Electronic Supplementary Material (ESI) for New Journal of Chemistry.

SUPPORTING INFORMATION FOR:

Redox Speciation of Uranyl in Citrate medium: Kinetics and reduction mechanism with In Situ Spectroelectrochemical investigation

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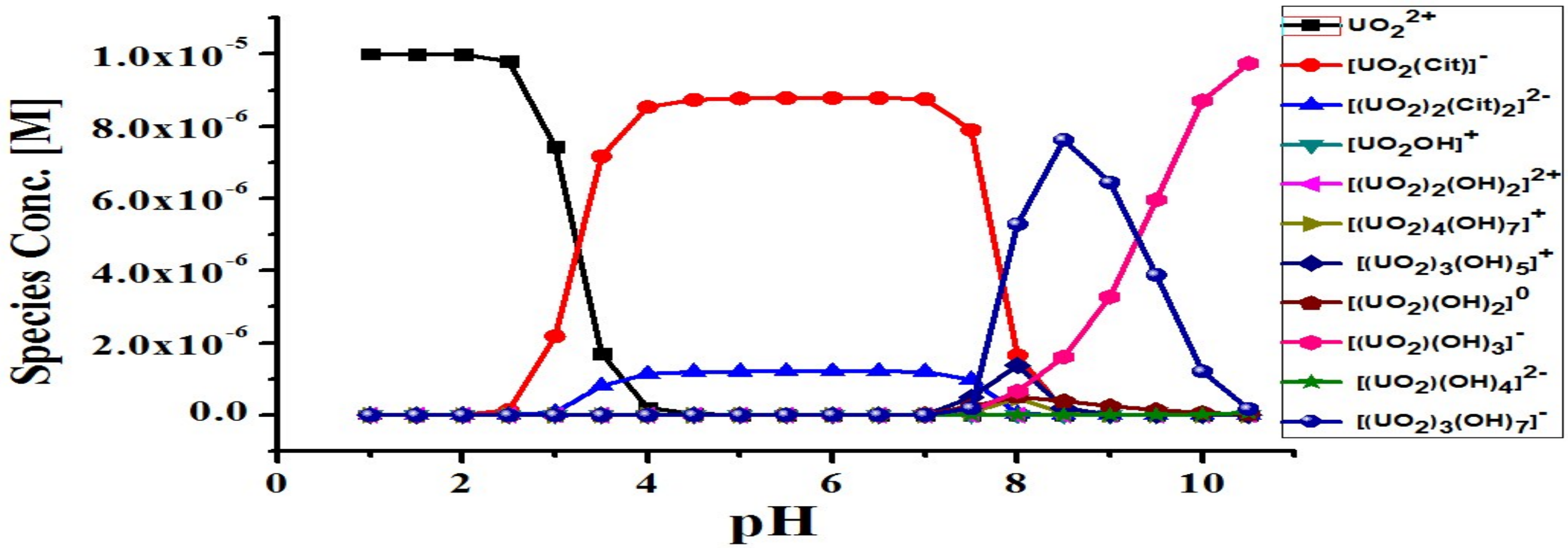
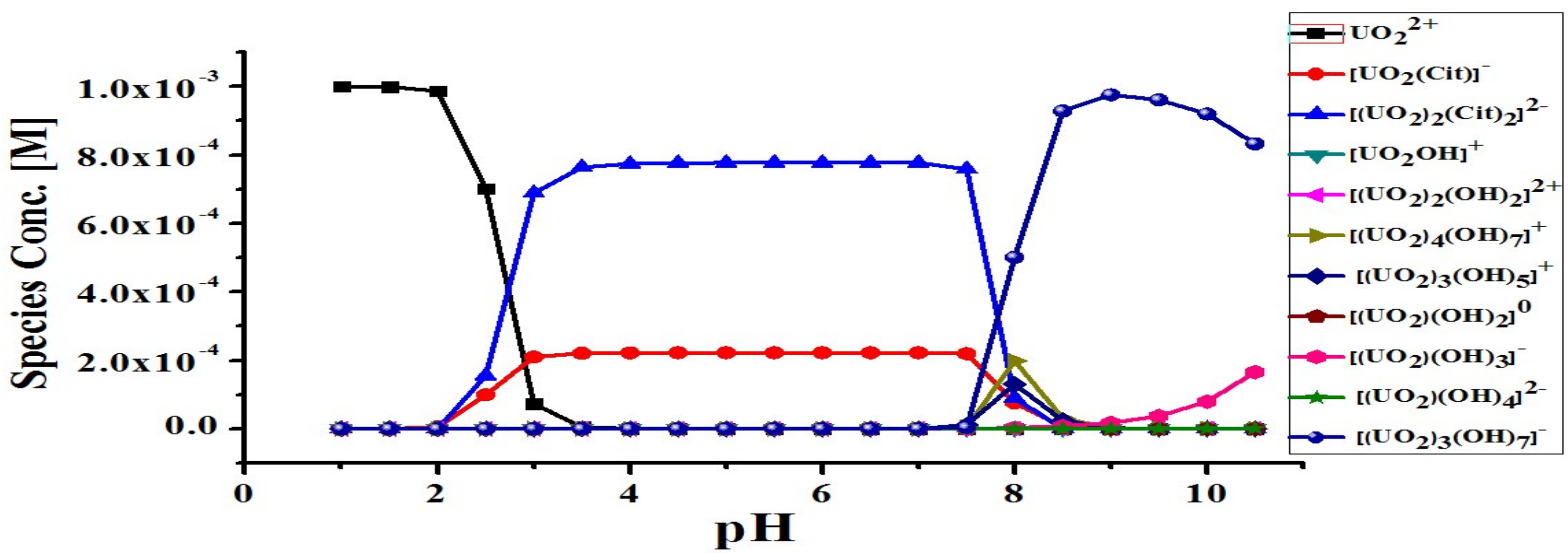


Species Conc. [M]
1.0x10^-5
8.0x10^-6
6.0x10^-6
4.0x10^-6
2.0x10^-6
0.0
0
2
4
6
8
10
pH
UO2 2+
[UO2(Cit)]-
[(UO2)2(Cit)2]2-
[UO2OH]+
[(UO2)2(OH)2]2+
[(UO2)4(OH)7]+
[(UO2)3(OH)5]+
[(UO2)(OH)2]0
[(UO2)(OH)3]-
[(UO2)(OH)4]2-
[(UO2)3(OH)7]-

(a)



Species Conc. [M]
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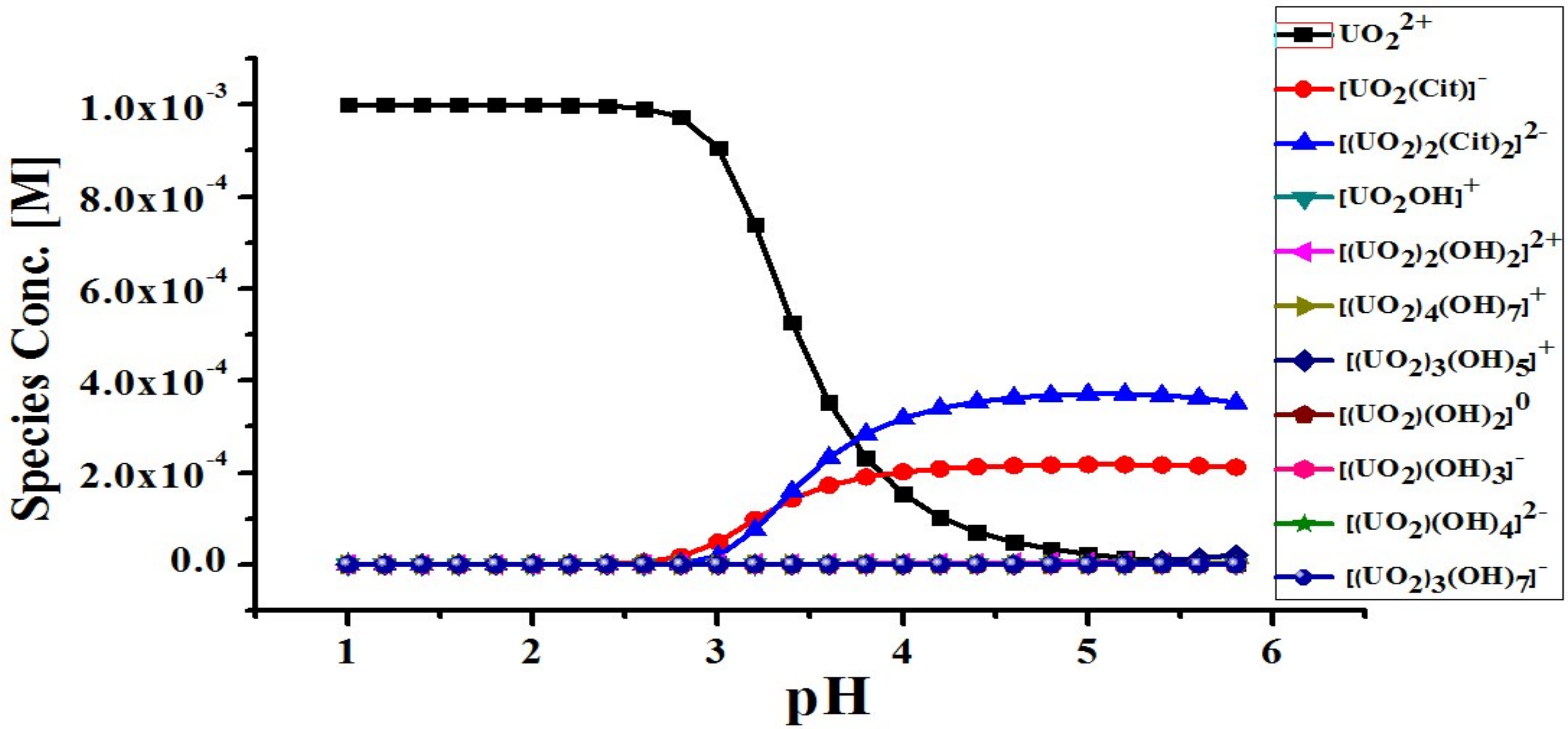
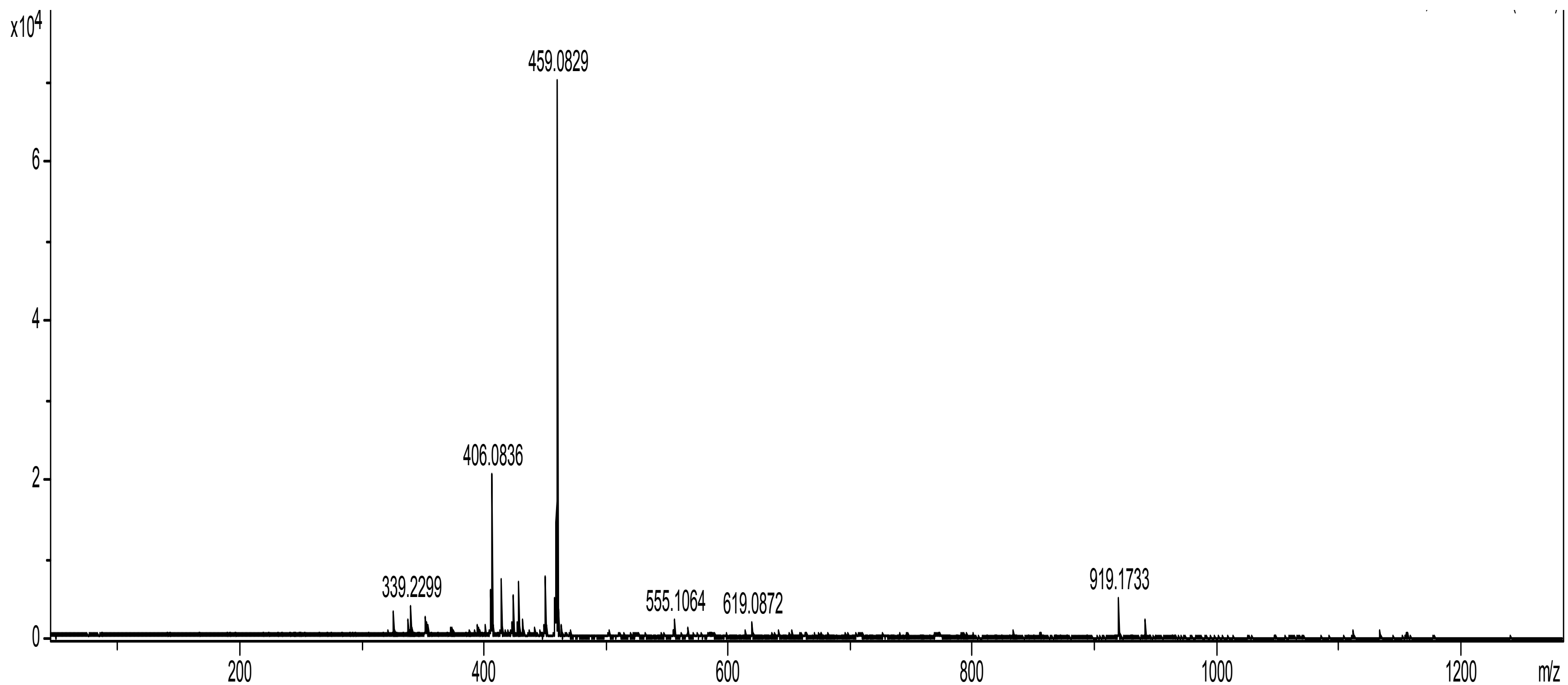
8.0x10^-4
6.0x10^-4
4.0x10^-4
2.0x10^-4
0.0
0
2
4
6
8
10
pH
UO2 2+
[UO2(Cit)]-
[(UO2)2(Cit)2]2-
[UO2OH]+
[(UO2)2(OH)2]2+
[(UO2)4(OH)7]+
[(UO2)3(OH)5]+
[(UO2)(OH)2]0
[(UO2)(OH)3]-
[(UO2)(OH)4]2-
[(UO2)3(OH)7]-

