Thermodynamics of vanadium (V) solvent extraction by mixture of D2EHPA and TBP

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ABSTRACT

In the present study, the thermodynamics and mechanisms of vanadium extraction by a mixture of bis-2-ethylhexyl phosphoric acid (D2EHPA) and tri-n butyl phosphate (TBP) from sulfate medium were investigated. It was found that the maximum extraction percent of vanadium occurs at pH 1.8 under ambient conditions; this phenomenon was ascribed to the predominant presence of cationic species of vanadium (VO_2^+) at this pH. Based on the Fourier Transform Infrared (FT-IR) spectrums, the $P-O-H$ bond of D2EHPA was found responsible for the extraction of VO_2^+ species through a cationic exchange mechanism. Employing the slope analysis method showed that the stoichiometric reaction between VO_2^+ and D2EHPA was $VO_2^+ + RH \leftrightarrow \overline{VO_2R} + H^+$ regardless of the D2EHPA concentration. It was also shown that the TBP has no synergistic effect on the VO_2^+ extraction except in the experiments conducted at 60 °C. This was further elucidated by applying a modifying factor for TBP in the slope analysis method. Results showed that vanadium extraction was an endothermic reaction with an apparent molar enthalpy of 22.76 kJ/mol.

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1. Introduction

Vanadium, a high melting-point element, exhibits corrosion resistance against different acids and alkalis, at low temperatures (Moskalyk and Alfantazi, 2003). It is considered an important alloying element in the steel industry (Zeng and Cheng, 2009) and a material with superior performance in the aerospace and chemical industry (Moskalyk and Alfantazi, 2003). Other applications in catalysis, ink, dye, paint, varnish, insecticide, photography, pharmaceutical and glass industry are of significance, as well (Biswas and Mondal, 2003).

Vanadium is scarcely distributed in the earth crust (Biswas and Mondal, 2003). There are no mineral deposits in the nature that contains high values of vanadium (Li et al., 2009). Its usual occurrence is in minerals such as carnotite, roscoelite, vanadinite, mottramite and patronite (Moskalyk and Alfantazi, 2003). High contents of vanadium can, therefore, be found in the tailings of the mineral processing systems (Ho et al., 1994; Lihua, 2008; Narayanan Remya and Lakshmipathy Reddy, 2004).

Vanadium belongs to the VB group of the periodic table. Its dominant valences are +4 and +5 (Rehder, 2003; Zeng et al., 2009). Having different valences, vanadium can form various complexes; especially in aqueous solutions. A pertinent factor affecting variation of the vanadium valence is medium pH (Olazabal et al., 1992; Tangri et al., 1998). Oxidation state of vanadium determines its toxicity. Vanadium pentoxide is more detrimental than the elemental form (Moskalyk and Alfantazi, 2003).

Solvent extraction has been employed for recovery of vanadium. Leaching solutions of stone-coal/black shale (Deng et al., 2010; He et al., 2007; Li et al., 2009, 2011), spent catalysts (Chen et al., 2006; El-Nadi et al., 2009; Ho et al., 1994; Lozano and Juan, 2001; Yanhai et al., 2009; Zeng and Cheng, 2009; Zeng and Cheng, 2010; Zeng et al., 2009) and ash (Akita et al., 1995; Al-Ghouti et al., 2011; Giavarini, 1982; Navarro et al., 2007). Regarding different solutions containing vanadium, various reagent classes have been utilized for implementing solvent-extraction process; phosphinic acids (CYANEX 272 (Li et al., 2012)), phosphonic acids (EHEHPA (Li et al., 2012)), hydroxyoximes (LIX 63 (Zeng and Cheng, 2010; Zhang et al., 1996)), primary amines (Primene JMT (Nekovar and Schrötterová, 2000) and Primene 81R (Lozano and Godínez, 2003; Lozano and Juan, 2001)), tertiary amines (Alamine 336 (Lozano and Godínez, 2003), trialkylamine (Chen et al., 2006; Yanhai et al., 2009)), quaternary amines (Aliquat 336, Adogen

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464 (Chatterjee and Basu, 1991), TOMAC (Hirai and Komasawa, 1990; Hirai and Komasawa, 1993)) and phosphorus–oxygen extractants (TBP (Ojo, 2007; Oluwasanjo, 2013; Tedesco and De Rumi, 1980), TOPO/TBP (Sato et al., 1980) and TBP (Ojo, 2007; Oluwasanjo, 2013; Tedesco and De Rumi, 1980), and Cyanex 923 (Narayanan Remya and Lakshmipathy Reddy, 2004; Remya et al., 2003; Wang et al., 2009)).

