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Relative Stabilities of Complexes of MO_2^{2+} ($M=U$, Np, and Pu) with Monocarboxylate Anions

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Stability data for complexes of yl(VI) ions MO_2^{2+} ($M=U$, *Np, and Pu) with monocarboxylic ligands L are reported and discussed* ($L=CH_3CO_2^-$, $C_2H_5CO_2^-$, *and* $CH_2ClCH_2CO_2^-$). *Stability constants refer to the formation equilibria of complexes in aqueous* $NaClO_4$ *solution at 20° and 1* M *ionic strenght. In the range of ligand concentrations examined, complexes are formed in which the highest average ligand number,* $\bar{n}$ *is three. The stability order of complexes of the various ligands examined is* $UO_2^{2+}>NpO_2^{2+}>PuO_2^{2+}$. *The stabilities of complexes of a given* MO_2^{2+} *ion increase with increasing ligand basicity, which suggests a strong* hard *character for these oxycations.*

Introduction

There have recently been reported some studies on the formation of complexes of oxycations PuO_2^{2+} and UO_2^{2+} with carboxylate ligands in aqueous solution. A strict dependence of the stabilities of such complexes on the basicities of the ligands was established.[1-6]

With the aim of comparing the relative stabilities of isostructural complexes of MO_2^{2+} ions with various metals ($M=U$, Np, Pu), we report herein some data relating to the formation of complexes of yl(VI) ions with monocarboxylate anions of various basicities.

We have studied the formation of complexes of NpO_2^{2+} by a potentiometric method, the following equilibria being involved:

$$NpO_2^{2+}+nL \rightleftarrows NpO_2L_n^{2-n}$$

where L = monochloroacetate, propionate, and β-chloropropionate in aqueous $NaClO_4$ solution at 20° and ionic strength $I=1$ *M*.

Experimental Section

(i) *Chemicals.* Neptunium (isotope ^{237}Np) was purified before use by absorption on Dowex 1X4 anion-exchange resin from 8 *M* nitric acid as neptunium(IV) and eluted in 0.3 *M* nitric acid.[7] A neptunium(V) solution was obtained by concentrating the eluate to about 1 *M* in nitric acid. Neptunium(V) hydroxide was then precipitated with sodium hydroxide, washed carefully with water and dissolved in 1 *M* perchloric acid to give a solution about 100 m*M* in neptunium(V).

The neptunium(VI) solutions were prepared by electrolytic oxidation of a neptunium(V) solution (electrodes of platinum wire; cathode and anode compartments separated by fine sintered glass discs; magnetic agitator in the anode compartment).

The oxidation state of neptunium was checked spectrophotometrically. The observed absorption spectra of neptunium(VI) in perchloric acid solution were very similar to those already reported by other authors.[8] The absence of appreciable amounts of neptunium(V) and (IV) was checked by the absence of absorption at the respective absorption bands for these species.[8]

The concentration of neptunium was determined by potentiometric titration of a separated aliquot of the NpO_2^{2+} solution (1 or 2 ml) with standard iron(II) solution.[9]

The concentration of the free perchloric acid in the neptunium(VI) solution was determined by ionic exchange analysis on a cationic resin in the hydrogen ion form (Dowex 50W-X4). For a total concentration of acid $[H^+]_t$, the original $[H^+]=[H^+]_t-2[NpO_2^{2+}]$.

Using standard solutions of NaOH and $NaClO_4$, the solutions containing NpO_2^{2+}, $HClO_4$, and $NaClO_4$ were eventually adjusted to the concentrations required for the measurements.

Spectrophotometric measurements at various times indicated that in these solutions neptunium(VI) is stable enough for our purposes. No appreciable reduction was observed during the first 24 hours; but after two days roughly 0.2% of neptunium(V) was detectable. The measurements were performed on fresh solutions.

Standard buffer solutions of monochloroacetic (Buffer 1:1), β-chloropropionic (Buffer 1:1), and propionic (Buffer 2:1) acid were prepared by exact neutralization of calculated amounts of acid with standard NaOH solutions.

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Monochloroacetic acid was distilled twice (b.p. 186-188° at 1 atm.) and dried *in vacuo* (equivalent weight: calcd. 94.5; found 94.5).

