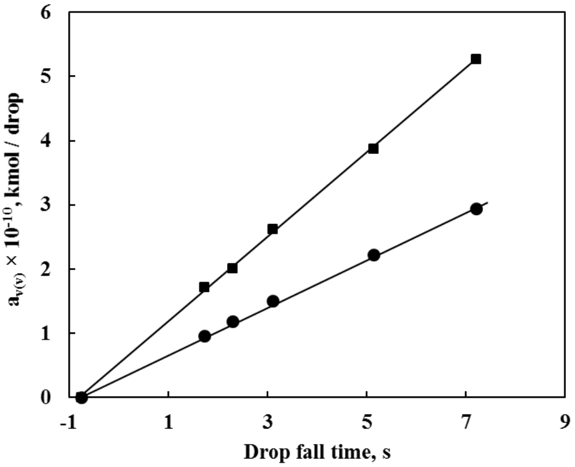

Fig. 1. Determination of time for drop formation and coalescence. [TOA] = 0.10 mol/L, $[NO_3^-]$ = 0.38 mol/L, pH = 1, Temp. = 294 K, Number of collected drops = 100; $[V(V)]_{(ini)}$ = 1.00 g/L (■); and 0.50 g/L (●).

3.2. *Effect of column height on the value of flux of V(V)-transfer*

The V(V) transfer flux has been calculated in two different ways for each column height used: flux (F') has been calculated on avoiding contribution from Δt value (F' = $a_{V(V)}$ transferred / (A.t)), whereas, flux (F) has been calculated on taking into account the contribution of Δt value (F = $a_{V(V)}$ transferred / A. (t + Δt)). The log (F' or F) vs column height plots are presented in Fig. 2. It is seen that the value of log F' decreases with column height, whilst log F is independent of column height but smaller than log F' value. It is concluded from this result that the calculated flux of V(V) transfer will be independent of column height if Δt is added to the drop fall time and the column of any height can be used for the flux measurement if F, in lieu of F' is measured.

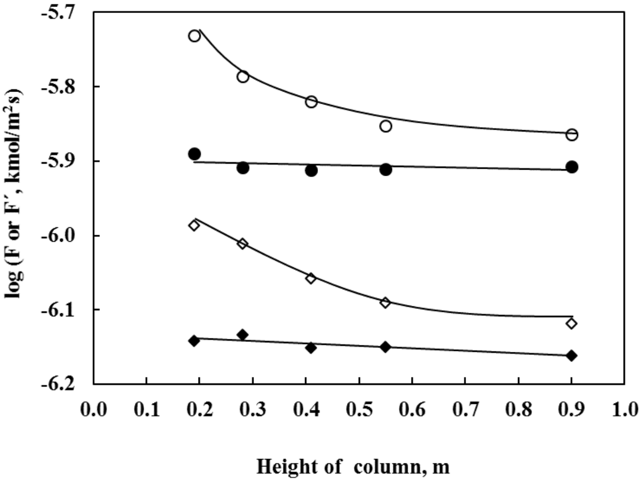

Fig. 2. Effect of column height on the flux of V(V) transfer. Δt = 0.75 s, (○) and (●), $[V(V)]_{(ini)}$ = 1.00 g/L; (◇) and (◆), $[V(V)]_{(ini)}$ = 0.50 g/L. Open symbol for F' and closed symbol for F. Other parameters are as in Fig. 1.

3.3. *Effect of initial [V(V)] in the aqueous phase on the flux of V(V) transfer*

On varying V(V) concentration between 0.10 and 2.00 g/L, the single drop experiments have been conducted keeping all other conditions identical. Three sets of experiments involving aqueous pH of 1, 2 and 3 using 0.10 mol/L TOA solution are investigated. The log (F, $kmol/m^2s$) vs log ($[V(V)]_{(ini)}$, $kmol/m^3$) plots are shown in Fig. 3. It is seen that the plots are of similar behavior. At lower concentration region of V(V), the limiting slope is about 1 and with increase in V(V) concentration, the slope gradually decreases. Thus, at lower concentration region of V(V), the rate is directly proportional to its concentration. With the increase in V(V) concentration, the slowly extractable or non-extractable V(V) species is formed gradually resulting the decrease in rate.