(b)

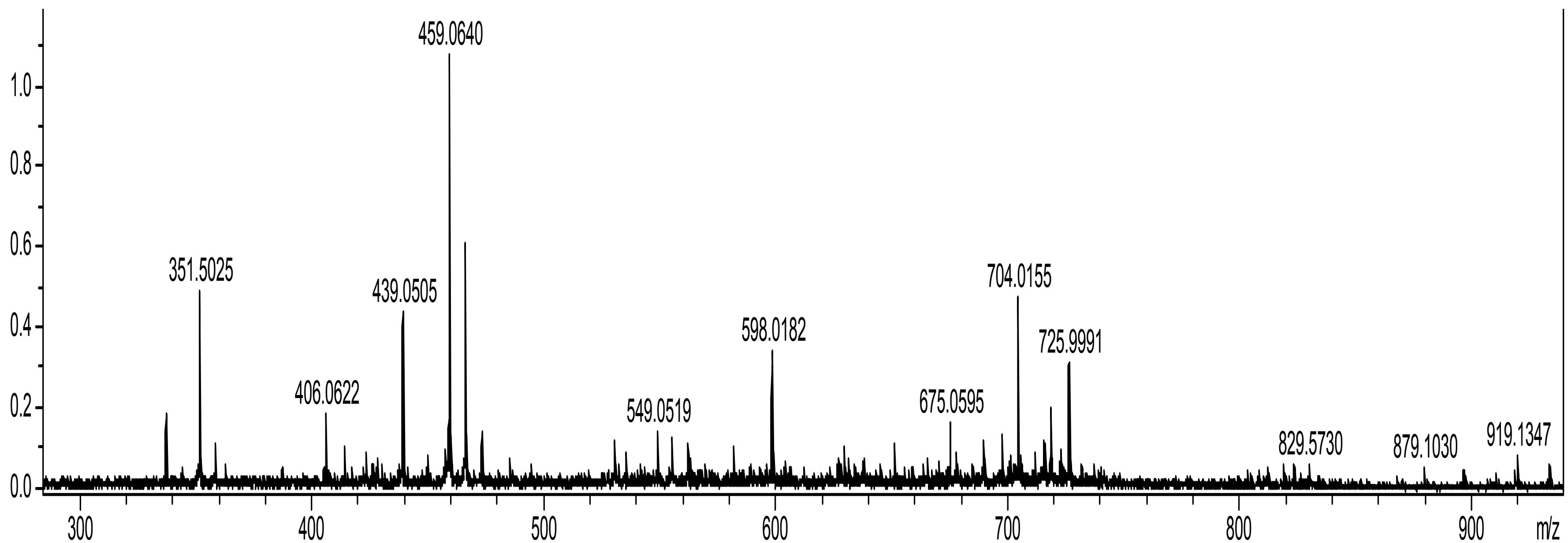


(c)

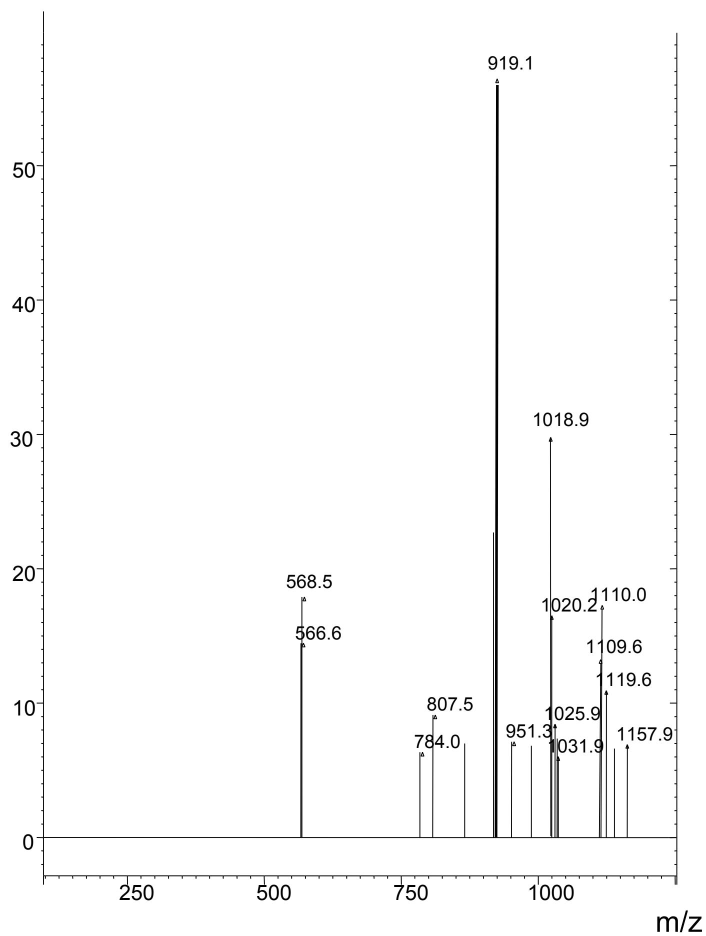
Figure S1. Speciation plots: **(a)** At $[UO_2^{2+}]$= 10^{-5} M in presence of [Citrate]= $5x10^{-3}$ M; **(b)** At $[UO_2^{2+}]$= 10^{-3} M in presence of [Citrate]= $5x10^{-2}$ M; **(c)** At $[UO_2^{2+}]$= 10^{-3} M in presence of [Citrate]= $1x10^{-3}$ M.


x10^4
459.0829
406.0836
339.2299
555.1064
619.0872
919.1733
0
2
4
6
200
400
600
800
1000
1200
m/z

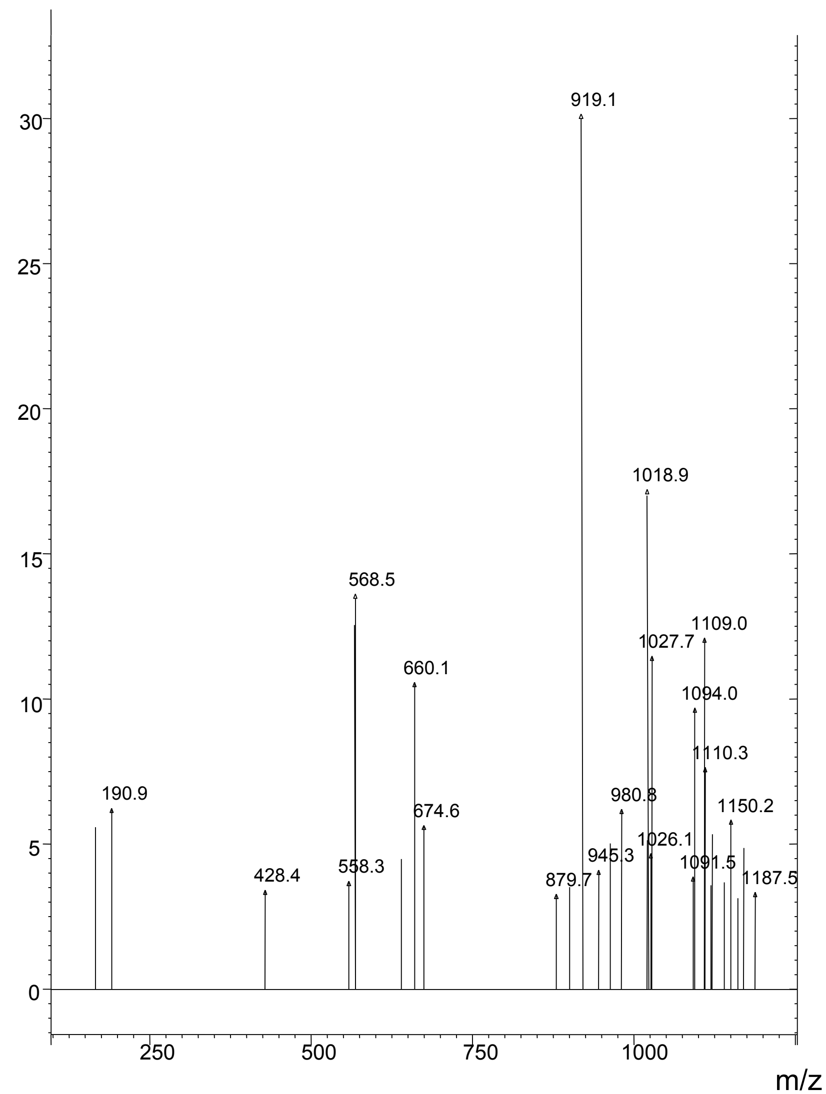
(a)


459.0640
351.5025
439.0505
406.0622
549.0519
598.0182
675.0595
704.0155
725.9991
829.5730
879.1030
919.1347
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
800
900
m/z

(b)