D2EHPA, a cheap and stable phosphoric acid extractant, can extract vanadium from various media including chloride (Ojo, 2007; Rigg and Garner, 1967; Sato et al., 1978), nitric (Brunette et al., 1979; Ojo, 2010, 2007) and sulfate (Alibrahim et al., 2008; Biswas and Mondal, 2003; Crouse and Brown, 1959; Deng et al., 2010; Ho et al., 1994; Hughes and Biswas, 1991; Ipinmoroti and Hughes, 1990; Islam and Biswas, 1980; Li et al., 2009, 2012, 2011; Sato and Takeda, 1970) solutions. It may be used alone or in combination with other extractants such as TBP (Alibrahim et al., 2008; Crouse and Brown, 1959; Deng et al., 2010; Giavarini, 1982; Li et al., 2009, 2011; Ojo, 2010, 2007). The addition of TBP to D2EHPA reduces the unfavorable effects of M2EHPA presents in commercial D2EHPA (Keshavarz Alamdari et al., 2004). TBP is also an effective organic phase modifier which improves the phase separation conditions (Crouse and Brown, 1959; Haghshenas Fatmehsari et al., 2009; Li et al., 2011).

A literature review shows that D2EHPA–TBP has been employed for vanadium extraction from a solution obtained through leaching process implemented under optimized conditions (Deng et al., 2010; Li et al., 2009). Alibrahim et al. (2008) and Li et al. (2011) could effectively separate iron from vanadium leaching solution. Additionally, Ojo (2007) has studied and optimized the separation of vanadium and molybdenum in chloride and nitrate media using D2EHPA. According to the results obtained by Ojo (2010), the extraction mechanism in nitrate media depends on the D2EHPA concentration in which the stoichiometric coefficient of D2EHPA equals 1 at concentrations lower than 0.574 M and 2 at higher concentrations. Thermodynamics and mechanisms of VO^{2+} extraction by D2EHPA from sulfate media was also investigated by Li et al. (2012) employing slope analysis method. Their results indicate that the mechanism is affected by pH.

In the present work, the mechanism and thermodynamics of vanadium extraction from aqueous solutions by mixtures of D2EHPA–TBP are evaluated based on the slope analysis method. The interactions between active species in $D2EHPA–TBP–VO_2^+$ is identified by FT-IR spectroscopy. Results obtained through mathematical–analytical analyses are applied for estimation of apparent enthalpy, as well as apparent entropy of the extraction reaction.

2. Materials and methods

2.1. Materials

In order to prepare various organic phases, different volumes of D2EHPA, TBP and kerosene were mixed together. D2EHPA was supplied by Shandong Chemical (China), TBP was supplied by Fluka (Switzerland), kerosene was purchased from Tehran Refinery Co. (Iran). All chemicals were used without further purification. NH_4VO_3 of analytical grade (Merck, GmbH) was dissolved in distilled water to produce a solution of 5 g/L vanadium. During the experiments, pH was adjusted by using H_2SO_4 and NH_4OH.

2.2. Methods

Equal volumes of aqueous and organic solutions (25 mL) were effectively mixed in a mechanical shaker for 60 min (Deng et al., 2010; Li et al., 2012; Ojo, 2010). Experiments were conducted at 25, 40 and 60 °C. Aqueous and organic solutions were separated isothermally via separating funnels. After achievement of equilibrium, detected by pH measurement (Metrohm 827), concentration of vanadium in the aqueous phase was analyzed by atomic absorption (GBC Awanta).

Equilibrium concentrations of vanadium in the organic phase were determined by mass balance calculations.

3. Results and discussions

Fig. 1 illustrates the extraction percentage of vanadium against pH of the mixture composed of D2EHPA (0.6 M) and TBP (0.18 M) diluted in kerosene, at ambient temperature. Maximum extraction occurs at pH ≈ 1.8 according to the diagram. Although D2EHPA and Cyanex 923 extract vanadium via different mechanisms, an almost similar optimum is reported for Cyanex 923 (Wang et al., 2009).

