

Solvent Extraction Studies of Molybdenum and Tungsten as Homologues of Seaborgium (Element 106)

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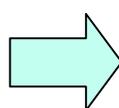
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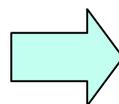
Element 106, Seaborgium (Sg)

4	5	6	7	8
22 Ti	23 V	24 Cr	25 Mn	26 Fe
40 Zr	41 Nb	42 Mo	43 Tc	44 Ru
72 Hf	73 Ta	74 W	75 Re	76 Os
104 Rf	105 Db	106 Sg	107 Bh	108 Hs

- Seaborgium belongs to the group 6
- ^{265}Sg ($T_{1/2} = 9 \text{ s}$) is mainly used in the chemical experiment
- Nuclear reaction: $^{248}\text{Cm}(^{22}\text{Ne}, 5\text{n})^{265}\text{Sg}$
 $\sigma = \text{several hundreds pb}$



The chemical properties of Sg are poorly known.



It is expected that Sg can be reduced

There is no report on the redox experiments of superheavy elements

Lighter homologues

Molybdenum(Mo)

Tungsten(W)

Various oxidation states
(**VI**, V, IV, III ...)

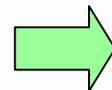
Solution chemistry of Sg

Example of solution chemistry of Sg

Experiment 1

Cation exchange experiment

0.1 M HNO₃/
5 × 10⁻⁴ M HF solution

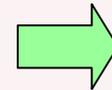
 Sg showed typical behavior
of group 6 element

Radiochim. Acta **77**, 149 (1997).

Experiment 2

Cation exchange experiment

0.1 M HNO₃ solution

 Sg showed non-tungsten
like behavior

Radiochim. Acta **83**, 163 (1998).



There is no report on solution chemistry of Sg following these works

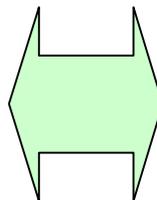
Chemical studies of Mo and W

Molybdenum Tungsten

In neutral to acid solution



Formation of polynuclear species



Seaborgium

The production rate is the order of one atom per hour

Sg cannot form polynuclear species

Investigation of the chemical behavior of mononuclear Mo and W is required for the comparison with that of Sg



Solvent extraction behavior of Mo and W under extremely low concentration was examined to investigate extraction behavior of mononuclear Mo and W

Contents of this study

Solvent extraction experiments with carrier-free Mo and W produced by heavy-ion induced nuclear reactions

Extraction system : Ion-pair extraction
from hydrochloric acid (HCl)

Experimental section

1. Dependence of distribution ratios (D) of Mo and W on HCl concentration
2. Dependence of D values of Mo and W on extractant concentration

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- 1. Dependence of distribution ratios (D) of Mo and W on HCl concentration**
2. Dependence of D values of Mo and W on extractant concentration

Dependence of D values of Mo and W as a function of HCl concentration

Experimental conditions

Place: RIKEN AVF cyclotron

RCNP AVF cyclotron

Nuclear reaction: ${}^{\text{nat}}\text{Ge}({}^{22}\text{Ne}, \text{xn}) {}^{90}\text{Mo}$ ($T_{1/2} = 5.7$ h)

${}^{\text{nat}}\text{Gd}({}^{22}\text{Ne}, \text{xn}) {}^{173}\text{W}$ ($T_{1/2} = 7.6$ min), ${}^{174}\text{W}$ ($T_{1/2} = 31$ min)

${}^{\text{nat}}\text{Dy}({}^{16}\text{O}, \text{xn}) {}^{173}\text{W}$ ($T_{1/2} = 7.6$ min), ${}^{174}\text{W}$ ($T_{1/2} = 31$ min)