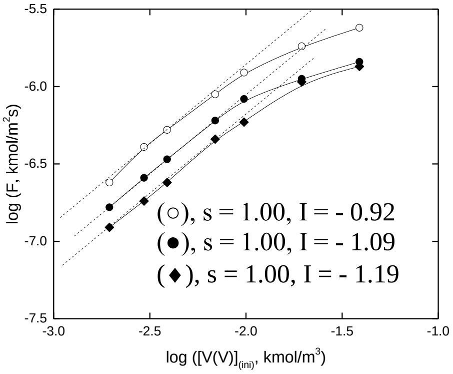

Fig. 3. Effect of initial V(V) concentration in the aqueous phase on the flux of V(V) transfer. Δt = 0.75 s. (◆), pH = 1; (○), pH = 2; (●), pH = 3. Other parameters are as in Fig. 1.

3.4. *Effect of initial [TOA] in the organic phase on the flux of V(V) transfer*

On varying the initial TOA concentration between 0.02 and 0.20 kmol/m^3, the fluxes of V(V) transfer have been measured for aqueous solutions containing 1 g/L V(V) and 0.38 mol/L NO_3^- at pH 1, 2 and 3, respectively. Fig. 4 shows the log (F, kmol/m^{2}s) vs log ([TOA]$_{(ini)}$, kmol/m^3) plots. It is seen that straight lines are obtained in all cases with slope of approximately 0.35. Rate of V(V) extraction by TOA is therefore directly proportional to the cube root of TOA concentration in the organic phase.

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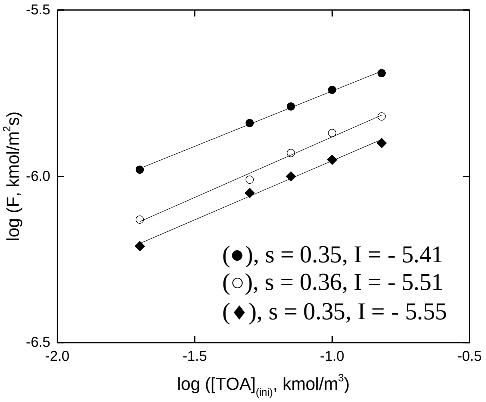

Fig. 4. Effect of initial [TOA] in the organic phase on the f lux of V(V) transfer. $[V(V)]_{(ini)}$ = 1.00 g/L, Δt = 0.75 s. (○), pH = 1; (●), pH = 2; (◆), pH = 3. Other parameters are as in Fig. 1.

3.5. *Effect of aqueous pH on the flux of V(V) transfer*

Effects of aqueous pH on the flux of V(V) transfer from an aqueous solution containing 1.00 g/L V(V) and 0.38 mol/L NO_3^- at 294 K by kerosene solution of either 0.05, 0.10 or 0.15 mol/L tri-n-octylamine (TOA) have been investigated. Fig. 5 shows the log (F, kmol/m^{2}s) vs. pH$_{(ini)}$ plots. The experimental points do not produce a straight line in neither of the cases. The plots show maxima at pH 2. It is realized from this result that the most extraction favorable V(V) species exists in maximum amount at pH 2. Moreover, the result indicates that the species existing below pH 2 is extracted by a cation exchange mechanism in the slow step since the limiting slope in this region is ~ 0.20 (indicating the release of a proton per 5 V(V) species being reacted in the rate determining reaction step), whereas, that existing above pH 2 is extracted by solvated ion-pair formation mechanism in the slow step as the limiting slope in this region is ~ -0.25 (indicating the association of a proton per 4 V(V) species being reacted in the rate determining reaction step).