Employing an activity-pH diagram, Li et al. (2012) have concluded that VO^{2+} – V(IV) – is predominant species present at pH <2; while VO_2^+ – V(V) – is the predominant species at higher activities of the aqueous solution. This has been the matter of debate. Olazabal et al. (1992) and Tangri et al. (1998) have stated, for example, that at pH <2, VO_2^+ is the predominant species of the solution. Qinggang et al. have related the presence of the vanadium species to the color of the solution: VO_2^+ showing yellow color while VO^{2+} displays the blue color (Qinggang et al., 2007). This has been the last reason for consideration of the VO_2^+ as the predominant species in our SX solutions.

Our experiments, neither before nor after SX extraction, did not show aqueous-solution blue color. The color of the solution, in all stages was yellow, instead. It was noteworthy that the concentration had strong effect on species predominance in the solution. The difference in results of Li et al. (2012) with that of ours was simply attributable to the unequal initial concentrations used in the two investigations (0.5 vs. 5 g/L).

Revealing optimum pH of 1.8, as shown in Fig. 1, indicated the relevance of the type of vanadium ion to pH of the aqueous solution. At pH <2, the ionic form of vanadium in the aqueous solutions was VO_2^+. When pH exceeded 2, anionic species like $V_{10}O_{28}^{6-}$ (Olazabal et al., 1992; Tangri et al., 1998) became predominant. Formation of different complexes is also affected by vanadium concentration and higher vanadium concentration leads to a lower pH range for VO_2^+ to be stable (Zeng et al., 2009); this could be the reason that at 5 g/L vanadium concentration, the pH range shifts to less than 1.8 (instead of 2). Based on the results shown in Fig. 1, the solvent extraction of D2EHPA–TBP–vanadium obeys a cation exchange mechanism at pHs between 0.5 and 1.8. Dropping the extraction percentage by pH, can indicate the absence of the cationic complexes at these pHs.

3.1. FT-IR spectroscopy analysis

FT-IR spectroscopy is a chemical micro-environment sensitive tool and a functional-group characterizing technique (Shen et al., 2007) that can be employed for exploring the existence of interactions
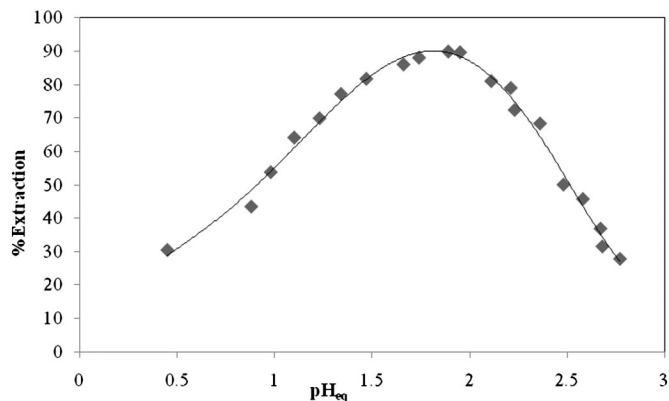

Fig. 1. The extraction of vanadium in sulfate media by 0.6 M D2EHPA and 0.18 M TBP diluted in kerosene at 25 °C.

between D2EHPA and TBP. These measurements can be used for recognizing the band-change during the solvent extraction.

According to the representative spectra of TBP, the bands from 1200 to 1350 cm^{-1} are related to the P═O stretching vibration of the TBP constituent (Alibrahim and Shlewit, 2007; Jiang et al., 2003; Shen et al., 2007). The decrease in intensity of P═O stretching vibration leads to shifting of the corresponding peak to the lower wave numbers. This is assigned to the presence of a second component which is involved in phosphoryl (P═O) band (Shen et al., 2007).

The characteristic vibration bands of pure D2EHPA are P═O, P–O–C or P–O–H and O–H. Based on the results shown in Fig. 2, these characteristic vibration bands are indexed as 1229, 1033 and 1639 cm^{-1}, respectively. The FT-IR spectrum of a mixture of D2EHPA and TBP (shown in Fig. 2) indicates decrease of the intensity of P═O vibration band of D2EHPA (1232 cm^{-1} in the pure mixture of D2EHPA and TBP spectra). It seems that the P═O vibration band of TBP in the mixture of D2EHPA and TBP influences the P═O vibration band of D2EHPA. It can be concluded that there is an interaction between D2EHPA and TBP (Haghshenas Fatmehsari et al., 2009).