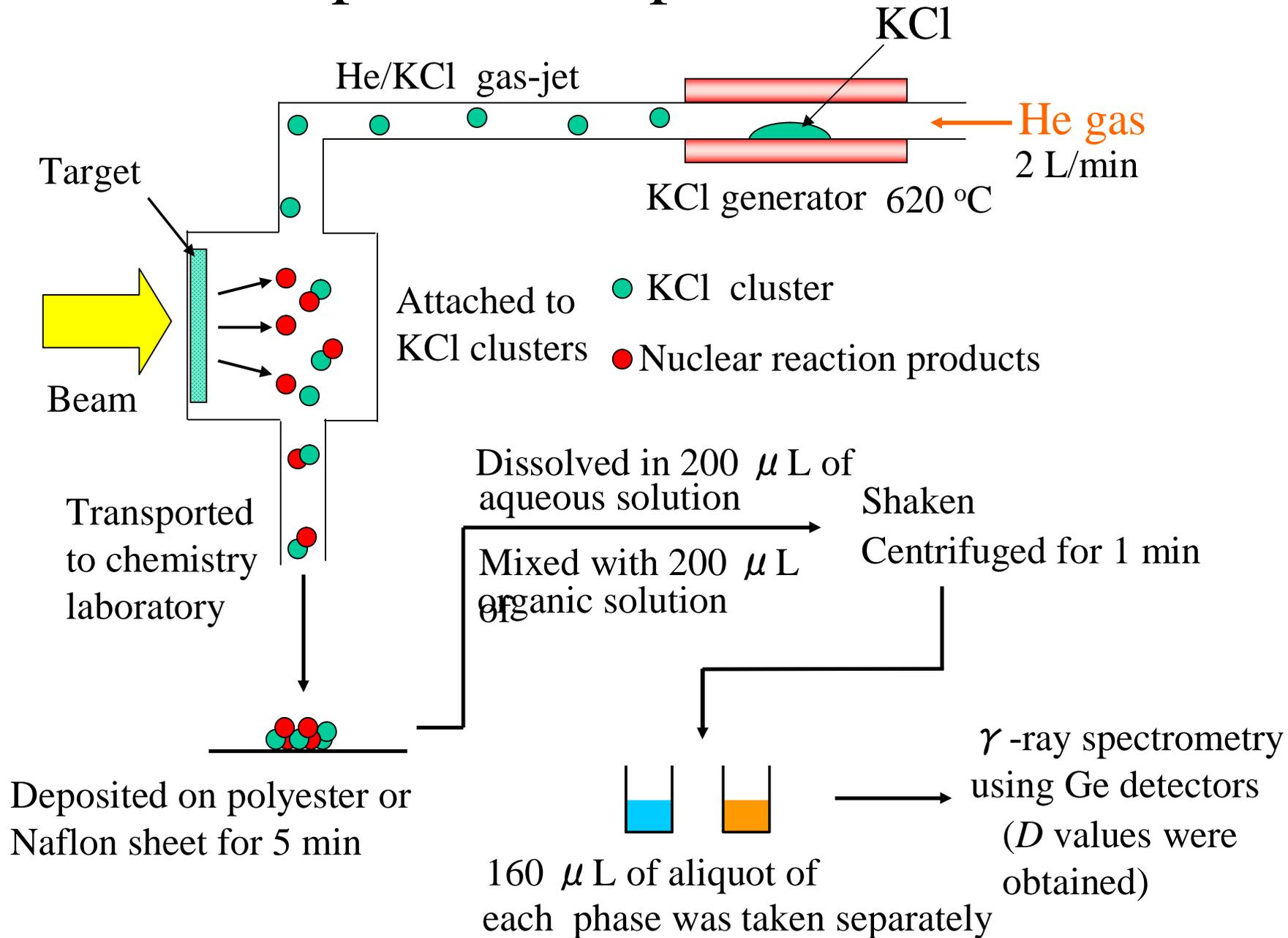
Aqueous phase: HCl (Wako for Ultratrace analysis Mo, W < 10 ppt)

