

# Electronic Supplementary Material

## Highly efficient and selective removal of vanadium from tungstate solutions by microbubble floating-extraction

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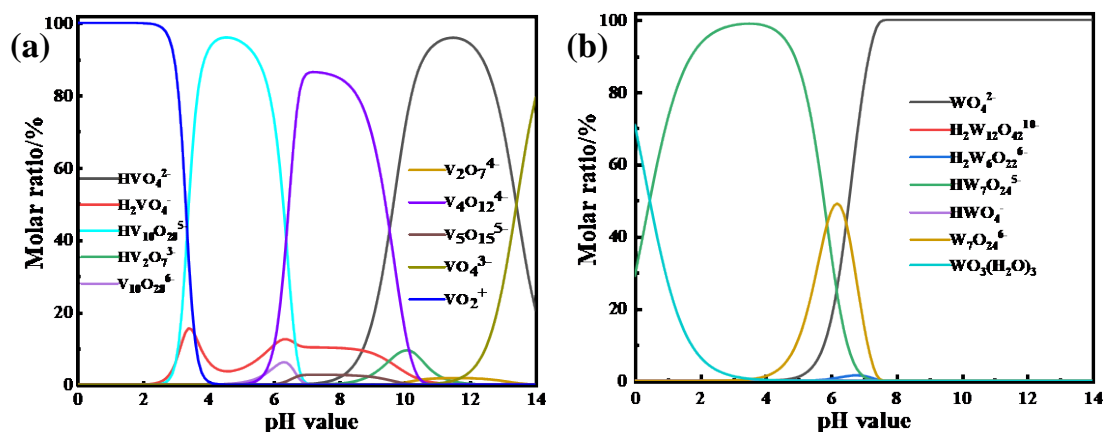
\*These authors contributed equally to this work.

### 1. Composition of spent SCR catalysts

**Table S1** Summary of the composition of spent SCR catalysts.

NO.	Composition of tungsten and vanadium	Concentration of tungsten	Concentration of vanadium	Reference
1	7.7% of WO <sub>3</sub> , 1.2% of V <sub>2</sub> O <sub>5</sub>	8.64 g/L	1.24 g/L	[1]
2	8.2% of WO <sub>3</sub> , 2.2% of V <sub>2</sub> O <sub>5</sub>	13.18 g/L	0.59 g/L	[2]
3	2.8% of WO <sub>3</sub> , 1.3% of V <sub>2</sub> O <sub>5</sub>	7.91 g/L	3.29 g/L	[3]
4	3.1% of WO <sub>3</sub> , 1.2% of V <sub>2</sub> O <sub>5</sub>	7.00 g/L	1.50 g/L	[4]
5	--	11.47 g/L	1.10 g/L	[5]

## 2. Ionic species and thermodynamic data



**Fig. S1** Molar ratio of tungsten (a) and vanadium (b) species as function of pH value in W-H<sub>2</sub>O and V-H<sub>2</sub>O system. ( $C_W = 10$  g/L,  $C_V = 1.0$  g/L, 25 °C).