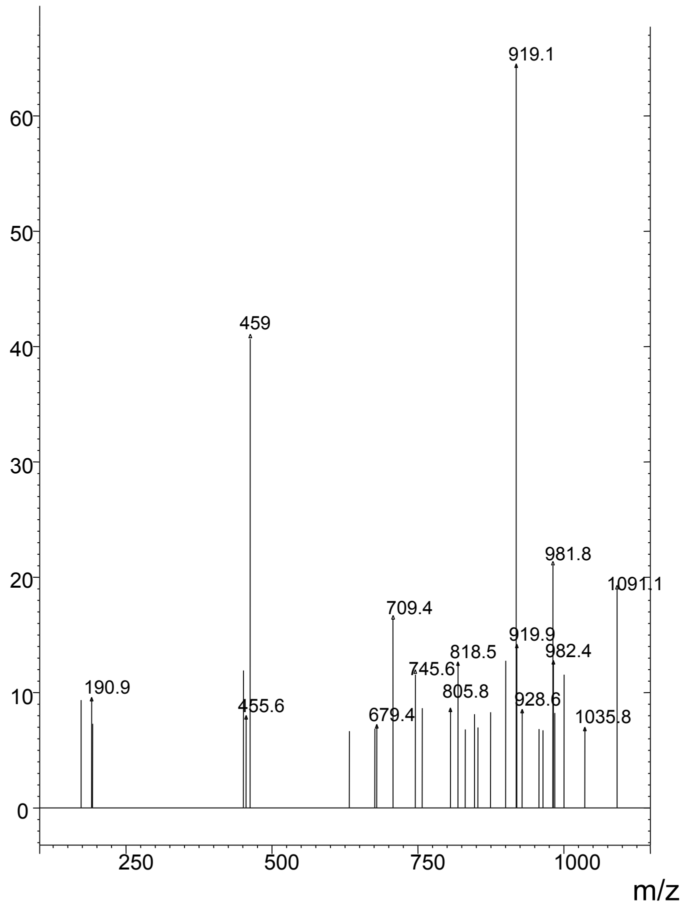

919.1
1018.9
568.5
566.6
1020.2
1110.0
1109.6
1119.6
807.5
1025.9
951.3
784.0
1031.9
1157.9
0
10
20
30
40
50
250
500
750
1000
m/z

(c)



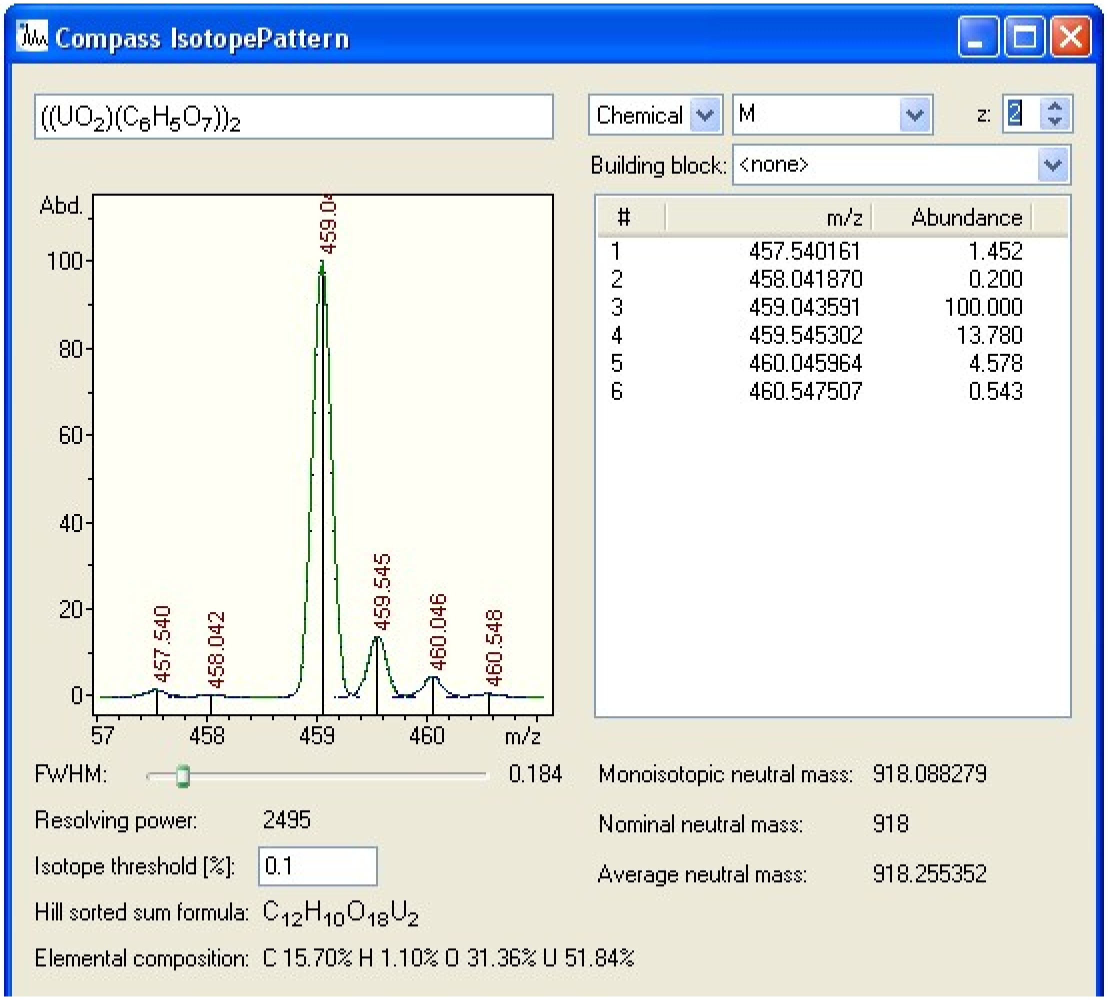
919.1
1018.9
568.5
1109.0
1027.7
660.1
1094.0
1110.3
190.9
980.8
674.6
1150.2
1026.1
945.3
558.3
1091.5
428.4
879.7
1187.5
0
5
10
15
20
25
30
250
500
750
1000
m/z

(d)

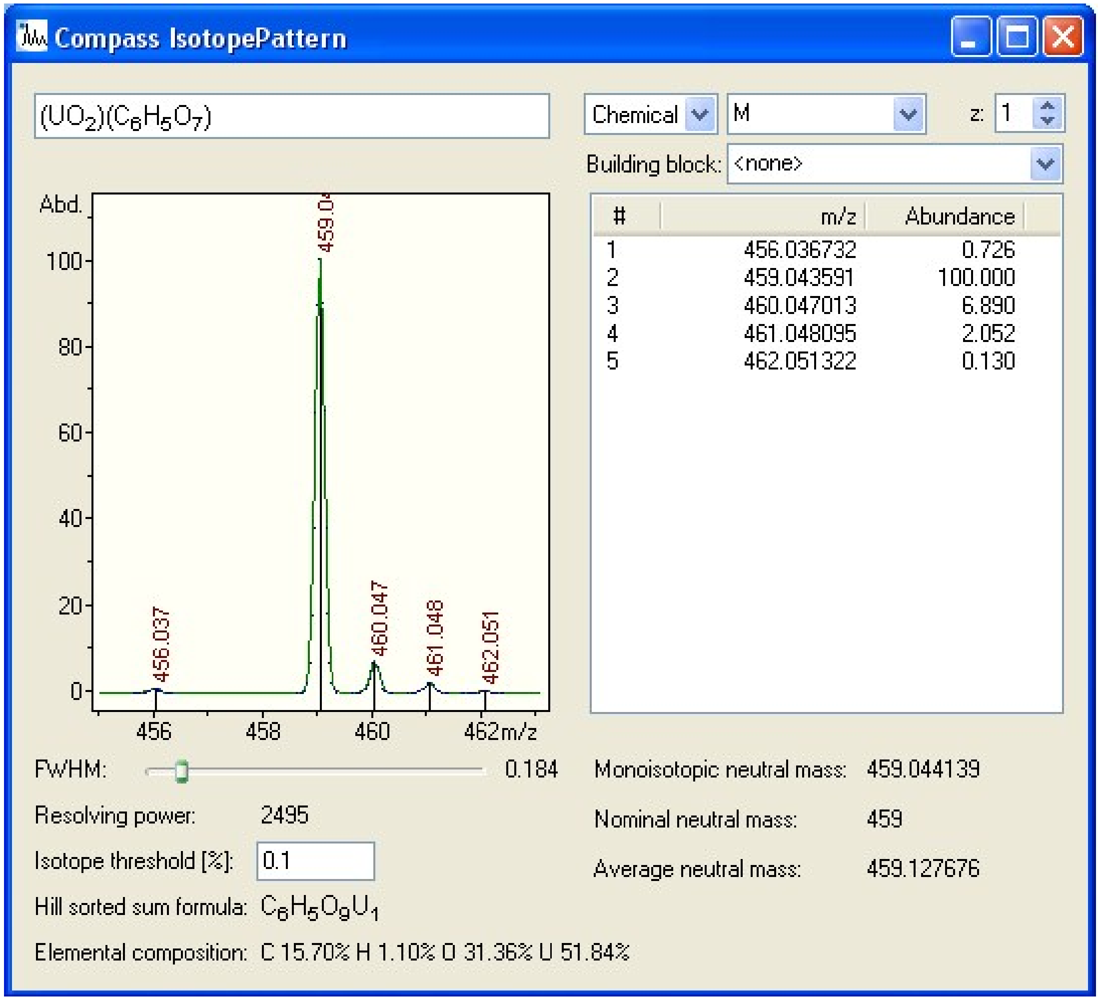


919.1
459
981.8
1091.1
709.4
919.9
818.5
982.4
745.6
190.9
805.8
455.6
928.6
679.4
1035.8
0
10
20
30
40
50
60
250
500
750
1000
m/z

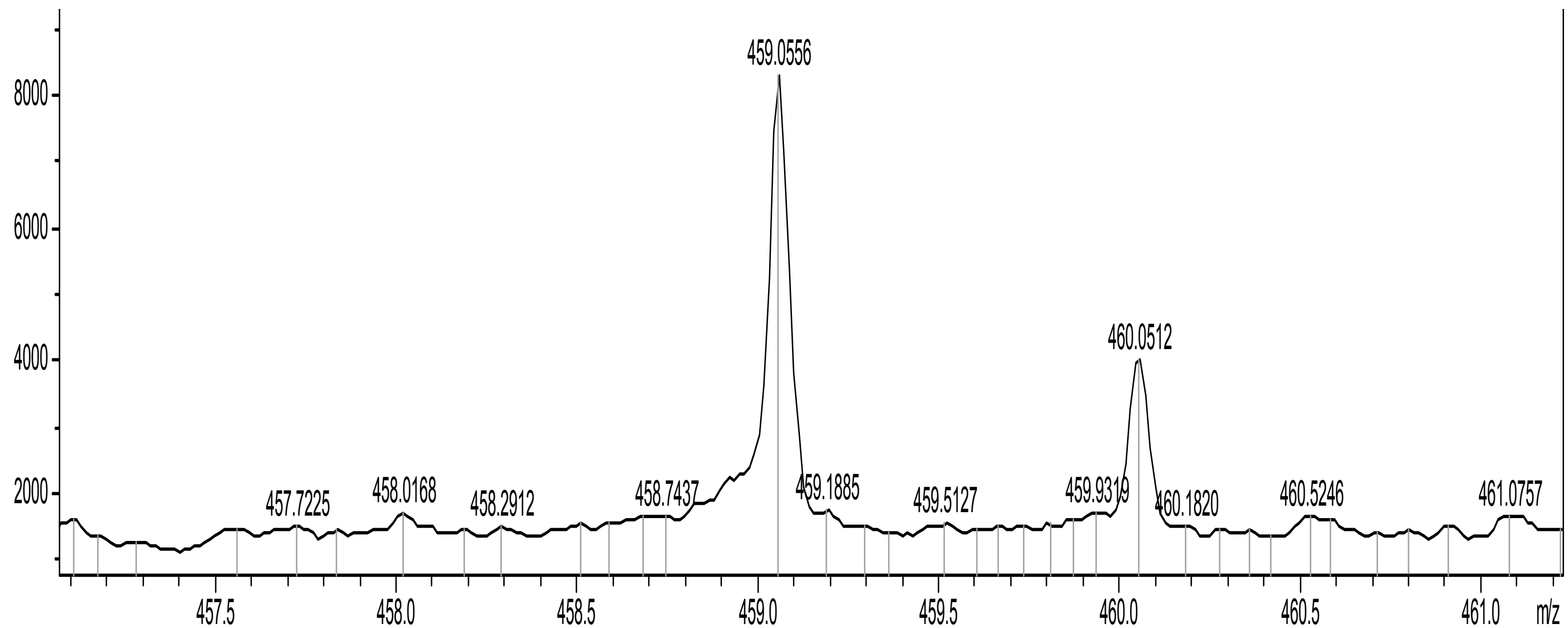
(e)