Concentration: 0.1–11 M

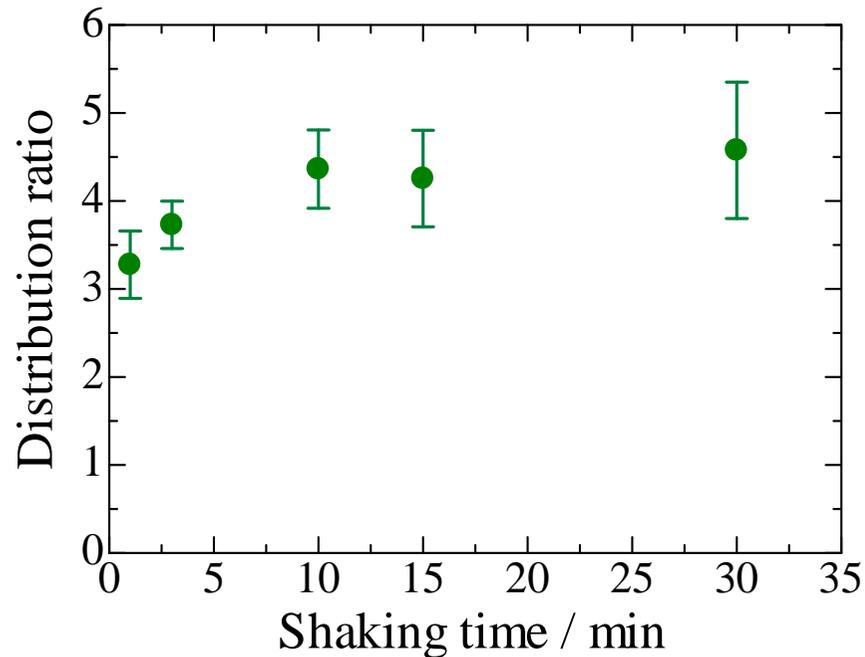
**Organic phase: 0.05 M Tetraphenylarsonium chloride
(TPAC)-chloroform solution**