**Table S2** Chemical reaction and calculation formulas of the concentration of substances (25 °C) [6, 7].

Reaction No.	Relevant reaction	lgk	Formula
1	$WO_4^{2-} + H^+ = HWO_4^-$	3.5	$[HWO_4^-] = 10^{3.5} [WO_4^{2-}][H^+]$
2	$WO_4^{2-} + 2H^+ = H_2WO_4$	8.1	$[H_2WO_4] = 10^{8.1} [WO_4^{2-}][H^+]^2$
3	$6WO_4^{2-} + 6H^+ = W_6O_{21}^{6-} + 4H_2O$	49.07	$[W_6O_{21}^{6-}] = 10^{49.07} [WO_4^{2-}]^6 [H^+]^6$
4	$6WO_4^{2-} + 7H^+ = HW_6O_{21}^{5-} + 4H_2O$	56.48	$[HW_6O_{21}^{5-}] = 10^{56.48} [WO_4^{2-}]^6 [H^+]^7$
5	$7WO_4^{2-} + 8H^+ = W_7O_{24}^{6-} + 4H_2O$	65.19	$[W_7O_{24}^{6-}] = 10^{65.19} [WO_4^{2-}]^7 [H^+]^8$
6	$7WO_4^{2-} + 9H^+ = HW_7O_{24}^{5-} + 4H_2O$	69.96	$[HW_7O_{24}^{5-}] = 10^{69.96} [WO_4^{2-}]^7 [H^+]^9$
7	$12WO_4^{2-} + 18H^+ = H_2W_{12}O_{40}^{6-} + 8H_2O$	135.02	$[H_2W_{12}O_{40}^{6-}] = 10^{135.02} [WO_4^{2-}]^{12} [H^+]^{18}$
8	$12WO_4^{2-} + 14H^+ = H_2W_{12}O_{42}^{10-} + 6H_2O$	115.38	$[H_2W_{12}O_{42}^{10-}] = 10^{115.38} [WO_4^{2-}]^{12} [H^+]^{14}$
9	$VO_4^{3-} + H^+ = HVO_4^{2-}$	13.36	$[HVO_4^{2-}] = 10^{13.36} [VO_4^{3-}][H^+]$
10	$2VO_4^{3-} + 2H^+ = V_2O_7^{4-} + H_2O$	27.38	$[V_2O_7^{4-}] = 10^{27.38} [VO_4^{3-}]^2 [H^+]^2$
11	$2VO_4^{3-} + 3H^+ = HV_2O_7^{3-} + H_2O$	37.17	$[HV_2O_7^{3-}] = 10^{37.17} [VO_4^{3-}]^2 [H^+]^3$
12	$2VO_4^{3-} + 4H^+ = H_2V_2O_7^{2-} + H_2O$	45.4	$[H_2V_2O_7^{2-}] = 10^{45.4} [VO_4^{3-}]^2 [H^+]^3$
13	$10VO_4^{3-} + 24H^+ = V_{10}O_{28}^{6-} + 12H_2O$	264.82	$[V_{10}O_{28}^{6-}] = 10^{264.82} [VO_4^{3-}]^{10} [H^+]^{24}$