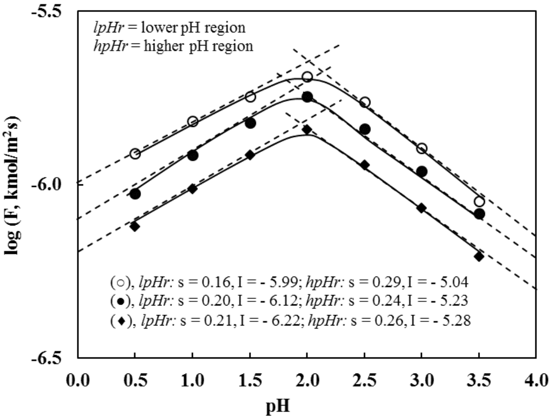

Fig. 5. Effect of aqueous pH on the flux of V(V) transfer. $[V(V)]_{(ini)}$ = 1.00 g/L, Δt = 0.75 s. (◆), $[TOA]_{(o,ini)}$ = 0.05 mol/L; (●), $[TOA]_{(o,ini)}$ = 0.10 mol/L; (○), $[TOA]_{(o,ini)}$ = 0.15 mol/L. Other parameters are as in Fig. 1.

3.6. ***Effect of nitrate ion concentration on the flux of V(V) transfer***

The effect has been measured at three sets of parametric conditions. The log (F, kmol/m^{2}s) vs log ($[NO_3^-]$, kmol/m^3) plots are displayed in Fig. 6. Although the equilibrium study indicates the enhancement of extraction with increasing NO_3^- concentration in the aqueous phase [1], the flux of V(V) transfer in most cases is found to be decreased with increasing $[NO_3^-]$. At pH = 1, the flux is, however, increased with increasing $[NO_3^-]$ in its lower concentration region. At higher concentration region of nitrate ion in the aqueous phase, the limiting slope is –(1.00±0.40), whilst that in the lower concentration region is –(0.40±0.08) for two cases and ~ 1 in another set of experimental parameters.

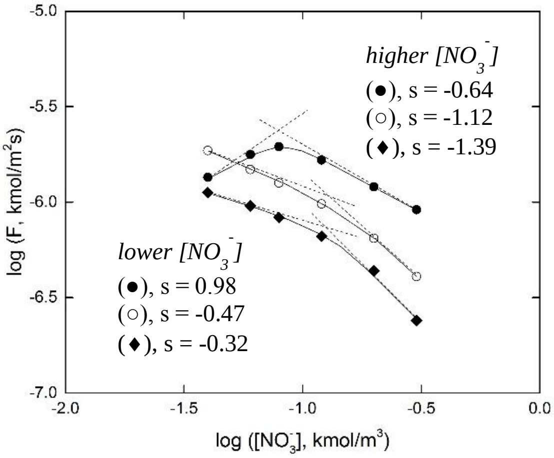

Fig. 6. Effect of nitrate ion concentration on the flux of V(V) transfer. $[V(V)]_{(ini)} = 1.00$ g/L, [TOA] = 0.10 mol/L, $\Delta t = 0.75$ s. (●), pH = 1; (○), pH = 2; (◆), pH = 3. Other parameters are as in Fig. 1.

3.7. *Effect of temperature on the flux of V(V) transfer*

The effect of temperature has been measured at three sets of parametric conditions. The Arrhenius plots (log F vs 1/T) are shown in Fig. 7. In all cases, straight line with a positive slope (rate being decreased with increasing temperature) is obtained. Slopes of these lines yield activation energy of ~ -(12.00±1.20) kJ/mol. The negative value of activation energy at the first sight, is unacceptable as rates of all chemical or diffusional processes increase with increasing temperature. However, it is presumably for the variation of the extractable species with temperature. With the rise of extraction temperature, virtually, during the pre-equilibration of the aqueous phase at different higher temperatures, the distribution of V(V)-species is changed so that the % of non-extractable species, such as, $V_{10}O_{27}(OH)^{5-}$ is increased with the rise of temperature, resulting in lower rate at higher temperature. On the other hand, with lowering of extraction temperature, virtually, during the pre-equilibration of the aqueous phase at different lower temperatures (by ice cooled water), the distribution of V(V)-species is so changed that the % of extractable species, such as, VO_2^+ is increased with the rise of temperature, resulting in higher rate at lower temperature.