0.05 M Aliquat 336-chloroform solution

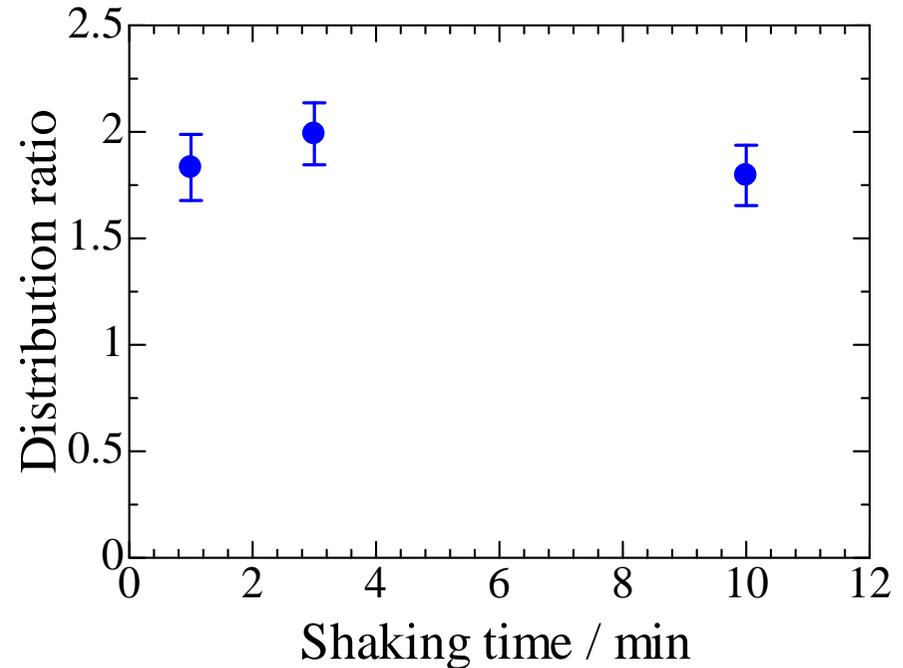
Experimental procedure



D value of Mo as a function of shaking time

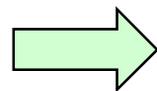


Extractant: TPAC 6 M HCl



Extractant: Aliquat 336 11 M HCl

- Mo concentration was $\sim 10^{-13}$ M (calculated from radioactivity)
- Extraction equilibrium is obtained within 10 min (TPAC) or 1 min (Aliquat 336)

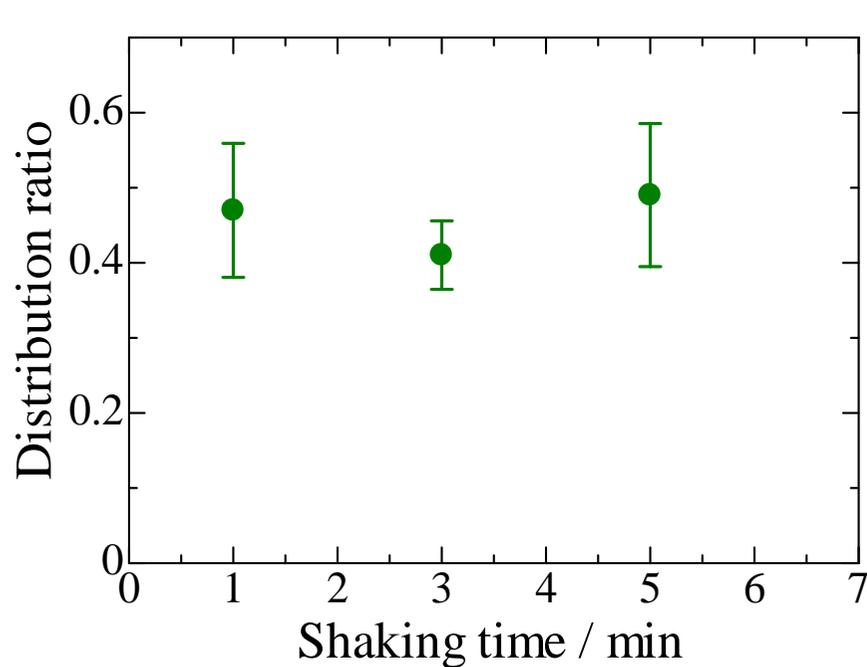


Shaking time for Mo in subsequent experiments :

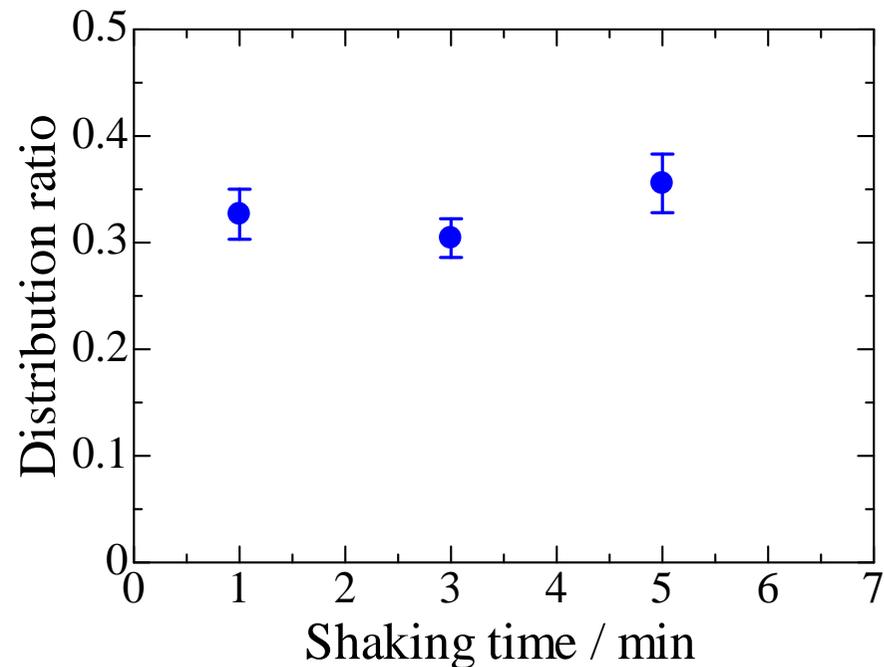
15 min (TPAC) or 3 min (Aliquat 336)