14	$10\text{VO}_4^{3-} + 25\text{H}^+ = \text{HV}_{10}\text{O}_{28}^{5-} + 12\text{H}_2\text{O}$	270.89	$[\text{HV}_{10}\text{O}_{28}^{5-}] = 10^{270.89}[\text{VO}_4^{2-}]^{10}[\text{H}^+]^{25}$
15	$10\text{VO}_4^{3-} + 26\text{H}^+ = \text{H}_2\text{V}_{10}\text{O}_{28}^{5-} + 12\text{H}_2\text{O}$	274.49	$[\text{H}_2\text{V}_{10}\text{O}_{28}^{5-}] = 10^{274.49}[\text{VO}_4^{2-}]^{10}[\text{H}^+]^{26}$
16	$4\text{VO}_4^{3-} + 8\text{H}^+ = \text{V}_4\text{O}_{12}^{4-} + \text{H}_2\text{O}$	95.11	$[\text{V}_4\text{O}_{12}^{4-}] = 10^{95.11}[\text{VO}_4^{2-}]^4[\text{H}^+]^8$
17	$5\text{VO}_4^{3-} + 10\text{H}^+ = \text{V}_5\text{O}_{15}^{4-} + 5\text{H}_2\text{O}$	118.69	$[\text{V}_5\text{O}_{15}^{4-}] = 10^{118.69}[\text{VO}_4^{2-}]^5[\text{H}^+]^{10}$
18	$\text{VO}_4^{3-} + 4\text{H}^+ = \text{VO}_2^+ + 2\text{H}_2\text{O}$	28.23	$[\text{VO}_2^+] = 10^{28.23}[\text{VO}_4^{2-}][\text{H}^+]^4$
19	$2\text{VO}_4^{3-} + 4\text{WO}_4^{2-} + 10\text{H}^+ = \text{V}_2\text{W}_4\text{O}_{19}^{4-} + 5\text{H}_2\text{O}$	99.29	$[\text{V}_2\text{W}_4\text{O}_{19}^{4-}] = 10^{99.29}[\text{VO}_4^{2-}]^2[\text{WO}_4^{2-}]^4[\text{H}^+]^{10}$
20	$2\text{VO}_4^{3-} + 4\text{WO}_4^{2-} + 11\text{H}^+ = \text{HV}_2\text{W}_4\text{O}_{19}^{3-} + 5\text{H}_2\text{O}$	101.52	$[\text{HV}_2\text{W}_4\text{O}_{19}^{3-}] = 10^{101.52}[\text{VO}_4^{2-}]^2[\text{WO}_4^{2-}]^4[\text{H}^+]^{11}$
21	$3\text{VO}_4^{3-} + 3\text{WO}_4^{2-} + 10\text{H}^+ = \text{V}_3\text{W}_3\text{O}_{19}^{5-} + 5\text{H}_2\text{O}$	105.49	$[\text{V}_3\text{W}_3\text{O}_{19}^{5-}] = 10^{105.49}[\text{VO}_4^{2-}]^3[\text{WO}_4^{2-}]^3[\text{H}^+]^{10}$
22	$3\text{VO}_4^{3-} + 3\text{WO}_4^{2-} + 11\text{H}^+ = \text{HV}_3\text{W}_3\text{O}_{19}^{4-} + 5\text{H}_2\text{O}$	112.48	$[\text{HV}_3\text{W}_3\text{O}_{19}^{4-}] = 10^{112.48}[\text{VO}_4^{2-}]^3[\text{WO}_4^{2-}]^3[\text{H}^+]^{11}$
23	$3\text{VO}_4^{3-} + 3\text{WO}_4^{2-} + 24\text{H}^+ = \text{V}_9\text{WO}_{28}^{5-} + 12\text{H}_2\text{O}$	257.31	$[\text{V}_9\text{WO}_{28}^{5-}] = 10^{257.31}[\text{VO}_4^{2-}]^9[\text{WO}_4^{2-}][\text{H}^+]^{24}$
24	$3\text{VO}_4^{3-} + 3\text{WO}_4^{2-} + 25\text{H}^+ = \text{HV}_9\text{WO}_{28}^{4-} + 12\text{H}_2\text{O}$	259.46	$[\text{HV}_9\text{WO}_{28}^{4-}] = 10^{259.46}[\text{VO}_4^{2-}]^9[\text{WO}_4^{2-}][\text{H}^+]^{25}$

### 3. Effects of impurity ions

In addition to tungsten and vanadium, the spent SCR catalyst also contains some impurities including titanium, iron, molybdenum, silicon [8], and may affect the removal of vanadium from tungstate solutions. According to previous reports, titanium is hardly leached in both acid leaching and alkaline leaching [9, 10]. In addition, the mineralization mechanism of Aliquat336 is mainly through anion exchange reaction, while iron ion is a cation [11]. Therefore, we discussed the effect of molybdenum and silicon oxyanions on the separation of tungsten and vanadium. As

can be seen from Fig. S5, molybdenum had almost no effect on the mineralization efficiency of vanadium, and the mineralization efficiency of vanadium decreases slightly with increasing silicon concentration. This phenomenon may be caused by the competition between the  $\text{SiO}_3^{2-}$  and the target oxyanions for the Aliquat336 binding sites [12]. Overall, Aliquat336 surfactant exhibited higher mineralization efficiency toward vanadium.