The FT-IR spectra of the pure organic phase (D2EHPA–TBP) and that loaded by vanadium (D2EHPA–TBP–vanadium) are shown in Fig. 3 at ambient temperature. As can be seen, the extraction of vanadium affects the characteristic vibrational band of D2EHPA (P–O–H, 1033 cm^{-1} in loaded spectra). It is also observed that that there is no change in the characteristic vibration of the other bands such as P═O (1232 cm^{-1}). Consequently, TBP does not participate in extraction reaction of vanadium species and only D2EHPA is responsible for the formation of organometallic complexes.

3.2. Extraction mechanism and thermodynamics of the process

Based on the results obtained in Section 3.1, the extraction reaction of VO$_2^+$ by D2EHPA can be simply represented as (Darvishi et al., 2005):

$$M^+ + n(RH) \leftrightarrow \overline{M(R)_1(RH)_{n-1}} + H^+ \tag{1}$$
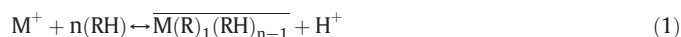
where RH and M$^+$ stand for D2EHPA and VO$_2^+$, respectively.

The equilibrium concentration of the organic phase [RH]$_{equilibrium}$ can be defined according to the following equation:

$$[RH]_{equilibrium} = [RH]_{initial} - n\overline{[M]}_{org} \tag{2}$$

in which [RH]$_{initial}$ is the initial concentration of D2EHPA, n is the stoichiometric coefficient of RH in Eq. (1) and $\overline{[M]}_{org}$ is the concentration of vanadium extracted by the D2EHPA.

According to the extraction constant of the reaction:

$$K_{ex} = \frac{\left[\overline{M(R)_1(RH)_{n-1}}\right][H^+]}{[M^+][\overline{RH}]^n_{equiblirium}} \tag{3}$$

and the distribution coefficient:

$$D_M = \frac{\left[\overline{M(R)_1(RH)_{n-1}}\right]}{[M^+]}. \tag{4}$$

The following expression can thus be obtained:

$$\log K_{ex} = \log D_M - pH - n\log[\overline{RH}]_{equilibrium}. \tag{5}$$

Since "$-RT \ln K_{ex} = \Delta H° - T\Delta S°$", Eq. (5) can be written as:

$$\log K_{ex} = \log D_M - pH - n\log[\overline{RH}]_{equilibrium} = \frac{\Delta H°}{2.3RT} + \frac{AS°}{2.3R} \tag{6}$$

where $\Delta H°$ and $\Delta S°$ are the apparent standard enthalpy and entropy of the extraction, respectively.

3.2.1. Effect of D2EHPA concentration on vanadium extraction

Figs. (5) and (6) show the plots of $\log D_M - n\log[\overline{RH}]_{eq}$ against pH$_{eq}$ for various values of n at different D2EHPA concentrations and constant TBP concentration (0.18 M). The line that most closely exhibits a slope equal to 1 is then selected (because of the stoichiometry of the hydrogen ion – H$^+$ – in Eq. (5)). This slope is related to the stoichiometric coefficient of the hydrogen ion – H$^+$ – throughout the extraction.

As can be seen in Figs. 4–6, the value of n = 1 is the best choice for all concentrations of D2EHPA. Eq. (7) can, thus, be proposed for the extraction reaction of vanadium by D2EHPA:

$$VO_2^+ + RH \leftrightarrow \overline{VO_2R} + H^+. \tag{7}$$

Ojo (2010) has indicated, however, that the stoichiometric coefficient of D2EHPA equals 1 below 0.574 M and 2 at higher concentrations. This result is not consistent with that of ours. This nonconcurrence could be the outcome of different media used in different investigations (nitrate vs. sulfate). Different initial solutions of vanadium (2.5 vs. 5 g/L) or TBP could have resulted in the difference. Ojo (2010) has not also considered the equilibrium concentration of the D2EHPA ([RH]$_{equilibrium}$). Li et al. (2012) state that at pH range 0.9–1.1 – the beginning range of our study – the stoichiometric coefficient of D2EHPA equals 2 and that of pH range 2–2.1 equals 1. As discussed before, Li et al. (2012) have made a model based on the assumption of VO^{2+} – V(IV) – as the predominant
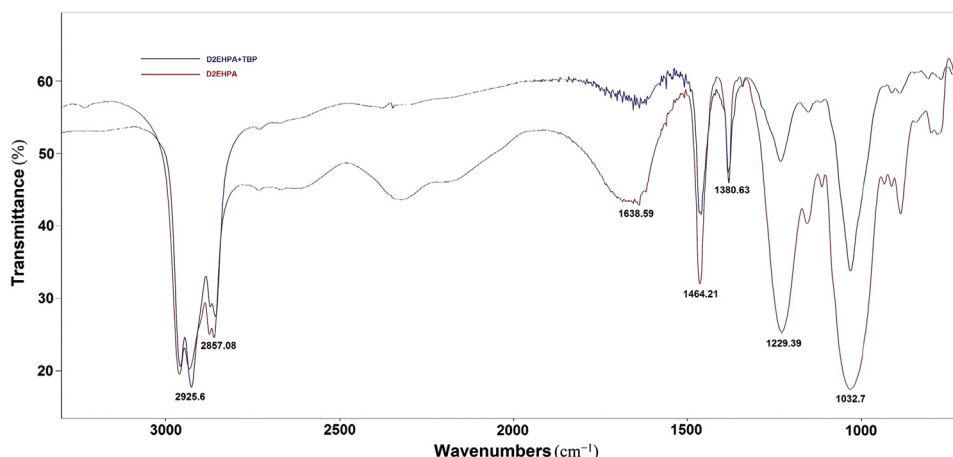

Fig. 2. FT-IR spectra of mixture of D2EHPA and TBP (20 and 5 vol.% respectively) as compared with pure D2EHPA.
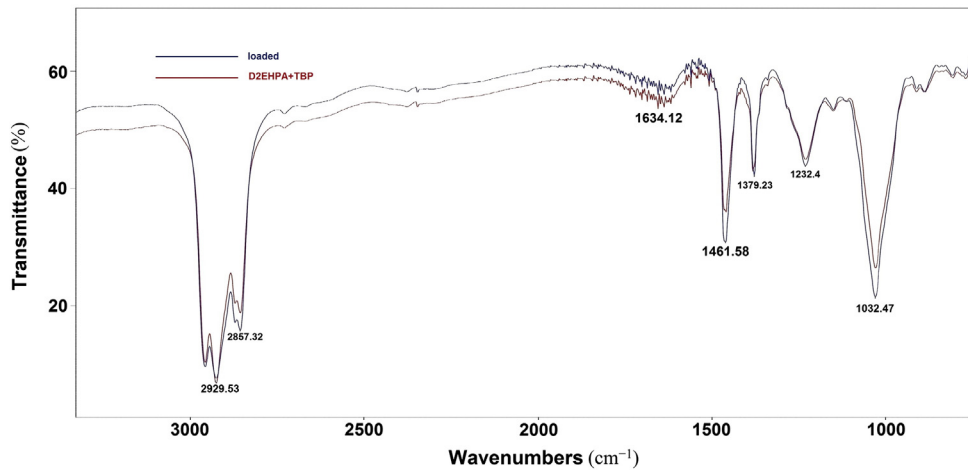
Fig. 3. Comparison between FT-IR spectra of pure organic phase and organic phase loaded with vanadium at pH = 1.7.
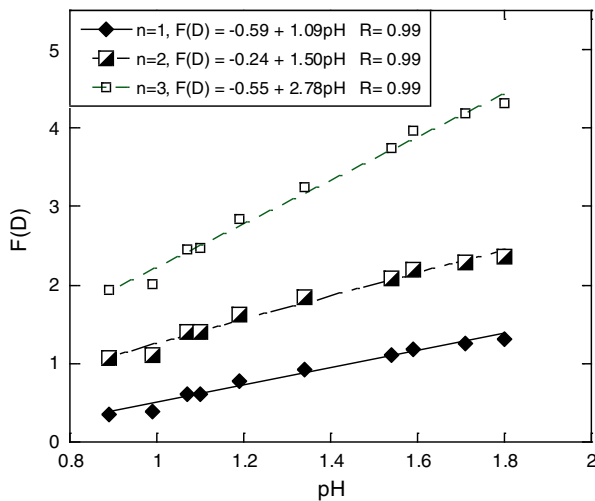