Compass IsotopePattern
((UO2)(C6H5O7))2
Chemical
M
z: 2
Building block: <none>
Abd.
100
80
60
40
20
0
459.04
457.540
458.042
459.545
460.046
460.548
57
458
459
460
m/z
m/z Abundance
1 457.540161 1.452
2 458.041870 0.200
3 459.043591 100.000
4 459.545302 13.780
5 460.045964 4.578
6 460.547507 0.543
FWHM: 0.184
Resolving power: 2495
Isotope threshold [%]: 0.1
Hill sorted sum formula: C12H10O18U2
Elemental composition: C 15.70% H 1.10% O 31.36% U 51.84%
Monoisotopic neutral mass: 918.088279
Nominal neutral mass: 918
Average neutral mass: 918.255352

(f)


Compass IsotopePattern
(UO2)(C6H5O7)
Chemical
M
z: 1
Building block: <none>
Abd.
100
80
60
40
20
0
456
458
460
462 m/z
459.04
456.037
460.047
461.048
462.051
m/z Abundance
1 456.036732 0.726
2 459.043591 100.000
3 460.047013 6.890
4 461.048095 2.052
5 462.051322 0.130
FWHM: 0.184
Resolving power: 2495
Isotope threshold [%]: 0.1
Hill sorted sum formula: C6H5O9U1
Elemental composition: C 15.70% H 1.10% O 31.36% U 51.84%
Monoisotopic neutral mass: 459.044139
Nominal neutral mass: 459
Average neutral mass: 459.127676

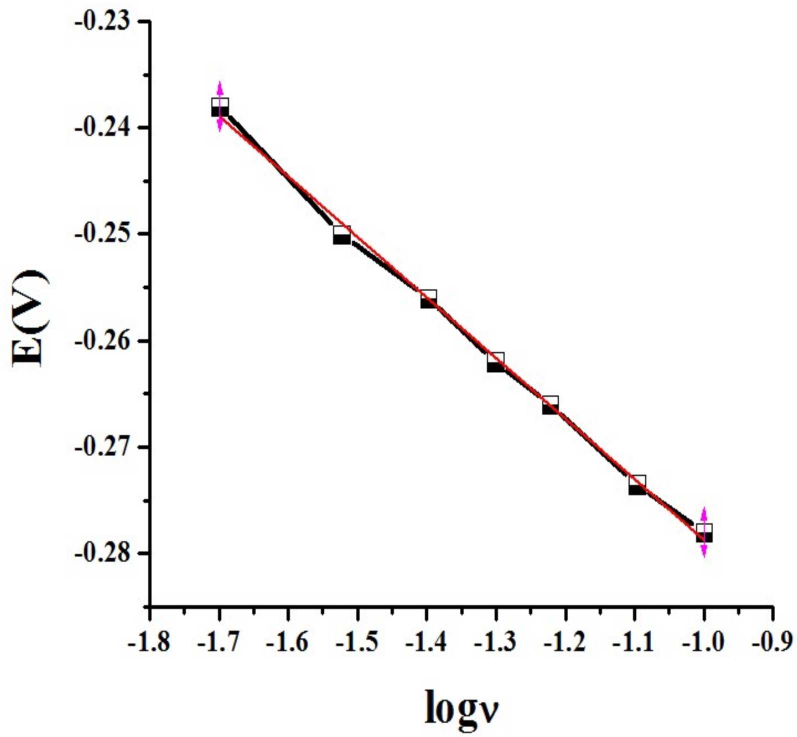
(g)



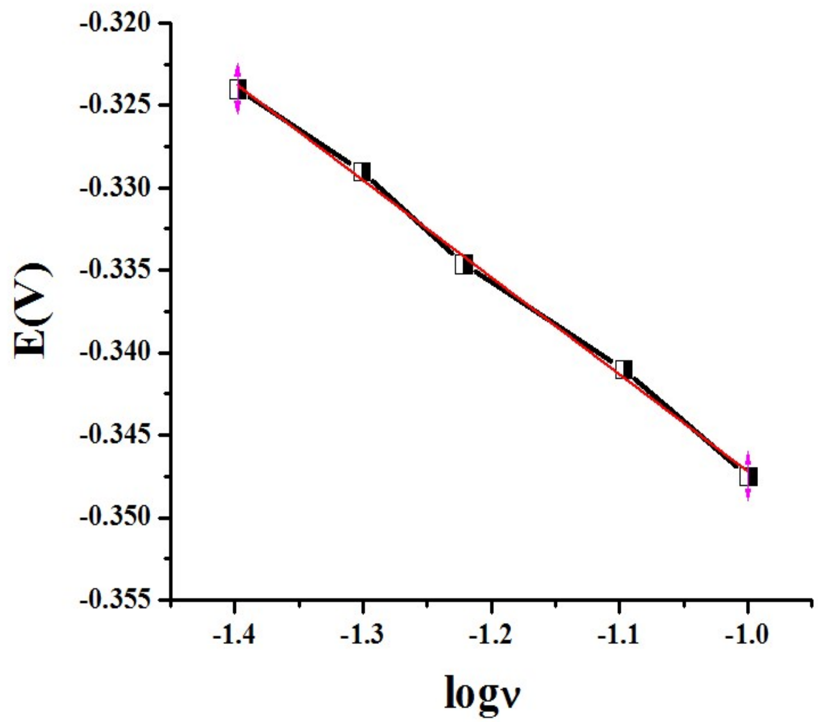
(h)

Figure S2. ESI-MS data conditions: **(a)** $[UO_2^{2+}]$= 10^{-5} M in presence of [Citrate]= $5x10^{-3}$ M at pH 4, **(b)** Same as **(a)** at pH 6.5, **(c)** $[UO_2^{2+}]$= 10^{-3} M in presence of [Citrate]= $5x10^{-2}$ M at pH 4, **(d)** Same as **(c)** at pH 6.4, **(e)** $[UO_2^{2+}]$= 10^{-3} M in presence of [Citrate]=

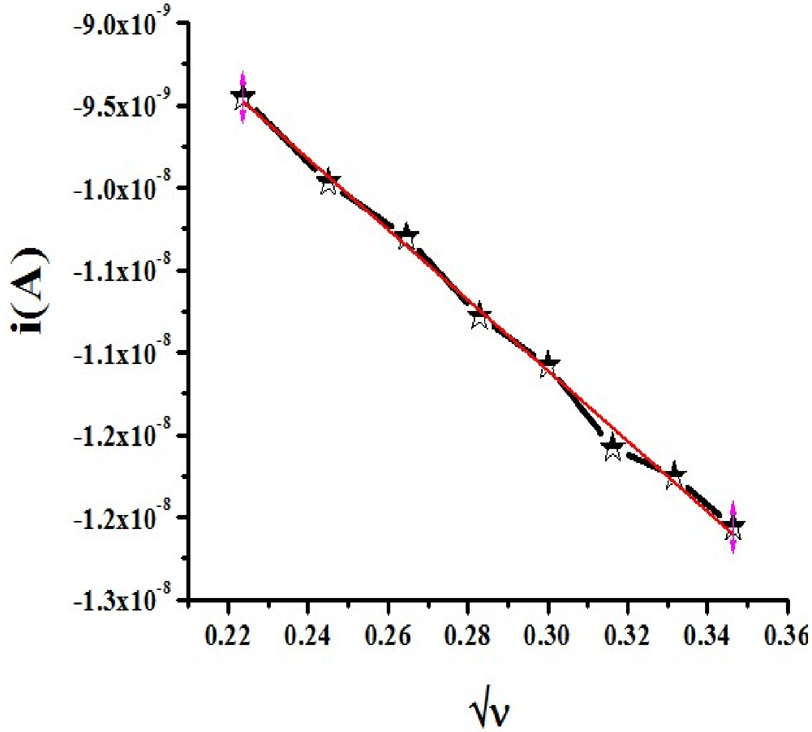
1x10^{-3} M at pH 3.25, **(f)** & **(g)** Theoretically calculated m/z value of isotopic peak for $[(UO_2)_2Cit_2]^{2-}$ and $[UO_2Cit]^{-}$ respectively, **(h)** Experimentally observed isotopic peak pattern.



(a)

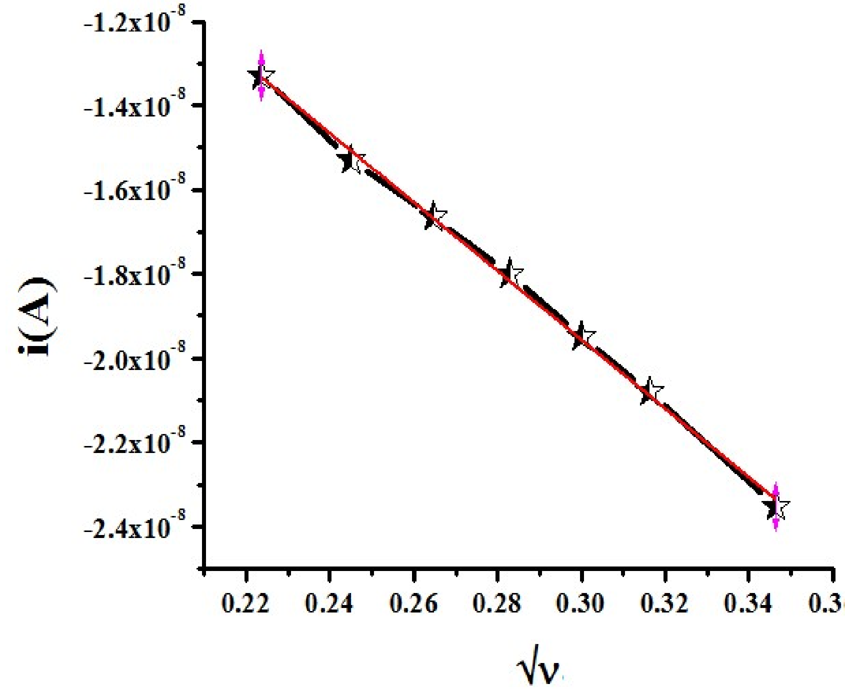


(b)



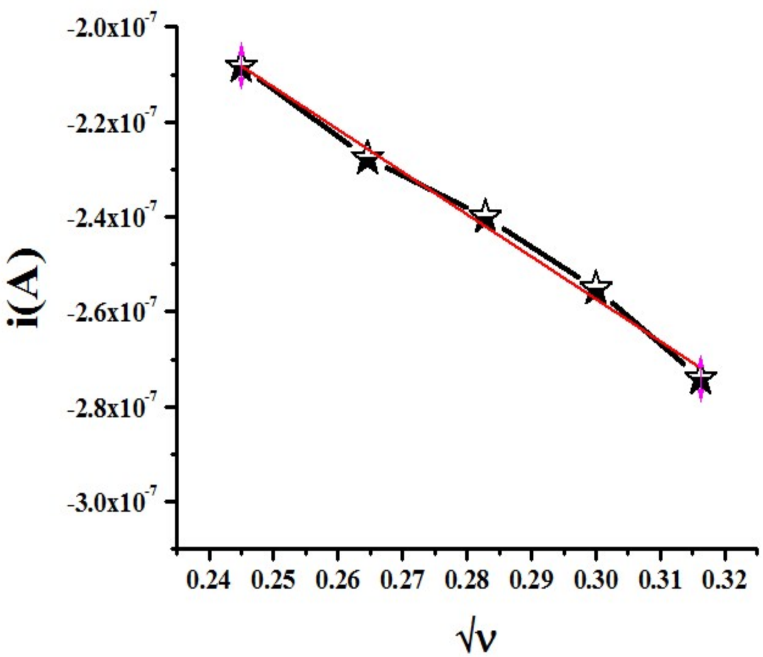
-9.0x10^-9
-9.5x10^-9
-1.0x10^-8
-1.1x10^-8
-1.1x10^-8
-1.2x10^-8
-1.2x10^-8
-1.3x10^-8
i(A)
0.22 0.24 0.26 0.28 0.30 0.32 0.34 0.36
√ν