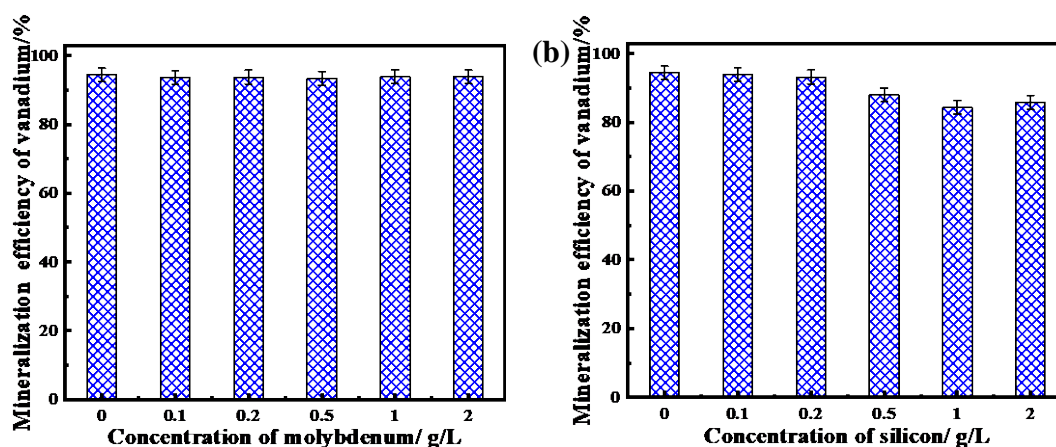


Fig. S2 Effects of impurity ions molybdenum and silicon concentrations on vanadium mineralization efficiency.

#### 4. Scrubbing experiment results

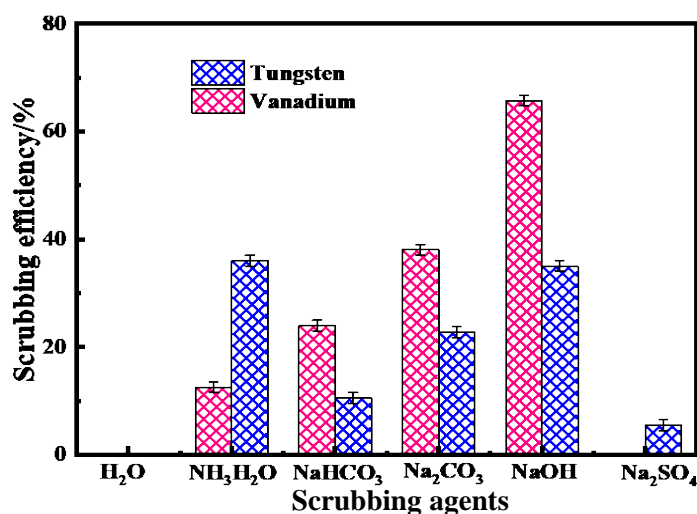


Fig. S3 Effect of the type of scrubbing agents on scrubbing efficiency.

## 5. Controlled-variables experiment results

**Table S3** Controlled-variables experiment results.

NO.	Metals concentration of initial solutions (g/L)		Metals concentration of raffinate (g/L)		Flotation efficiency (%)	
	tungsten	vanadium	tungsten	vanadium	Tungsten	Vanadium
A <sub>1</sub>	21.15	1.07	19.90	0.10	5.93	90.24
A <sub>2</sub>	15.62	1.06	15.00	0.09	4.01	92.03
A <sub>3</sub>	10.14	1.03	9.72	0.09	4.23	92.52
A <sub>4</sub>	5.08	1.04	4.87	0.07	4.09	93.67
A <sub>5</sub>	1.03	1.02	0.842	0.04	18.25	96.21
A <sub>6</sub>	0.00	1.05	0.00	0.03	0.00	97.01
B <sub>1</sub>	11.91	2.38	11.97	0.91	0.00	61.70
B <sub>2</sub>	11.61	1.81	11.55	0.36	0.56	80.22
B <sub>3</sub>	11.90	0.51	10.88	0.025	8.56	95.10
B <sub>4</sub>	11.69	0.11	9.99	0.003	14.61	97.02
B <sub>5</sub>	11.77	0.00	9.63	0.00	18.23	0.00