β-chloropropionic acid (Fluka *purum*) was purified by recrystallization from ethylether-light petroleum (twice) and dried *in vacuo.*[10] Its purity was checked by melting point (41.8°) and equivalent weight determination (calcd. 108.52; found 108.5).

Buffer solutions of the above acids were prepared immediately prior to use to avoid the presence of Cl^- that might be formed by hydrolysis. Propionic acid was dried over anhydrous Na_2SO_4 and fractionally distilled. The fraction distilling at 139-141° was collected and fractionated over $KMnO_4$. The middle fraction, which distilled at 140.7°/760 mmHg,[11] was employed in the measurements.

(ii) *Measurements.* The procedure adopted for experimental measurements and treatment of data is analogous to that used earlier by Ahrland[4,5] and then by us.[1-3,12]

The hydrogen ion concentration was determined by use of the cell

$$\begin{array}{l|l|l||l||l|l}
\mathrm{Ag} & \mathrm{AgCl} & 50\ \mathrm{m}M\ \mathrm{NaCl} & \mathrm{NaClO_4} & C_M\ \mathrm{m}M\ \mathrm{NpO_2(ClO_4)_2} & \text{glass} \\
 & & 950\ \mathrm{m}M\ \mathrm{NaClO_4} & 1000\ \mathrm{m}M & C_H\ \mathrm{m}M\ \mathrm{HClO_4} & \text{electrode} \\
 & & & & C_L\ \mathrm{m}M\ \mathrm{NaL} & \\
 & & & & C_{HL} = \delta C_L\ \mathrm{m}M\ \mathrm{HL} & \\
 & & & & I = 1\ M\ \mathrm{NaClO_4} &
\end{array}$$

L = CH_2ClCOO^-, $CH_2ClCH_2COO^-$, and $CH_3CH_2COO^-$; $\delta = C_{HL}/C_L$ Buffer ratio. The solution on the right-hand side of the cell was prepared by adding known volumes of buffers with a microburette to a known volume (15 ml) of a starting solution of composition:

$$C_M^\circ\ \mathrm{m}M\ \mathrm{NpO_2(ClO_4)_2}, \qquad C_H^\circ\ \mathrm{m}M\ \mathrm{HClO_4},$$
$$(1000-3\,C_M^\circ-C_H^\circ)\mathrm{m}M\ \mathrm{NaClO_4}$$

E.m.f. measurements were carried out with the same cell and with $C_M=C_H=O$ in order to determine the dissociation constants of monochloroacetic, β-chloropropionic, and propionic acid in these ionic solutions. The behavior of the glass electrode was checked in the pH range 2 - 3.5 with standard solutions of $HClO_4$ ($I = 1\,M$ by $NaClO_4$) both before and after each set of measurements.

The e.m.f. is given by the relationship $E = E^\circ + 58.16 \log [H^+] - 0.06[H^+]$.

The oxidation state of neptunium was checked both before and after each set of measurements by recording the absorption spectrum of a sample in the wavelength range 360-1000 mμ. No reduction of Np^{VI} was detected.

(iii) *Treatment of Data.* Values obtained for each buffer system when $C_M = C_H = O$ are reported here as E′ and $[H^+]'$ whereas the corresponding values for $C_M \neq O$ are reported as E and $[H^+]$. The free ligand equilibrium concentration, [L], in solutions of NpO_2^{2+} was determined from the relationship:

$$[L] = \frac{[H^+]'}{[H^+]} \times \frac{(C_L+[H^+]')(\delta C_L+C_H-[H^+])}{\delta C_L-[H^+]'} \qquad (1)$$

The average ligand number, $\bar{n}$, was calculated from the equation:

$$\bar{n} = \frac{C_L+[H^+]-C_H-[L]}{C_M} \qquad (2)$$

Results and Discussion

The experimental values of E′, obtained by increasing the concentrations of the three buffer systems when $C_M = C_H = O$, are given in Table I, together with the calculated dissociation constants, K_C, of the corresponding acids. Experimental results for neptunyl(VI) complexes are listed in Table II.