Due to non-linearity of plots in Figs. 3, 5 and 6, it is not possible to elucidate the value of rate constant. But the nature of these plots, particularly, the pH dependence rate plots in Fig. 5 clearly points out that there are two types of processes depending on aqueous acidity; one below pH 2 where the rate increases with increasing pH (limiting order with respect to $[H^+]$ being around -0.20) and the other above pH 2, where the rate decreases with increasing pH (limiting order with respect to $[H^+]$ being around 0.25).

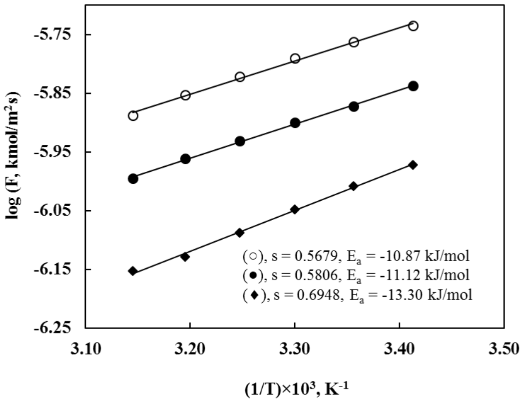

Fig. 7. Effect of temperature on the flux of V(V) transfer. $[V(V)]_{(ini)}$ = 1.00 g/L, Δt = 0.75 s. (●), pH = 1; (○), pH = 2; (◆), pH = 3. Other parameters are as in Fig. 1.

According to Zeng and Cheng [18], yellow colored VO_2^+ exists within pH <1 – 2, whereas, within pH 2 - 6.50, orange – red $V_{10}O_{28}^{6-}$ exists. However, it is also reported [19] that with the gradual increase in pH, VO_2^+ is gradually transformed to $VO(OH)_3$ (to a small extent), $V_{10}O_{26}(OH)_2^{4-}$, $V_{10}O_{27}(OH)^{5-}$, $V_{10}O_{28}^{6-}$, $V_3O_9^{3-}$, $V_4O_{12}^{4-}$, $VO_2(OH)_2^-$ etc. $V_{10}O_{26}(OH)_2^{4-}$ is virtually doubly protonated $V_{10}O_{28}^{6-}$, whilst, $V_{10}O_{27}(OH)^{5-}$ is single protonated $V_{10}O_{28}^{6-}$. The distribution of these species as function of pH is available graphically (species % vs pH plots) [19]. Based on this graph, the approximate % of species existing at a pH have been estimated and collected in Table 1. It is seen from this table that the predominant species around and below pH 2 is the cationic species, VO^{2+}. This forms anionic species with nitrate ion of type $[VO_2(NO_3)_2]^-$, which in turn forms the ion-pair $H^+[VO_2.(NO_3)_2]^-$ and is diffused to the interface. A part of TOA extracts HNO_3 by forming ion pair of type $TOAH^+.NO_3^-$ at the interface, where, it forms the solvated ion-pair of the type $TOAH^+[VO_2.(NO_3)_2]^-$ with the already diffused $H^+[VO_2.(NO_3)_2]^-$.

Table 1. Distribution of V(V) species at different acidic pH values [20].

pH	% (approximate)								Theoretical pH dependence in Eq. study
	VO_2^+	$VO(OH)_3$	$V_{10}O_{26}(OH)_2^{4-}$	$V_{10}O_{27}OH^{5-}$	$V_{10}O_{28}^{6-}$	$V_3O_9^{3-}$	$VO_2(OH)^{2-}$	$V_4O_{12}^{4-}$	
1.0	99	1	-	-	-	-	-	-	0.99
1.5	98	2	-	-	-	-	-	-	0.98
2.0	65	3	31	-	-	-	-	-	0.526
2.5	24	2	74	-	-	-	-	-	-0.056
3.0	4	1	80	15	-	-	-	-	-0.355
3.5	-	-	65	35	-	-	-	-	-0.435
4.0	-	-	35	65	-	-	-	-	-0.455
4.5	-	-	13	85	1	-	-	-	-0.477
5.0	-	-	4	87	6	1	2	-	-0.517
5.5	-	-	2	81	12	2	3	-	-0.535
6.0	-	-	-	57	32	6	4	1	-0.577