## 6. Computation details and results

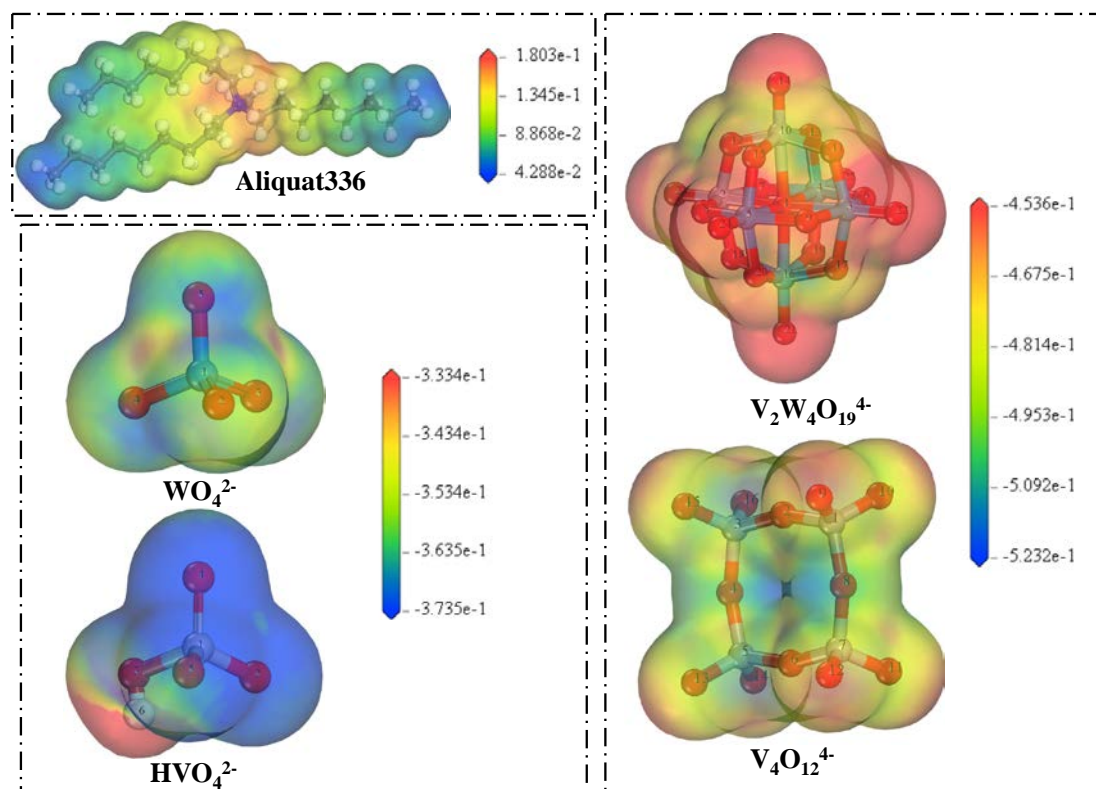
Molecular dynamics simulations of Aliquat336 with different species of W and V were carried out using COMPASS force field as implemented in the Forcite module of Materials Studio 2017 (Accelrys Software Inc. (2016)). The system was subjected to molecular dynamics equilibration for 50 ns at 298 K using a canonical NVT ensemble.

The interaction energy ( $\Delta E$ ) was used to indicate the strength of Aliquat336 and different species binding ability, and the increasingly negative  $\Delta E$  values indicates more favorable interactions between Aliquat336 and species [13]. The  $\Delta E$  for the Aliquat336 and species was calculated using the following expression:

$$\Delta E = E_{\text{total}} - (E_{\text{Aliquat336}} + E_{\text{species}}) \quad (1)$$

Where  $E_{\text{total}}$  is the total energy of systems.  $E_{\text{Aliquat336}}$ ,  $E_{\text{species}}$  is the total energy of Aliquat336 and different species of W and V, respectively.