In Figure 1 are plotted the $\bar{n}$ values *vs.* log [L] for the three systems studied. Formation of successive complexes containing respectively 1, 2 and 3

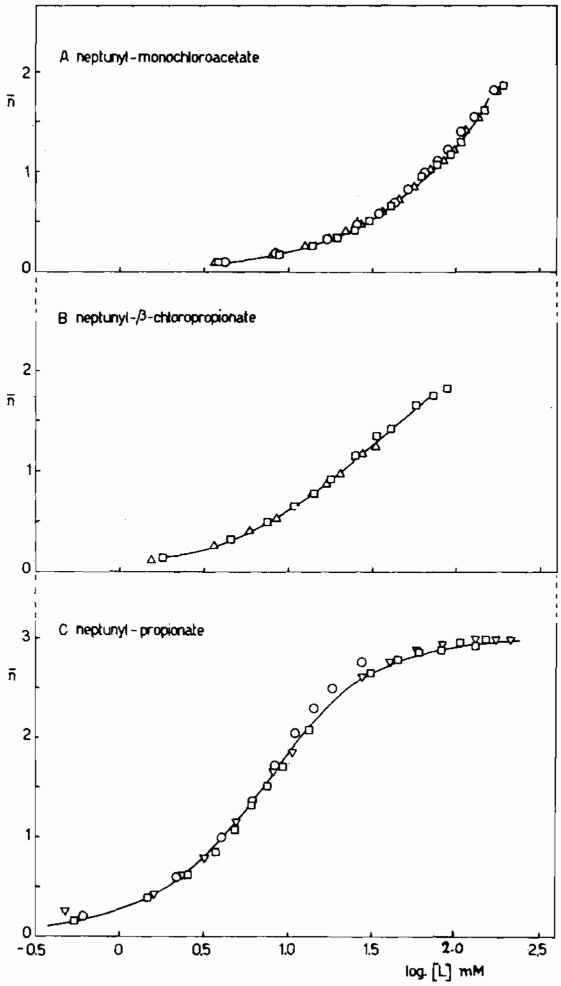

Figure 1. The complex formation curves of: (A) the neptunyl-monochloroacetate system; (B) the neptunyl-β-chloropropionate system; (C) the neptunyl-propionate system. The symbols relate to Table II. Fulldrawn curves obtained from calculated complexity constants.

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Table I. E′ and the dissociation constants K_c for the ligands as a function of C_L

	Monochloroacetate Buffer		Propionate Buffer		β-Chloropropionate Buffer	
C_L m*M*	E′ mV	$K_c \times 10^3$	E′ mV	$K_c \times 10^5$	E′ mV	$K_c \times 10^4$
6.62	+169.6	2.15	+82.7	1.93	+130.1	1.32
13.16	174.2	2.17	82.7	1.92	129.6	1.26
19.61	176.0	2.17	82.6	1.91	129.2	1.22
25.97	177.0	2.17	82.7	1.92	128.8	1.20
32.26	177.5	2.15	82.3	1.88	128.7	1.19
38.46	177.8	2.14	82.0	1.86	128.5	1.18
44.59	178.1	2.14	81.8	1.85	128.3	1.17
50.63	178.4	2.14	81.8	1.85	128.2	1.16
62.50	178.6	2.12	81.5	1.82	127.9	1.15
74.07	178.4	2.10	81.2	1.80	127.6	1.14
90.91	178.4	2.07	80.8	1.77	127.2	1.12
107.14	178.4	2.06	80.5	1.75	126.7	1.09
122.81	178.4	2.06	80.1	1.73	126.3	1.08
142.86	178.0	2.00	79.6	1.69	125.7	1.05

Table II. Experimental values for the neptunyl(VI)-monochloroacetate, -β-chloropropionate, and -propionate systems