(c)

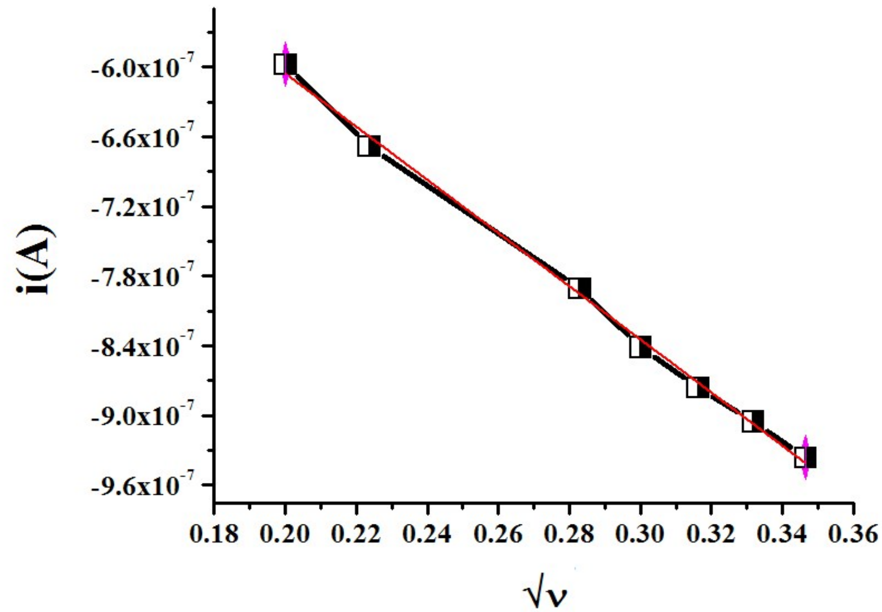


-1.2x10^-8
-1.4x10^-8
-1.6x10^-8
-1.8x10^-8
-2.0x10^-8
-2.2x10^-8
-2.4x10^-8
i(A)
0.22 0.24 0.26 0.28 0.30 0.32 0.34 0.36
√ν

(d)

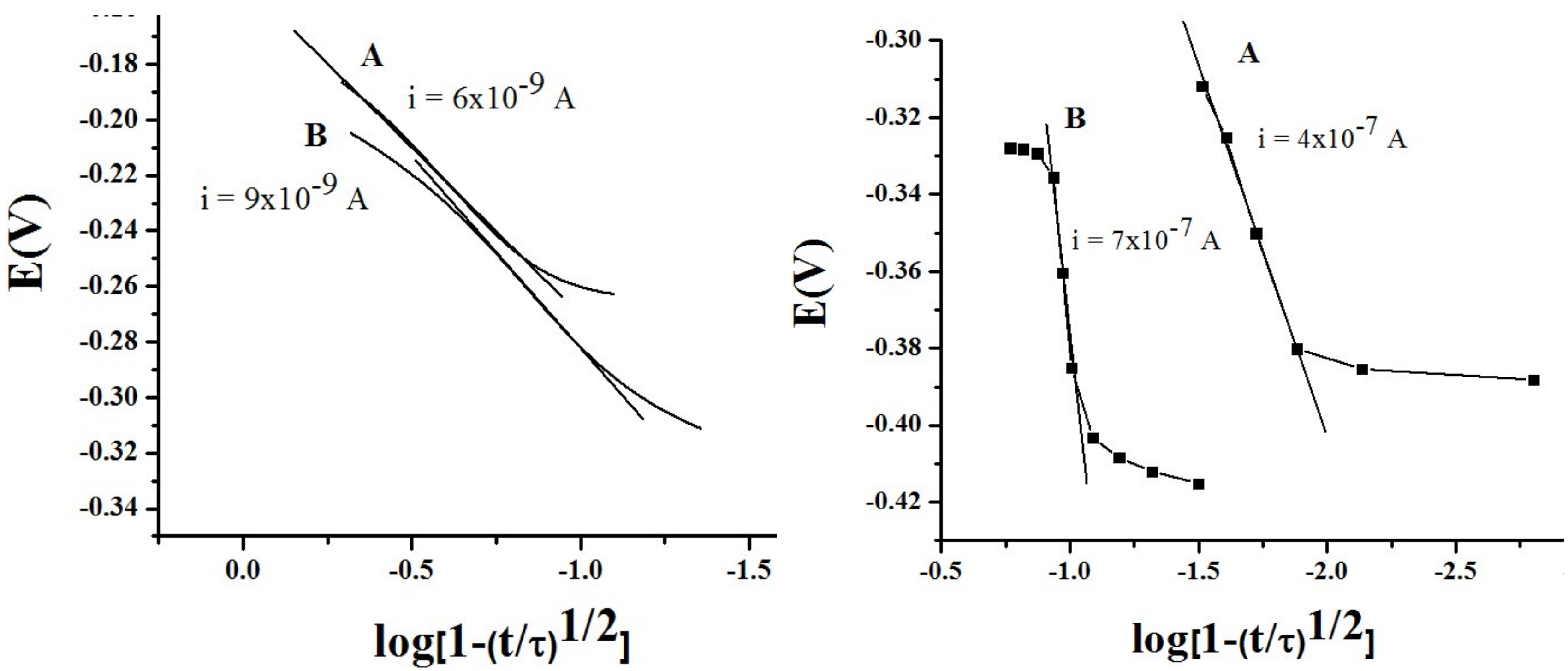


(e)



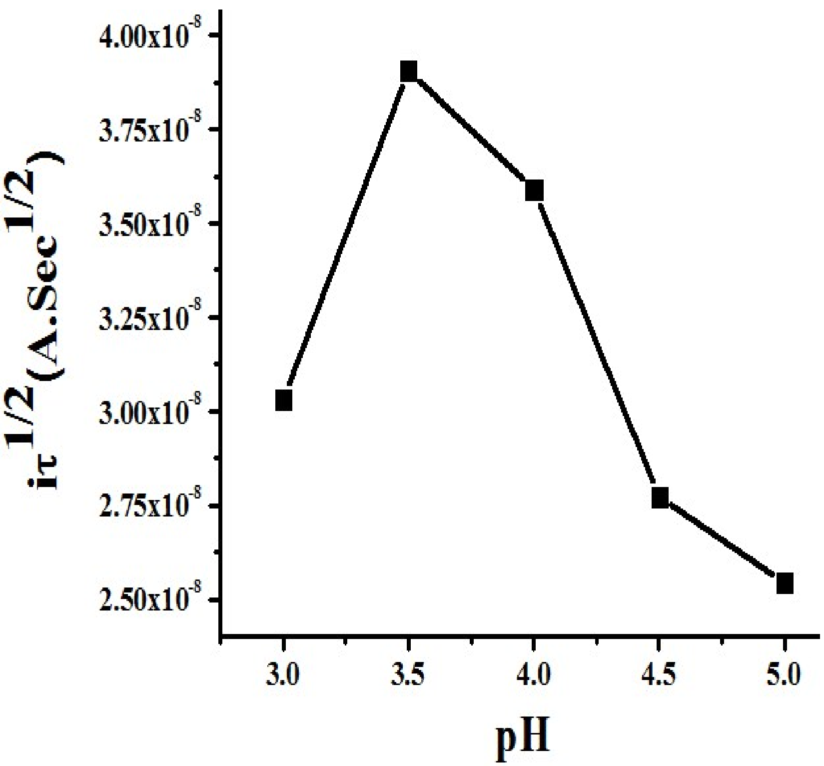
(f)

Figure S3. **(a)** & **(b)** are E vs. logν plot for peak I [U(VI)-U(V)] and **(c)-(f)** are i vs. √ν plot, Condition: **(a)** & **(c)** at [UO_2^{2+}]=10^{-5} M [Citrate]= $5x10^{-3}$ M, I= 0.1 M $NaClO_4$ at pH 4 while **(d)** same as **(c)** at pH 6.5; **(b)** & **(e)** at [UO_2^{2+}]= 10^{-3} M [Citrate]= $5x10^{-2}$ M, I= 0.1 M $NaClO_4$ at pH 4 while **(f)** same as **(e)** at pH 6.5.



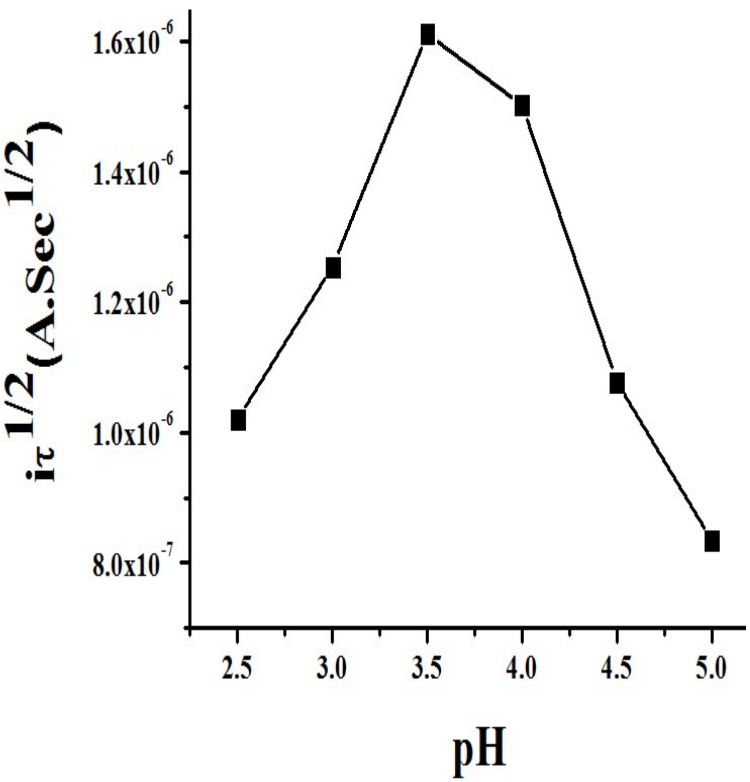
A
i = 6x10-9 A
B
i = 9x10-9 A
E(V)
log[1-(t/τ)1/2]
A
B
i = 4x10-7 A
i = 7x10-7 A
E(V)
log[1-(t/τ)1/2]

(a) (b)