Due to the presence of 24 C-atoms in the solvated ion pair, it possesses hydrophobicity and ultimately, is transferred into the organic phase. The process is as a whole diffusion controlled as fractional reaction order of magnitude -0.20 with respect to $[H^+]$ has been obtained at ~ pH 1 (for a chemical controlled process, a small value of reaction order with respect to $[H^+]$ would not be obtained). The basis for the formation of $[VO_2(NO_3)_2]^-$ is the positive reaction order (almost unity) with respect to $[NO_3^-]$. Moreover, a negative activation energy (which could never be for a chemical or diffusion process but indicating complexity of the system) points out at least that the process is diffusion controlled. If it would be a chemically controlled process, the activation energy should be over 50 kJ/mol.

Above pH 2, the extractable species is $V_{10}O_{26}(OH)_2^{4-}$. By taking up two H^+, it can be converted into $V_{10}O_{26}^{2-}$. This ion can take up another H^+ to form $HV_{10}O_{26}^-$, which is diffused to the interface. On the other hand, at the interface TOA takes up a H^+ to form $TOAH^+$ by forming a co-ordination bond between N of TOA (possessing lone pair of electrons) and H^+. $HV_{10}O_{26}^-$ and $TOAH^+$ form ion pair $TOAH^+$ $HV_{10}O_{26}^-$ which is being extracted into the kerosene phase. This mechanism is supported by positive reaction order with respect to H^+ (negative pH dependence of rate). As no high positive value of activation energy is obtained, the process might be diffusion controlled again.

Vinarov and Kirichenko [21] have reported kinetics of V(V)-extraction from HCl by tri-n-butyl phosphate. They have suggested that the process is diffusion controlled on the basis of obtaining low activation energy. However, no mechanism of extraction has been suggested.

4. Conclusion

The kinetics of the extraction of V(V) from HNO_3 medium by TOA have been measured using the single drop (falling) technique. The flux of V(V) transfer will be independent on column height if Δt (0.75 s) is added to the drop fall time in its calculation. When V(V) concentration is kept within 1 g/L, the flux is found to be directly proportional to [V(V)] and cube root of [TOA], but the reaction order with respect to $[H^+]$ varies widely from ~ -0.20 to 0.25. At lower pH region, flux is increased with increasing $[NO_3^-]$ in its lower concentration region, but it is inversely proportional to $[NO_3^-]$ in most cases. The temperature dependence of flux gives activation energy of -(12±1.3) kJ/mol. The negative value of activation energy is highly unacceptable at the first appearance. However, it points out the complexity of the system. With the rise of temperature, the percentage of extractable species is probably decreased resulting in lower rate of extraction at higher temperature. Due to variation of reaction orders, it is not possible to elucidate the value of rate constant. However, probable mechanisms of extraction of VO_2^+ and $V_{10}O_{26}(OH)_2^{4-}$ have been discussed. The first and second species are extracted by the formation of the solvated ion-pairs $TOAH^+[VO_2(NO_3^-)_2]^-$ and $TOAH^+.HV_{10}O_{26}^-$, respectively and diffusions are rate controlling.

Acknowledgment

Mottakin is grateful to the Ministry of Science and Technology, Bangladesh, for giving him the National Science and Technology Fellowship to carry out this work. The paper was presented in an International Conference on Engineering Materials and Metallurgical Engineering, ICEMME-2016 (held on December 22–24, 2016), organized by the Pilot Plant & Process Development Centre (PP & PDC), Bangladesh Council of Scientific and Industrial Research (BCSIR), Dr. Qudrat-i-Khuda Road, Dhanmondi, Dhaka, Bangladesh.

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Appendix

A schematic diagram of the single drop apparatus is shown below:

1 = Aqueous reservoir
2, 4 = Interface
3 = Falling drop
5 = Drop collecting beaker
6 = Stop-cocks
7 = Thermostated water jacket
8 = Thermostated water bath
9 = Pump
10 = Rubber tubing
11 = Column containing organic phase