In addition, based on the density functional theory, the DMol<sup>3</sup> tool was used to calculate the electron density, electrostatic potential during the mineralization process to further interpret interaction mechanisms. The spin-unrestricted generalized gradient approximation (GGA) functional by Perdew and Wang (PW91) and double numerical basis sets including p-polarization function (DNP) were employed for all calculations. The convergence threshold values for geometry optimization were set to be the maximum displacement of 0.005 Å, the maximum force of 0.002 Ha/Å, the maximum energy change of  $1.0 \times 10^{-5}$  eV/atom and the self-consistent field (SCF) convergence tolerance was set to be  $1.0 \times 10^{-6}$  eV/atom.

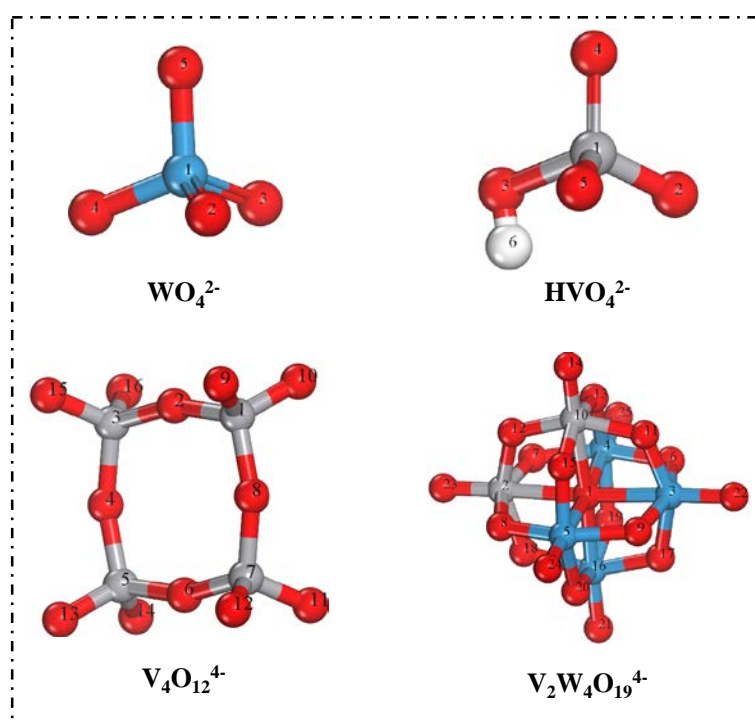


**Fig. S4** Electrostatic potential maps for surfactant and species.

**Table S4** Mulliken charge for each species.

NO.	$\text{WO}_4^{2-}$	$\text{HVO}_4^-$	$\text{V}_2\text{W}_4\text{O}_{19}^{4-}$	$\text{V}_4\text{O}_{12}^{4-}$
1	1.537	1.157	-0.913	1.321
2	-0.884	-0.859	1.251	-0.801
3	-0.884	-0.782	1.879	1.321
4	-0.884	-0.857	1.886	-0.802
5	-0.884	-0.859	1.886	1.321
6	-	0.201	-0.79	-0.801
7	-	-	-0.712	1.321
8	-	-	-0.712	-0.802
9	-	-	-0.79	-0.76
10	-	-	1.251	-0.76
11	-	-	-0.705	-0.76
12	-	-	-0.627	-0.76

13	-	-	-0.712	-0.76
14	-	-	-0.635	-0.76
15	-	-	-0.712	-0.76
16	-	-	1.879	-0.76
17	-	-	-0.781	-
18	-	-	-0.705	-
19			-0.79	
20			-1.548	
21			-0.758	
22			-0.758	
23			-0.635	
24			-0.755	
25			-0.755	