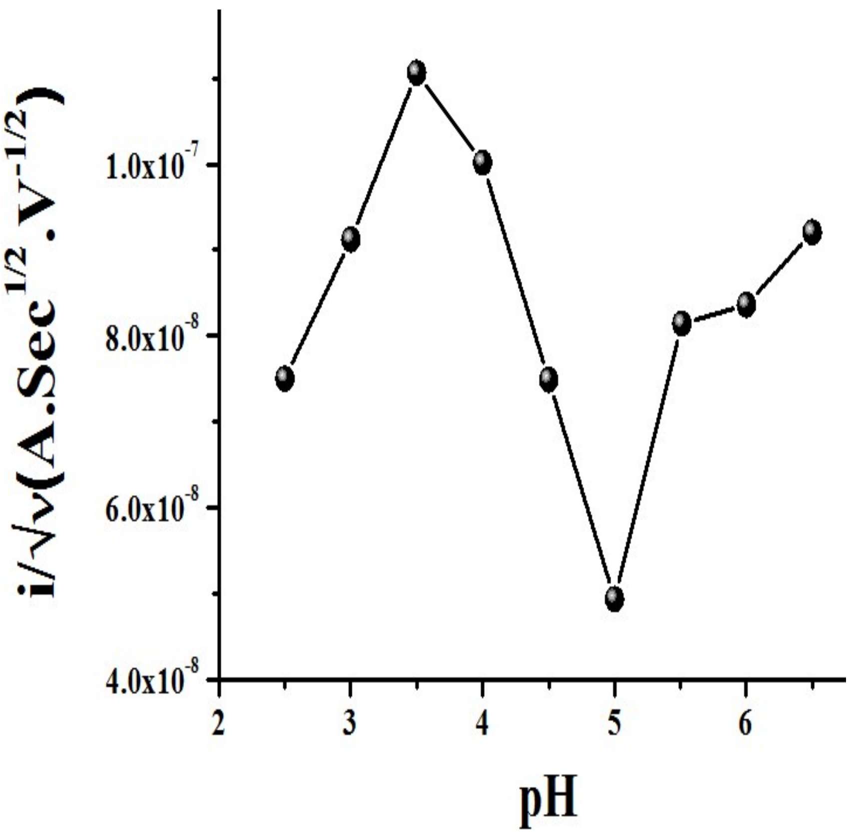
4.00x10-8
3.75x10-8
3.50x10-8
3.25x10-8
3.00x10-8
2.75x10-8
2.50x10-8
iτ1/2(A.Sec1/2)
3.0
3.5
4.0
4.5
5.0
pH

(c)

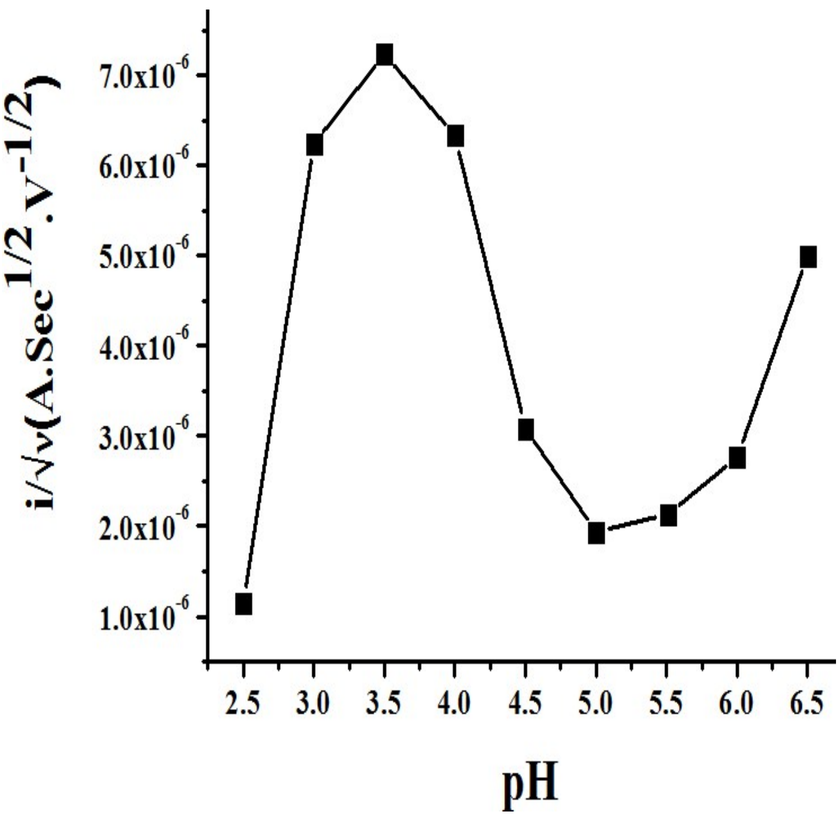


1.6x10-6
1.4x10-6
1.2x10-6
1.0x10-6
8.0x10-7
iτ1/2(A.Sec1/2)
2.5
3.0
3.5
4.0
4.5
5.0
pH

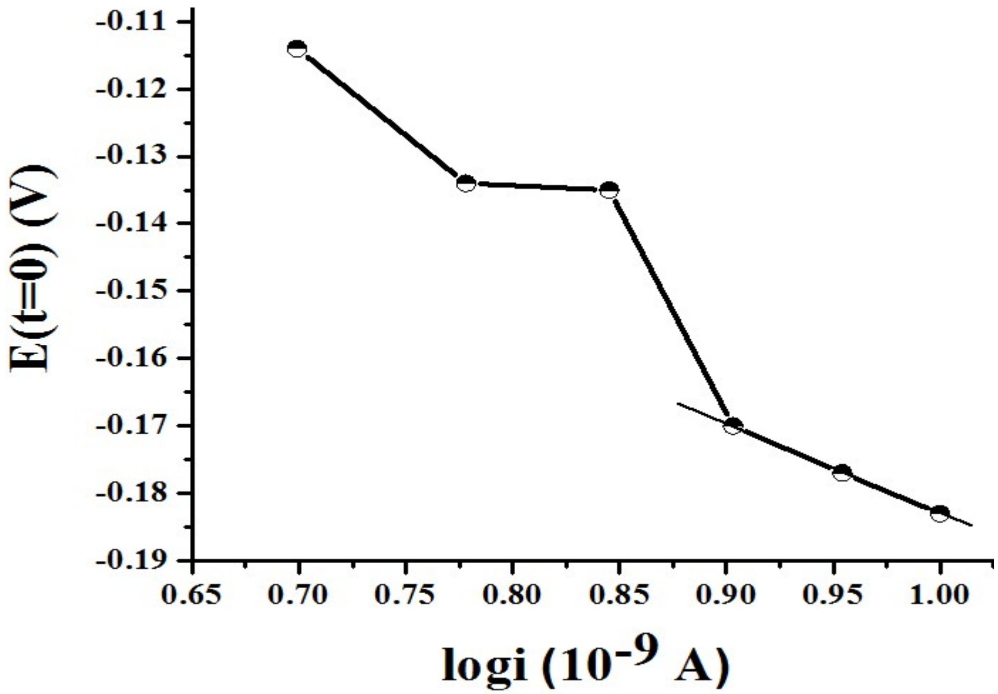
(d)


i/√ν(A.Sec^1/2.V^-1/2)
1.0x10^-7
8.0x10^-8
6.0x10^-8
4.0x10^-8
2
3
4
5
6
pH

(e)

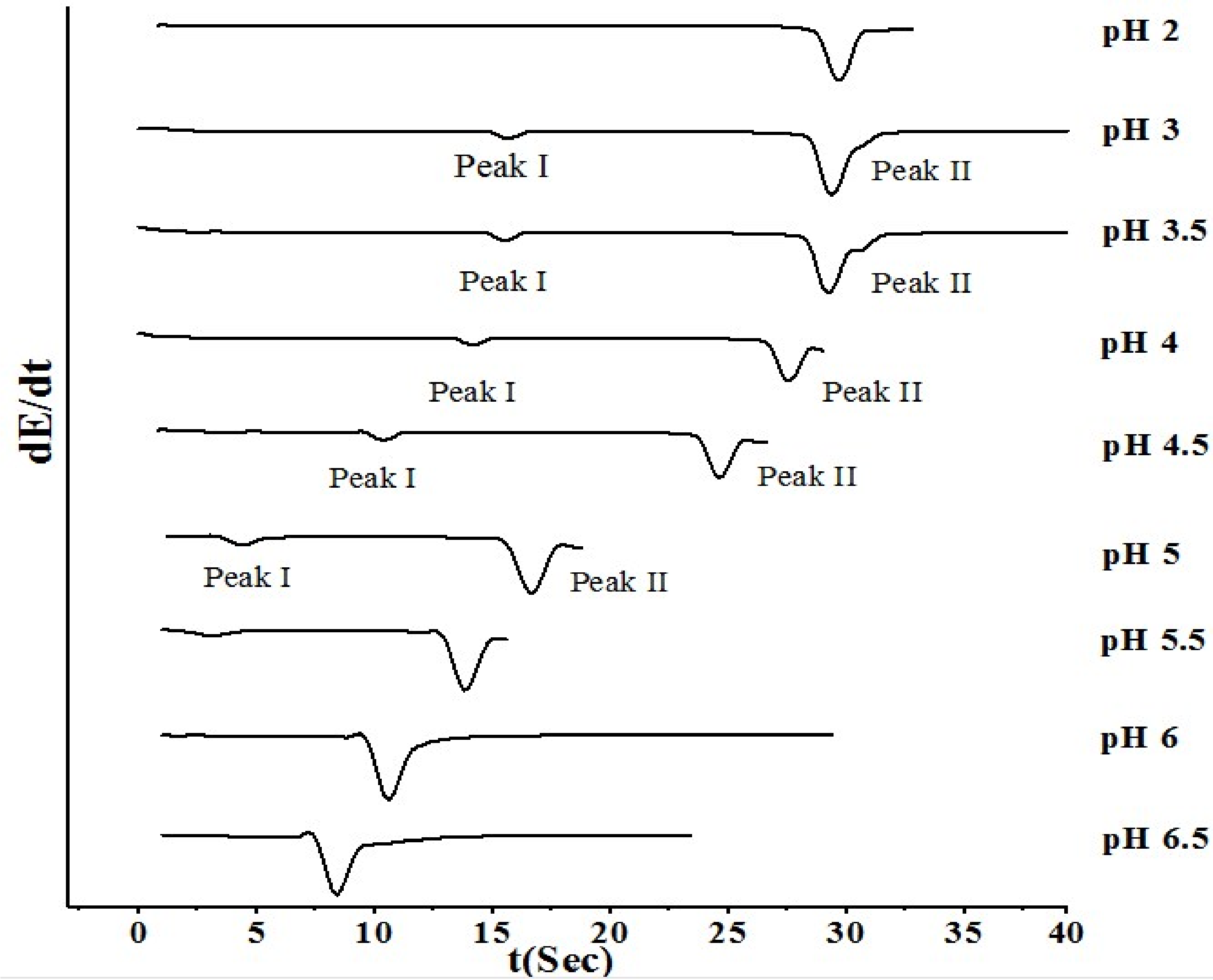

i/√ν(A.Sec^1/2.V^-1/2)
7.0x10^-6
6.0x10^-6
5.0x10^-6
4.0x10^-6
3.0x10^-6
2.0x10^-6
1.0x10^-6
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
pH

(f)