Extraction equilibrium of Mo with TPAC is slow

D value of W as a function of shaking time

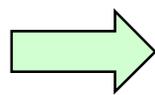


Extractant: TPAC 11 M HCl



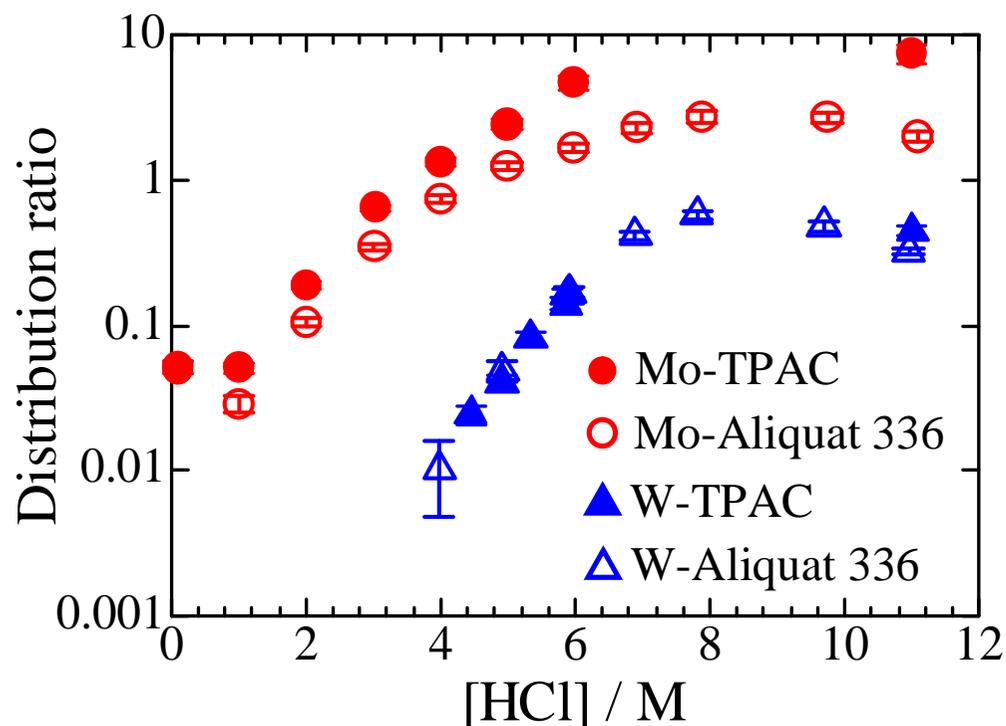
Extractant: Aliquat 336 11 M HCl

- W concentration was $\sim 10^{-13}$ M (calculated from radioactivity)
- Extraction equilibrium is obtained within 1 min with both extractants