**Fig. S5** Atomic number of the species.



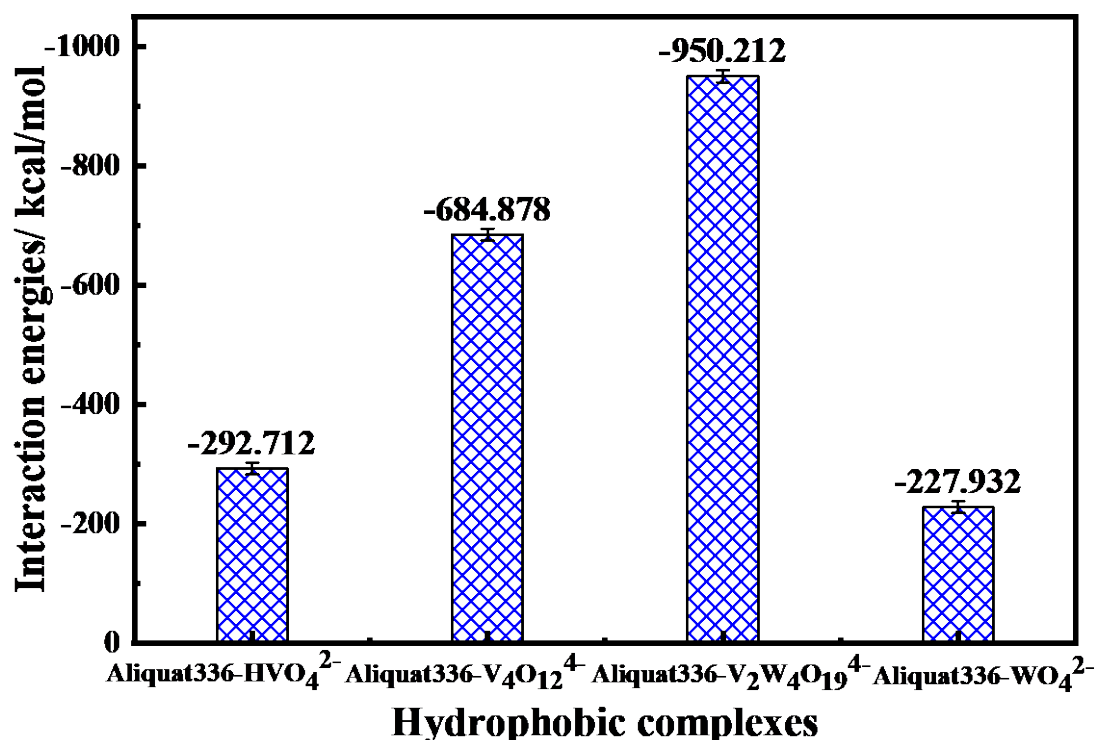
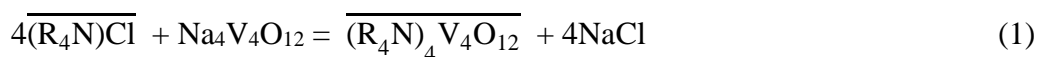


Fig. S6 Interaction energies of Aliquat336 with species in a homogeneous aqueous solution.

## 7. Stoichiometric ratio of the extractant to vanadium

Under optimal experimental conditions, the mineralized amounts of tungsten and vanadium were 0.983 g/L (0.0193 mol/L), 0.62 g/L (0.00337 mol/L), respectively. The molar concentration of 1% (m/m) Aliquat336 is calculated to be 0.0247 mol/L, assuming that all tungsten exists in the species of V<sub>2</sub>W<sub>4</sub>O<sub>19</sub><sup>4-</sup>, the molar concentration of remaining Aliquat336 and vanadium are 0.0217 mol/L and 0.0186 mol/L, respectively, and the molar ratio of Aliquat336 to vanadium and was 1.17, which was close to 1. Therefore, the mineralization reaction can be expressed in **Eq. (1)**. We hope this is acceptable for the reviewers and readers.



## Reference

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