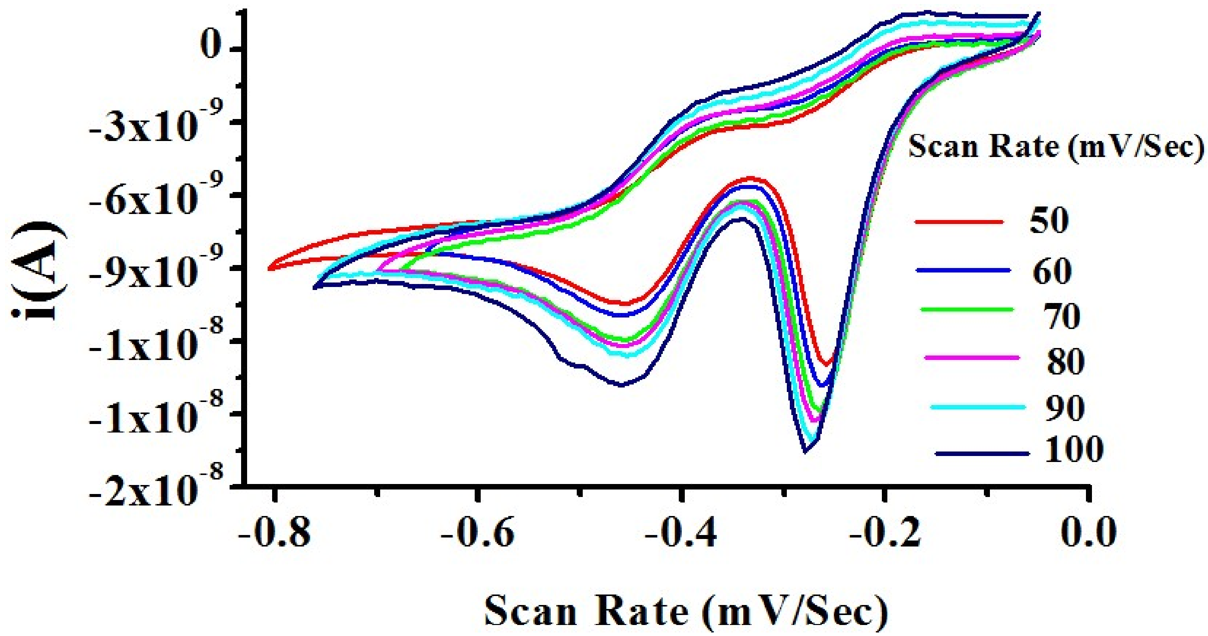
-0.11
-0.12
-0.13
-0.14
-0.15
-0.16
-0.17
-0.18
-0.19
E(t=0) (V)
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
logi (10-9 A)

(g)



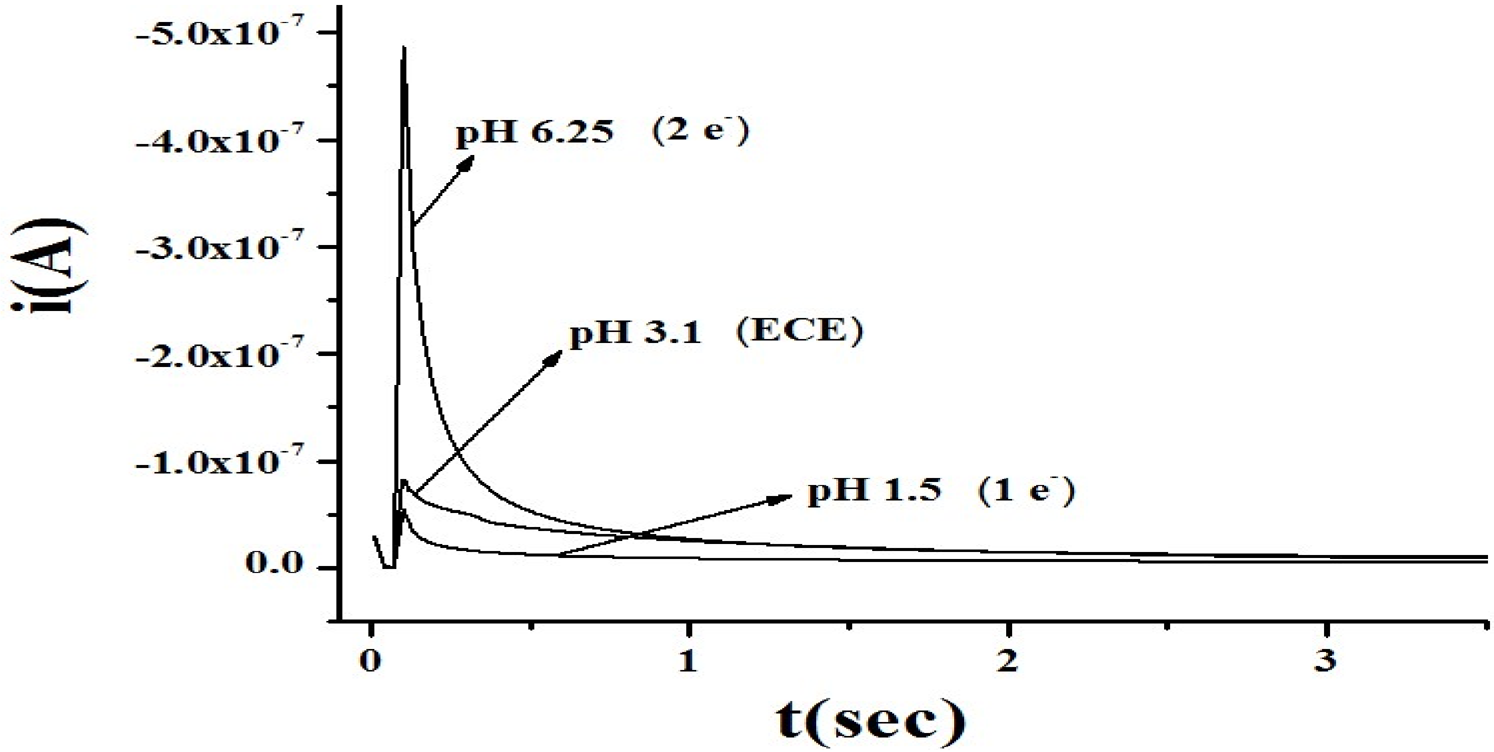
dE/dt
pH 2
pH 3
Peak I
Peak II
pH 3.5
Peak I
Peak II
pH 4
Peak I
Peak II
pH 4.5
Peak I
Peak II
pH 5
Peak I
Peak II
pH 5.5
pH 6
pH 6.5
0
5
10
15
20
25
30
35
40
t(Sec)

(h)

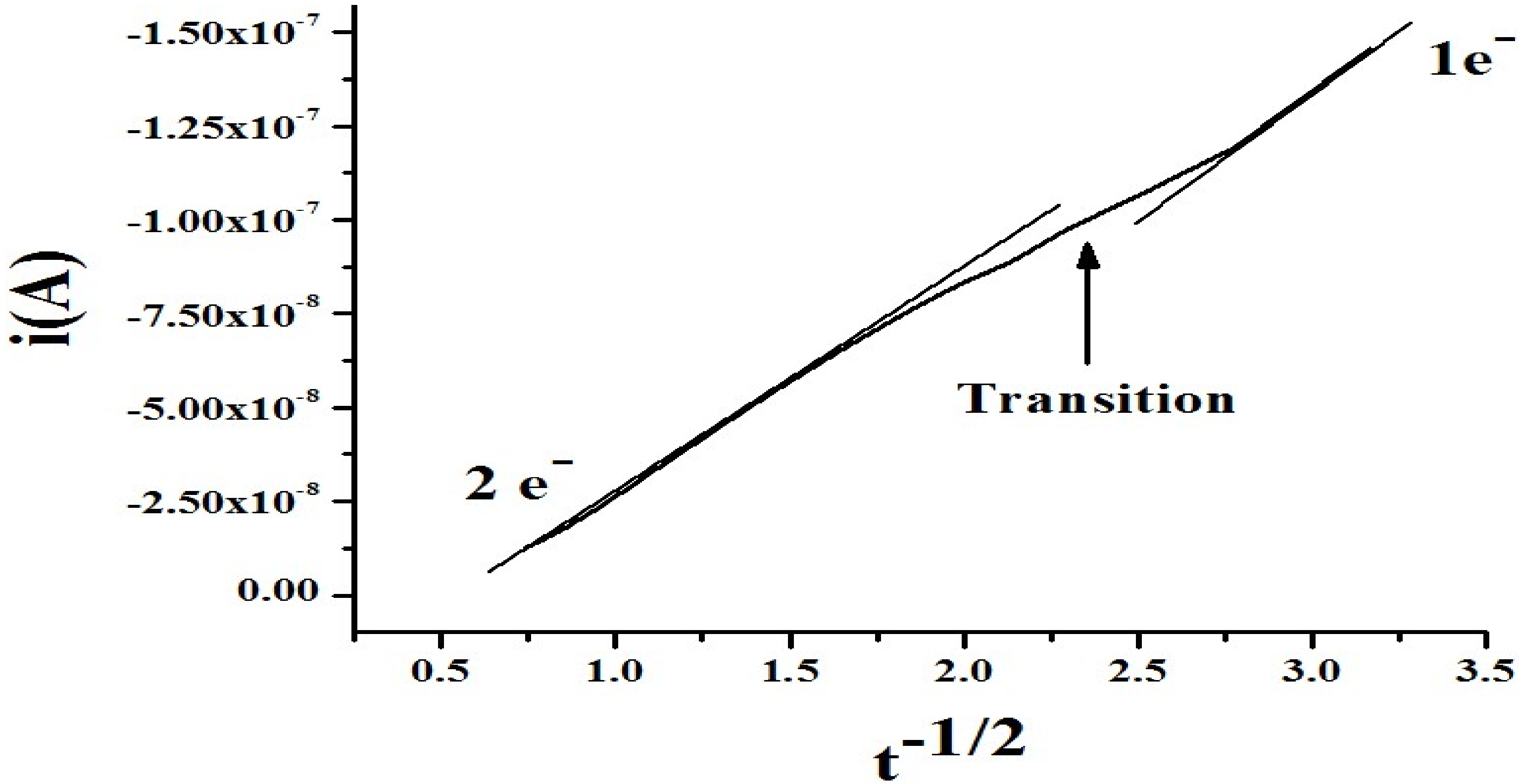


(i)

Figure S4. E(V) vs. log $[1-(t/\tau)^{1/2}]$ plots at pH 4 are in **(a)** & **(b)**. Variation of chronopotentiometric constant ($i\tau^{1/2}$) with pH **(c)** at fixed i = $10x10^{-8}$ A and **(d)** at fixed i = $10x10^{-7}$ A**.** Variation of Peak Current function ($i/\sqrt{v}$) with pH at 50 mV/sec scan rate are in **(e)** & **(f)**. Variation of E(t=0) with log i at pH 5 are in **(g).** The plot **(h)** is derivative chronopotentiometric peaks at several pH values and i = $5x10^{-7}$ A. The variation of cyclic voltammograms with scan rates are in (**i**). Conditions: **(a), (c)**, **(e), (g) & (i)** are at $[UO_2^{2+}]$= 10^{-5} M, [Citrate]= $5x10^{-3}$ M and I= 0.1 M $NaClO_4$ while **(b), (d), (f)** & **(h)** are at $[UO_2^{2+}]$= 10^{-3} M. [Citrate]= $5x10^{-2}$ M and I= 0.1 M $NaClO_4$.