C_M m*M*	C_L m*M*	E mV	[L] m*M*	$\bar{n}$
L = monochloroacetate				
$C_M^\circ = 29.84$ m*M*;		$C_H^\circ = 2.94$ m*M*		(○)
29.64	6.62	+190.7	4.21	0.09
29.44	13.16	191.2	8.42	0.17
29.06	25.97	191.1	16.92	0.33
28.69	38.46	190.5	25.47	0.47
28.33	50.63	190.0	34.33	0.59
27.97	62.50	189.4	43.18	0.70
27.63	74.07	188.9	57.34	0.83
27.13	90.91	188.1	64.54	0.98
26.64	107.1	187.5	77.64	1.11
26.17	122.8	186.7	91.18	1.21
25.57	142.9	185.9	107.1	1.40
24.86	166.7	185.1	128.3	1.55
23.56	210.5	183.7	167.9	1.82
$C_M^\circ = 20.15$ m*M*;		$C_H^\circ = 5.87$ m*M*		(△)
19.99	6.62	+199.8	3.63	0.09
19.86	13.16	196.4	8.01	0.17
19.73	19.61	194.3	12.61	0.25
19.61	25.97	192.9	17.35	0.33
19.48	32.26	191.8	22.07	0.40
19.35	38.46	190.8	27.00	0.47
19.11	50.63	189.6	36.78	0.59
18.87	62.50	188.7	46.44	0.72
18.64	74.07	187.8	55.64	0.85
18.30	90.91	186.8	70.08	1.00
17.97	107.1	185.9	84.65	1.11
17.66	122.8	185.3	98.70	1.22
17.25	142.9	184.4	115.8	1.42
16.77	166.7	183.6	138.3	1.54
15.89	210.5	182.3	179.3	1.82
$C_M^\circ = 10.18$ m*M*;		$C_H^\circ = 6.68$ m*M*		(□)
10.12	6.62	+200.5	3.84	0.09
10.05	13.16	195.7	8.73	0.18
9.98	19.61	192.9	13.91	0.27
9.92	25.97	191.0	19.40	0.34
9.85	32.26	189.7	24.75	0.42
9.79	38.46	188.7	30.10	0.50
9.67	50.63	187.6	40.67	0.67
9.43	74.07	185.6	61.48	0.96
9.26	90.91	184.6	77.41	1.08
9.09	107.1	183.8	93.04	1.17
8.93	122.8	183.2	107.7	1.30
8.49	166.7	181.7	149.7	1.61
8.04	210.5	180.6	192.5	1.86

Table II. (Continued)

C_M m*M*	C_L m*M*	E mV	[L] m*M*	$\bar{n}$
L = β-chloropropionate				
$C_M^\circ = 30.00$ m*M*;		$C_H^\circ = 2.94$ m*M*		(△)
29.80	6.62	+171.2	1.55	0.12
29.61	13.16	164.4	3.66	0.26
29.41	19.61	160.9	5.97	0.39
29.22	25.97	158.3	8.53	0.53
29.03	32.26	156.3	11.29	0.65
28.85	38.46	154.7	14.14	0.77
28.66	44.59	153.1	17.23	0.88
28.48	50.63	151.7	20.5	0.98
28.13	62.5	149.3	27.46	1.17
27.78	74.07	147.1	33.01	1.25
$C_M^\circ = 20.03$ m*M*;		$C_H^\circ = 3.32$ m*M*		(□)
19.90	6.62	+168.4	1.79	0.13
19.77	13.16	159.5	4.53	0.31
19.64	19.61	155.2	7.58	0.48
19.51	25.97	152.6	10.81	0.64
19.39	32.26	150.5	14.35	0.79
19.26	38.46	148.8	17.99	0.92
19.02	50.63	146.1	25.75	1.17
18.78	62.50	143.9	34.16	1.37
18.55	74.07	141.8	40.97	1.42
18.21	90.91	139.1	57.81	1.67
17.89	107.1	136.8	72.75	1.77
17.57	122.8	135.0	88.21	1.82
L = propionate				
$C_M^\circ = 32.06$ m*M*;		$C_H^\circ = 5.12$ m*M*		(▽)
31.85	6.62	+174.0	0.23	0.11
31.64	13.16	155.3	0.87	0.25
31.43	19.61	148.7	1.60	0.42
31.23	25.97	144.9	2.41	0.61
31.02	32.26	142.3	3.22	0.78
30.83	38.46	140.2	4.08	0.97
30.63	44.59	138.3	5.00	1.14
30.44	50.63	136.6	6.05	1.32
30.06	62.5	133.3	8.36	1.65
29.68	74.1	129.6	10.68	1.85
28.62	107.1	115.5	27.35	2.63
28.12	122.8	108.8	40.32	2.78
27.48	142.9	102.2	59.30	2.88
26.72	166.7	96.9	85.65	2.95
25.99	189.2	93.3	108.2	2.96
25.31	210.5	90.7	130.7	2.99
24.66	230.8	88.7	152.9	3.00
24.04	250.0	87.1	174.2	2.99
22.89	285.7	84.5	213.9	2.98