Fig. 4. Variation of $F(D) = \log D_M - n\log[RH]_{eq.}$ versus $pH_{eq.}$ for 0.3 M D2EHPA.

species of the aqueous solution. Moreover, they have added no TBP to the organic solution and an aqueous solution more dilute than this study has been employed by them (0.5 vs. 5 g/L).
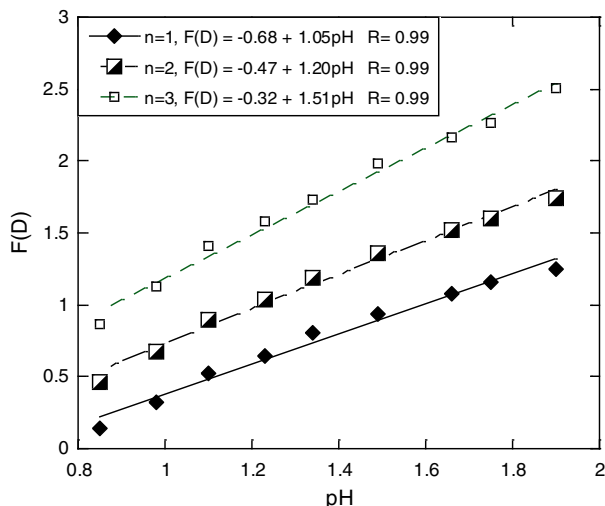
3.2.2. Effect of temperature on vanadium extraction

To explore the effect of temperature on vanadium extraction, some experimental runs were conducted using 0.6 M D2EHPA–0.18 M TBP mixture at three temperatures. F(D) versus pH_{eq} is plotted for 25, 40 and 60 °C in Figs. 7–9, respectively.

As can be seen in Figs. 7–9, the line related to n = 1 shows a slope equal to 1 for all concentrations of D2EHPA.

3.2.3. Effect of TBP

When TBP has a synergistic effect on the extraction of vanadium from solution with D2EHPA, Eq. (2) can be rewritten as the following equation (Haghshenas Fatmehsari et al., 2009):

$$[RH]_{equilibrium} = [RH]_{initial} - n[\overline{M}]_{org} - \alpha[TBP]. \qquad (8)$$

In other words:

$$\log D_M - n\log\left([RH]_{initial} - n[\overline{M}]_{org} - \alpha[TBP]\right) = \log K_{ex} + pH \qquad (9)$$

in which α is a coefficient depending on the concentration of TBP and the metal ion. It could be stated that in all experiments, when temperature and initial concentrations of the D2EHPA and TBP are constant, α
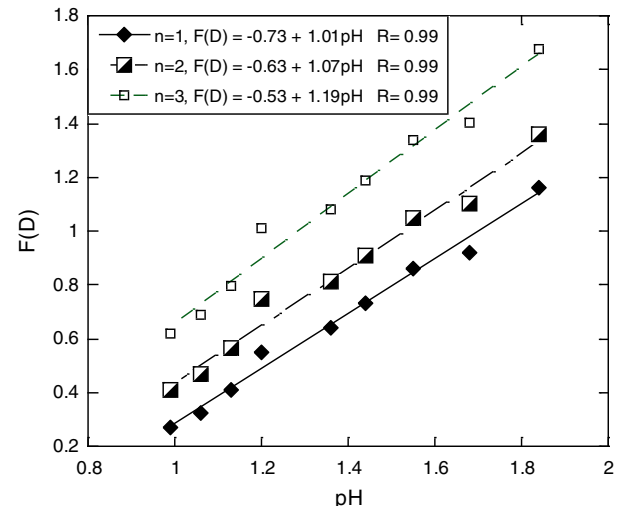

Fig. 5. Variation of of $F(D) = \log D_M - n\log[RH]_{eq.}$ versus $pH_{eq.}$ for 0.6 M D2EHPA.