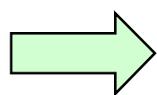


3 minutes are selected as shaking time for W in subsequent experiments

Dependence of D values on HCl concentration



- D values of Mo and W increase with an increase of HCl concentration



The anionic chloride complexes of Mo and W are formed

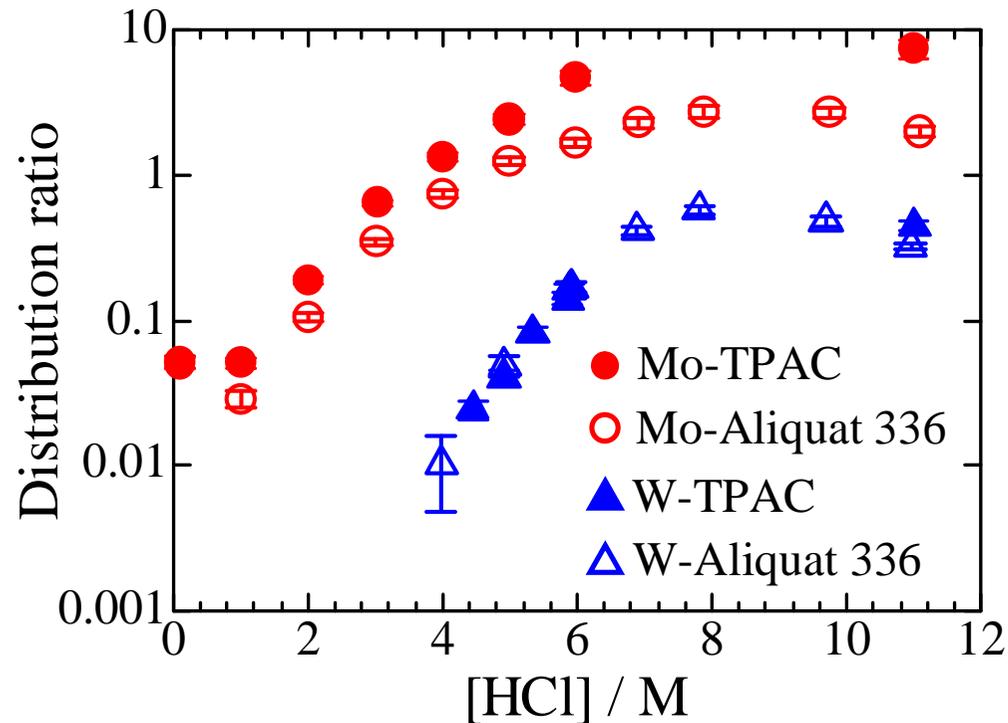
Expected extracted species: $\text{MoO}_2\text{Cl}_3^-$, $\text{MoO}_2\text{Cl}_4^{2-}$

WO_2Cl_3^- , $\text{WO}_2\text{Cl}_4^{2-}$, WCl_5^-

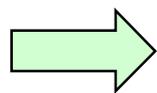
(anion exchange, absorption spectrum measurement)

J. Am. Chem. Soc. **77**, 3972 (1955). J. South Afr. Chem. Inst. **19**, 11 (1966). J. Radioanal. Nucl. Chem. **142**, 373 (1990.)