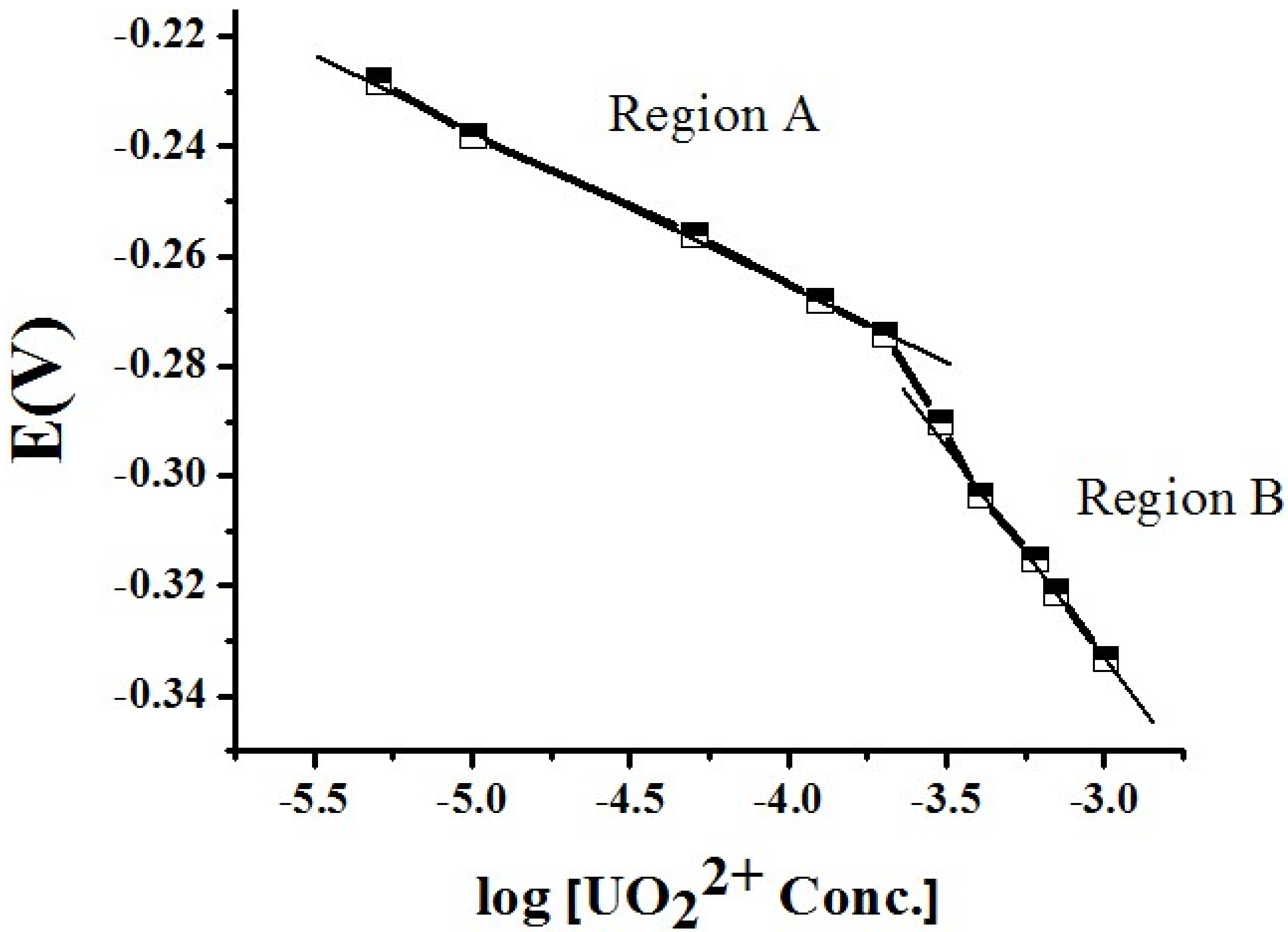

-5.0x10-7
-4.0x10-7
-3.0x10-7
-2.0x10-7
-1.0x10-7
0.0
i(A)
pH 6.25 (2 e-)
pH 3.1 (ECE)
pH 1.5 (1 e-)
0
1
2
3
t(sec)

(a)



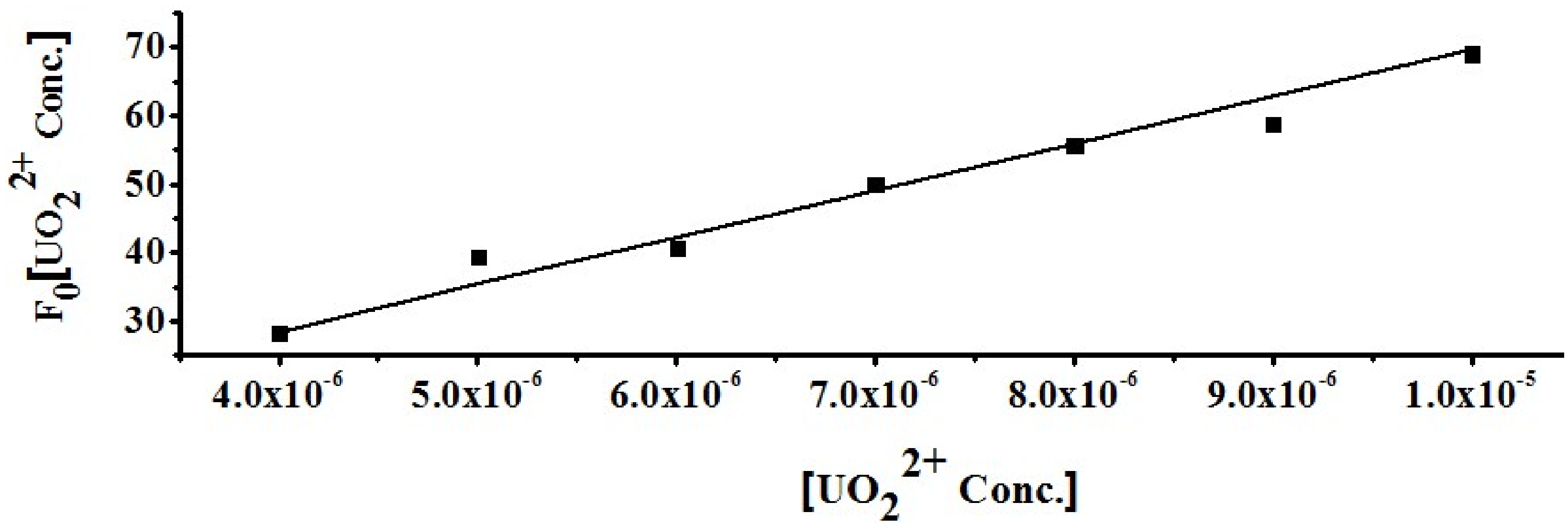
(b)

Figure S5. Plot of i(A) vs. t(sec) with varying pH is in **(a)** and **(b)** is the plot of i(A) vs. $t^{-1/2}$. Condition: **(a)** and **(b)** $[UO_2^{2+}]$= 1x10^{-5} M, [Citrate]= 5x10^{-3} M and I= 0.1 M $NaClO_4$.



E(V)
-0.22
-0.24
-0.26
-0.28
-0.30
-0.32
-0.34
Region A
Region B
-5.5
-5.0
-4.5
-4.0
-3.5
-3.0
log [UO2 2+ Conc.]

(a)



(b)

Figure S6. The Variation of E_p **(a)** with $[UO_2^{2+}]$ concentration at fixed [Citrate]= $1x10^{-2}$ M, I= 0.1 M $NaClO_4$ and pH 4; **(b)** The variation of $F_0[UO_2^{2+}$ Conc.] with $[UO_2^{2+}$ Conc.] at pH 4.

Table S1. The observed slope and calculated value of D_0 from i vs. $\sqrt{\nu}$ plot

Taken: **A= 4x10^{-3} cm^2,**						
pH	Monomer $[UO_2Cit]^-$			Dimer $[(UO_2)_2Cit_2]^{2-}$		
	Conc.(C_0^*) mol cm^{-3}	Slope	D_0 (cm^2/sec)	Conc.(C_0^*) mol cm^{-3}	Slope	D_0 (cm^2/sec)
4	7.26x10^{-9}	2.138x10^{-8}	1.21x10^{-5}	3.87x10^{-7}	8.70x10^{-7}	7.07x10^{-6}
6.5	8.76x10^{-9}	8.166x10^{-8}	9.39x10^{-6}	3.887x10^{-7}	2.29x10^{-6}	3.74x10^{-6}

Table S2. The value of αn and $k^0_{f,h}$ for $[UO_2Cit]^-$ and $[(UO_2)_2Cit_2]^{2-}$ at lower and higher current densities.

Applied Current (A)	Monomer $[UO_2Cit]^-$				Applied Current (A)	Dimer $[(UO_2)_2Cit_2]^{2-}$			
	Slope	αn	Intercept	$k^0_{f,h}$ (cm/sec)		Slope	αn	Intercept	$k^0_{f,h}$ (cm/sec)
Lower Current ($6x10^{-9}$)	0.14	0.42	-0.14	$6.16x10^{-6}$	Lower Current ($4x10^{-7}$)	0.11	0.52	-0.11	$1.20x10^{-5}$
Higher Current ($9x10^{-9}$)	0.13	0.45	-0.15	$8.69x10^{-6}$	Higher Current ($7x10^{-7}$)	0.13	0.45	-0.14	$1.13x10^{-5}$

Speciation Calculation: At $[UO_2^{2+}] = 4x10^{-3}$ M in presence of [Citrate] = $4x10^{-3}$ M at pH 4.

$[UO_2Cit]^{-}$: $[(UO_2)_2Cit_2]^{2-}$ = 11.5:82.3

```
*** System pH = 4.   *****************
System pH:           4.0
Ionic Strength:      1.000E-01 mol/L
Temperature:         25.0 Deg C
Charge Imbalance:    74.1 Percent

  Species in Solution       Molar Concentration
       H+1                          1.281E-04
       UO2+2                        2.300E-04
       Citrate                      8.282E-07
       H2[Citrate]                  1.644E-04
       H3[Citrate]                  1.684E-05
       (UO2)2(CITRATE)2)-2          1.647E-03
       UO2H(CITRATE)                6.361E-06
       UO2(CITRATE)-                4.581E-04
       OH-                          1.289E-10
       UO2OH+                       1.388E-06
       (UO2)2(OH)2+2                5.243E-06
       (UO2)3(OH)5+                 2.081E-08
       H[Citrate]                   5.986E-05

  Component Distribution Among Species
     For Component: Citrate
          4.1% is in species: H2[Citrate]
         82.3% is in species: (UO2)2(CITRATE)2)-2
         11.5% is in species: UO2(CITRATE)-
          1.5% is in species: H[Citrate]
     For Component: UO2+2
          5.7% is in species: UO2+2
         82.3% is in species: (UO2)2(CITRATE)2)-2
         11.5% is in species: UO2(CITRATE)-

  Component Distribution Among Phases
                                       ------ Percent in Each Phase ------
                                         Dissolved    Sorbed   Precipitated
    For Component: Citrate                100.0%       0.0%       0.0%
    For Component: UO2+2                  100.0%       0.0%       0.0%
    For Component: H+1                    100.0%       0.0%       0.0%
```

Parameters used for speciation modeling

The distribution of Uranyl in the Citrate solution, as shown in speciation plots [Figure S1(a-c)], is mainly dependent on thermodynamics data viz. stability constant of the species. Following are the reactions and parameters used in the speciation modelling:

1. UO_2^{2+} + $[Citrate]^{3-}$	= $[UO_2Citrate]^-$	log K= 6.70
2. $2UO_2^{2+}$ + $2[Citrate]^{3-}$	= $[(UO_2)(Citrate)_2]^{2-}$	log K= 19.02
3. $UO_2^{2+} + H_2O$	= $H^+ + [UO_2(OH)]^+$	log K= -5.89
4. $3UO_2^{2+} + 5H_2O$	= $5H^+ + [(UO_2)_3(OH)_5]^+$	log K= -15.58
5. $2UO_2^{2+} + 2H_2O$	= $2H^+ + [(UO_2)_2(OH)_2]^{2+}$	log K= -5.57
6. $UO_2^{2+} + 4H_2O$	= $4H^+ + [UO_2(OH)_4]^{2-}$	log K= -33.00
7. $3UO_2^{2+} + 7H_2O$	= $7H^+ + [(UO_2)_3(OH)_7]^-$	log K= -31.00
8. $4UO_2^{2+} + 7H_2O$	= $7H^+ + [(UO_2)_4(OH)_7]^+$	log K= -21.90
9. $UO_2^{2+} + 2H_2O$	= $2H^+ + [UO_2(OH)_2(aq)]$	log K= -12.0
10. $UO_2^{2+} + 3H_2O$	= $3H^+ + [UO_2(OH)_3]^-$	log K= -20.00
11. H^+ + Citrate	= H[Citrate]	log K= 6.39
12. $2H^+$ + Citrate	= H2[Citrate]	log K= 11.16
13. $3H^+$ + Citrate	= H3[Citrate]	log K= 14.28