Table II. (Continued)

$C_M° = 24.06$ m*M*;		$C_H° = 2.64$ m*M*		(□)
23.90	6.62	+149.9	0.54	0.17
23.74	13.16	139.9	1.49	0.40
23.59	19.61	135.5	2.56	0.73
23.43	25.97	132.7	3.76	0.85
23.28	32.26	130.7	4.93	1.08
23.13	38.46	128.9	6.20	1.29
22.98	44.59	127.1	7.61	1.51
22.84	50.63	125.3	9.29	1.71
22.55	62.50	121.0	13.36	2.08
21.87	90.91	108.5	17.22	2.65
21.48	107.1	102.5	30.66	2.78
21.10	122.8	98.2	45.14	2.86
20.62	142.9	94.2	60.24	2.88
20.05	166.7	90.9	81.36	2.96
19.51	189.2	88.6	105.1	2.92
19.00	210.5	86.8	130.0	2.98
$C_M° = 12.06$ m*M*		$C_H° = 4.14$ m*M*		(○)
11.98	6.62	149.4	0.61	0.20
11.91	13.16	131.1	2.22	0.60
11.83	19.61	124.6	4.09	0.99
11.75	25.97	120.9	6.17	1.36
11.67	32.26	117.8	8.39	1.71
11.06	38.46	114.7	11.06	2.03
11.53	44.59	111.6	14.32	2.29
11.45	50.63	108.5	18.31	2.49
11.31	62.5	103.1	27.49	2.76

coordinated ligands can be observed. The system NpO_2^{2+}–CH_2ClCOO^- could be studied at a maximum ligand concentration of up to 210 m*M*, since in more concentrated solutions the difference C_L–[L] in equation (2) becomes progressively smaller, thereby making the evaluation of $\bar{n}$ less and less accurate. For the system NpO_2^{2+}–$CH_2ClCH_2COO^-$ the ligand concentration range was limited by formation of a precipitate of $Na[NpO_2L_3]$.

The good overlap of data derived from measurements taken at different concentrations of NpO_2^{2+} indicates that $\bar{n}$ is a function of [L] only and hence that only mononuclear complexes are formed.[13a] An analogous behavior was observed for PuO_2^{2+} [1-3] under the same experimental conditions.

The present knowledge of the hydrolytic properties of NpO_2^{2+} in aqueous solutions[14] and previous results obtained with the acetate ion as ligand[12] indicate that hydrolysis of NpO_2^{2+} is negligible in the pH range examined in this work. By applying Fronaeus' extrapolation method[13b] to related values of $\bar{n}$, [L], we have determined the overall formation constants β_n of the successive equilibria

$$NpO_2^{2+} + nL \rightleftarrows NpO_2L_n^{2-n}$$

for n = 1, 2, and 3. The first-approximation constants obtained in this way were then elaborated by a computerized least-squares programme in order to determine refined values and standard deviations for each formation constant. Table III lists the resulting stability constants together with values of $1/K_C$ assessed under the same experimental conditions.

Figure 2 shows plots of logarithms of the stability constants K_1 for complexes of the yl(VI) ions *vs.*–log K_C for the various ligands L.

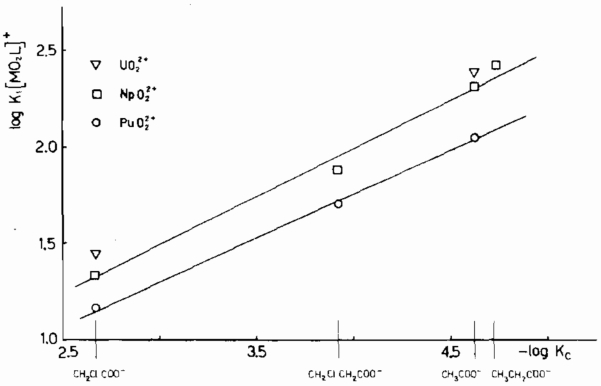

Figure 2. Relationship between log K_1 for the uranyl, neptunyl and plutonyl complexes and –log K_c for the monocarboxylic acid corresponding to the anionic ligand.