Fig. 6. Variation of $F(D) = \log D_M - n\log[RH]_{eq.}$ versus $pH_{eq.}$ for 0.9 M D2EHPA.
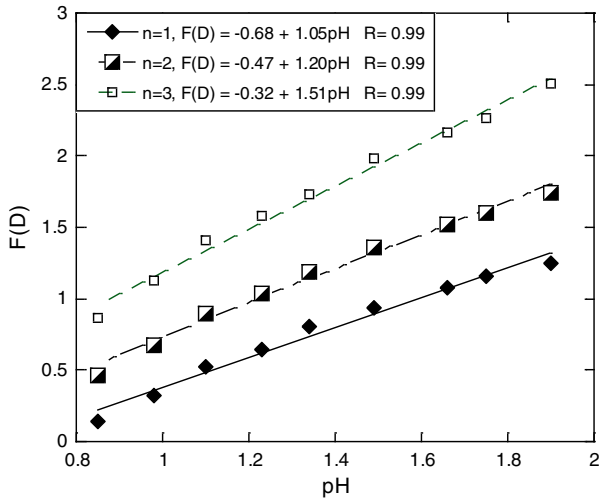
Fig. 7. Variation of $F(D) = \log D_M - n\log[RH]_{eq.}$ versus $pH_{eq.}$ at 25 °C.
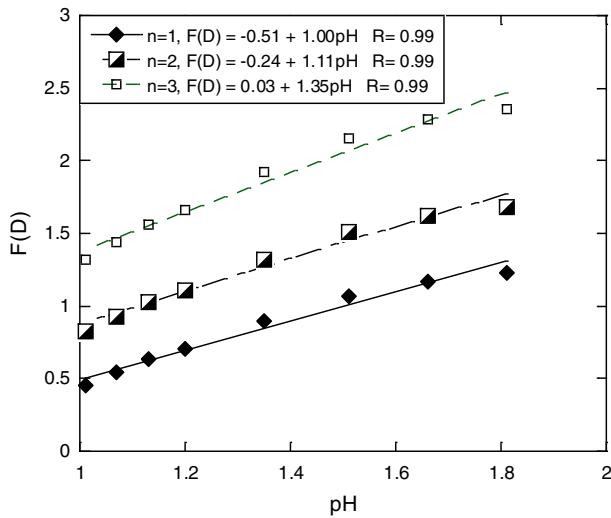

Fig. 8. Variation of $F(D) = \log D_M - n\log[RH]_{eq.}$ versus $pH_{eq.}$ at 40 °C.
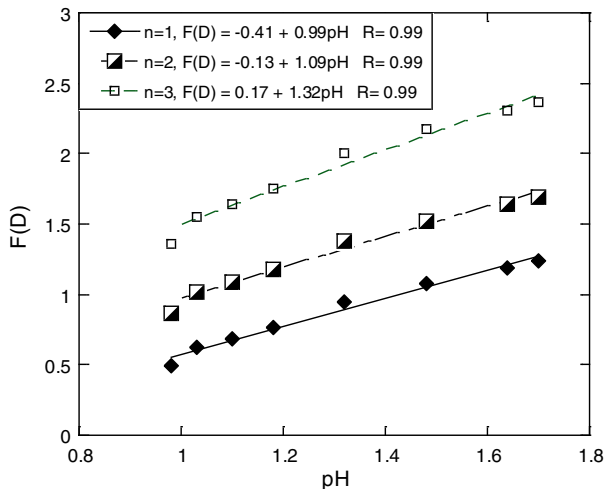

Fig. 9. Variation of $F(D) = \log D_M - n\log[RH]_{eq}$ versus pH_{eq} at 60 °C.

would also be constant. Considering $n = 1$ for the extraction mechanism, Eq. (9) would reduce to Eq. (10):

$$\log D_M - n\log\left([RH]_{initial} - n[\overline{M}]_{org} - C\right) = \log K_{ex} + pH \tag{10}$$

in which C is a positive constant. Applying trial and error method helps to obtain the best value of C in which the data fits well with a line of unit slope (coefficient of pH in Eq. (9)).

Trial and error results show that the value of C is zero in all experiments except the runs conducted at 60 °C. This result is consistent with FT-IR analysis and shows that TBP does not have any synergistic effect with the D2EHPA. For the experiments corresponding to T = 60 °C, the value of C would be 0.169 (Fig. 10 and Eq. (11); thus, α would be estimated equal to 0.94. As can be seen in Fig. 10, considering the effect of TBP and α value, the line exhibits a slope equal to 1.

$$\log D_M - n\log\left([RH]_{initial} - n[\overline{M}]_{org} - 0.169\right) = \log K_{ex} + pH \tag{11}$$

or:

$$\log D_M - n\log\left([RH]_{initial} - n[\overline{M}]_{org} - 0.94[TBP]\right) = \log K_{ex} + pH. \tag{12}$$

3.2.4. Thermodynamic parameters

Based on values of logK which was obtained through different temperatures, a plot of $\log K_{ex}$ versus 1000/T would result in the estimation of apparent $\Delta H°$ and $\Delta S°$ of vanadium extraction reaction. According to Fig. 11, the extraction is endothermic and $\Delta H°$ and $\Delta S°$ of vanadium extraction are 22.76 kJ/mol and 63.26 kJ/mol. K, respectively.

4. Conclusion

- Vanadium (VO_2^+) solvent extraction by D2EHPA strongly depends on the pH of solution due to the change in complex species of vanadium. It was found that the maximum extraction percent of vanadium occurs at pH 1.8 under ambient conditions.
- Fourier Transform Infrared (FT-IR) spectroscopy showed that P–O–H band of D2EHPA was responsible for the extraction of VO_2^+ species by cation exchange mechanism. Employing the slope analysis method, the stoichiometric coefficient of the extractant was found to be one:
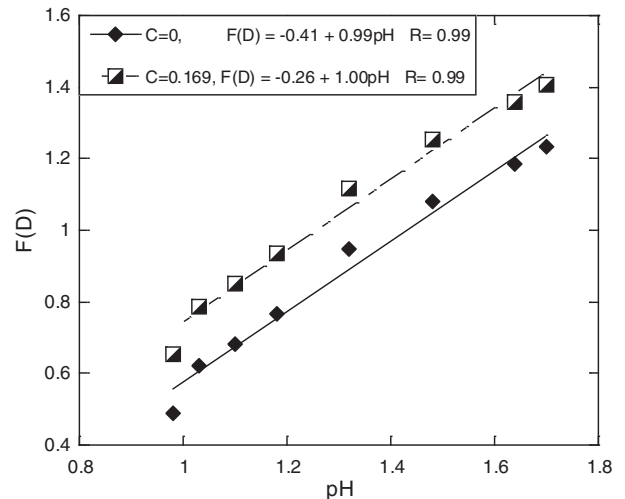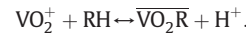
$$VO_2^+ + RH \leftrightarrow \overline{VO_2R} + H^+.$$

Fig. 10. F(D) versus pH for SX experiments at T = 60 °C with considering the effect of TBP (C = 0.169 or α = 0.94) and without considering the effect of TBP (C = 0 or α = 0).
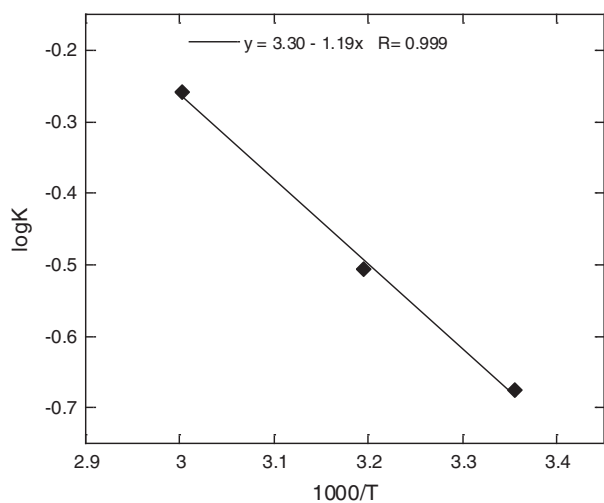
Fig. 11. Variation of logK versus 1000/T.

– Role of TBP in this solvent extraction system is modifier; i.e. it does not have any synergist effect at lower temperatures (25–40 °C).
– Based on the results obtained in the present work, the extraction of vanadium by D2EHPA is endothermic with apparent enthalpy of 22.76 kJ/mol. The value of the apparent entropy of the extraction reaction was estimated to be 63.26 kJ/mol K.

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