For PuO_2^{2+} and NpO_2^{2+} a satisfactory linear relationship is observed between log K_1 and –log K_C. For UO_2^{2+} the two points that are available for L = monochloroacetate and acetate and which were obtained with the same experimental approach indicate that this cation behaves in a similar manner to

Table III. Comparison of the stability constants of the uranium(VI), neptunium(VI), and plutonium(VI) complexes in aqueous solution at I = 1 *M* and 20° C.

Cation	β_n M^{-n}	CH_3COO^- $1/K_c = 4.1 \times 10^4$ M^{-1}		CH_2ClCOO^- $1/K_c = 460$ M^{-1}	$CH_3CH_2COO^-$ $1/K_c = 5.26 \times 10^4$ M^{-1}	$CH_2ClCH_2COO^-$ $1/K_c = 7.7 \times 10^3$ M^{-1}
UO_2^{2+} [a]	β_1	240 ± 10		27.5 ± 0.5		
	β_2	$(2.3 \pm 0.2) \cdot 10^4$		195 ± 20		
	β_3	$(2.2 \pm 0.3) \cdot 10^6$		625 ± 150		
NpO_2^{2+}	β_1	204 ± 8 [c]	[c]	21.4 ± 0.9	275 ± 15	75.0 ± 4.0
	β_2	$(1.7 \pm 0.2) \cdot 10^4$		126 ± 20	$(2.85 \pm 0.19) \cdot 10^4$	$(2.0 \pm 0.2) \cdot 10^3$
	β_3	$(1.0 \pm 0.4) \cdot 10^6$		605 ± 400	$(3.11 \pm 0.54) \cdot 10^6$	$(4.0 \pm 2.5) \cdot 10^3$
PuO_2^{2+} [b]	β_1	112 ± 4		14.6 ± 0.4		50.0 ± 5.0
	β_2	$(3.5 \pm 0.5) \cdot 10^3$		41.0 ± 6.0		900 ± 100
	β_3	$(9.2 \pm 2.0) \cdot 10^4$		100 ± 50		$(7.0 \pm 1.4) \cdot 10^3$

[a] Data from references 4,5; [b] data from references 1-3; [c] data from reference 12.

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(13) F. J. Rossotti and H. Rossotti, « The Determination of Stability Constants » a) p. 40; b) p. 108, Mc Graw-Hill,, New York (1961).

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PuO_2^{2+} and NpO_2^{2+}. From a general standpoint, the linear relationship between complex stability and ligand basicity should not be surprising. In fact, these cations are classified as « a »-type or « hard » ions,[15,16] forming strong bonds with bases that have a great affinity towards the proton. The values reported here indicate that for all of the anionic ligands examined the free energy of association with the hydrogen ion is far greater than that of formation of the first complex with each of the oxycations in aqueous solution. It can also be seen that straight lines drawn in Figure 2 have almost the same slope, the value of which is much smaller than 1. This clearly indicates that, as far as each oxycation in aqueous solution is concerned, the free energy of formation of the first complex increases with increasing ligand basicity to a far smaller extent than the increasing free energy of association of the corresponding ligands with the proton.

Finally, the data reported in Table III indicate that the tendency of these oxycations to form complexes with the ligands examined is in the order $UO_2^{2+} > NpO_2^{2+} > PuO_2^{2+}$. Such a stability trend is in agreement with Ahrland's findings that both Np^{4+} and NpO_2^{2+} display a lower affinity towards F^- than the corresponding uranium ions.[17] Therefore, a simple electrostatic interaction model cannot be applied to these systems since the observed stability trend is the reverse of what would have been expcted on th basis of the actinide contraction. Clearly, additional factors, beside ionic sizes and charges, must be taken into account. Probably, hydration of the central ion and of the complexes plays a primary role.

Acknowledgments. Thanks are due to Mr. Paolo Buso for his experimental assistance.

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