Dependence of D values on HCl concentration



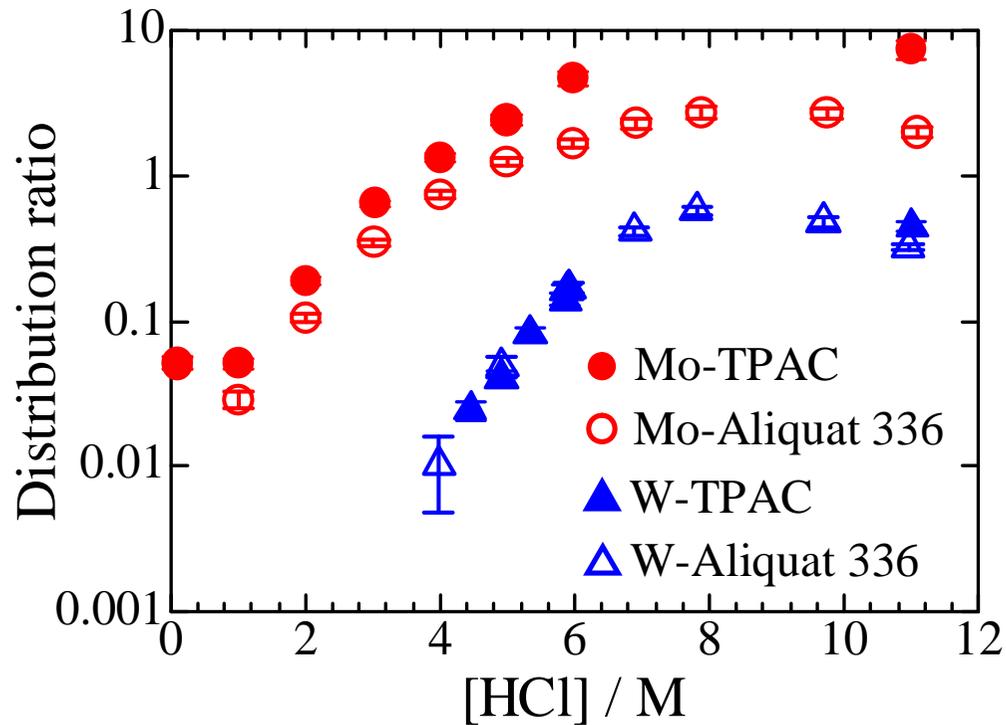
- W is little extracted in 0.1–4 M HCl



W exists as cationic and/or neutral species in the HCl concentration range

- Extraction of Mo is observed in all studied HCl concentration

Dependence of D values on HCl concentration

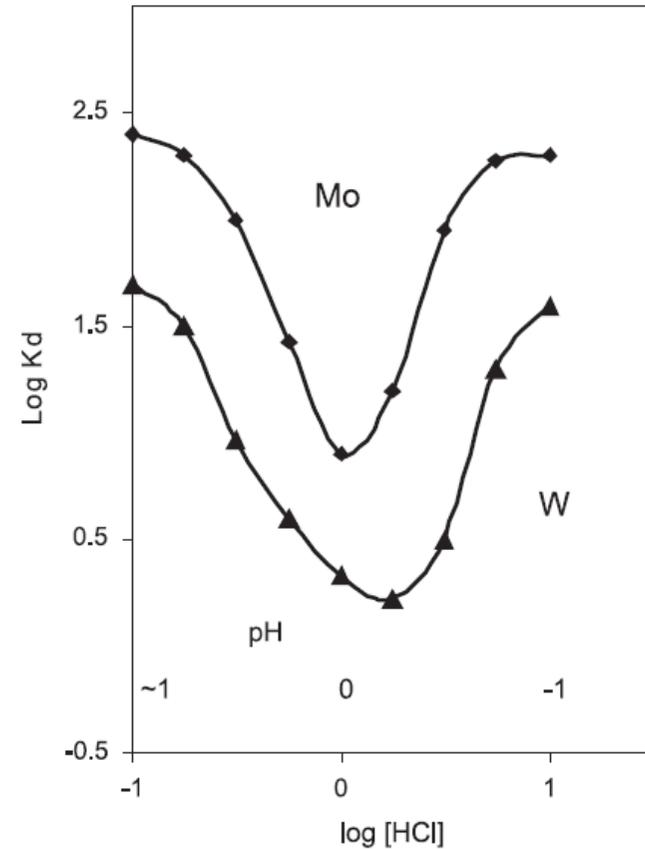


• The D value of Mo is greater than that of W under the studied conditions

- Present results are consistent with previous anion exchange study

- The trend in the chloride complex formation is Mo > W?

- It is required to determine the extracted species for investigation of the trend in the chloride complex formation



Result of previous anion exchange experiment

Radiochim. Acta **92**, 455 (2004).

J. Radioanal. Nucl. Chem. **142**, 373 (1990).

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Aqueous phase: 11.1 M HCl (Wako for Ultratrace analysis
Mo, W < 10 ppt)

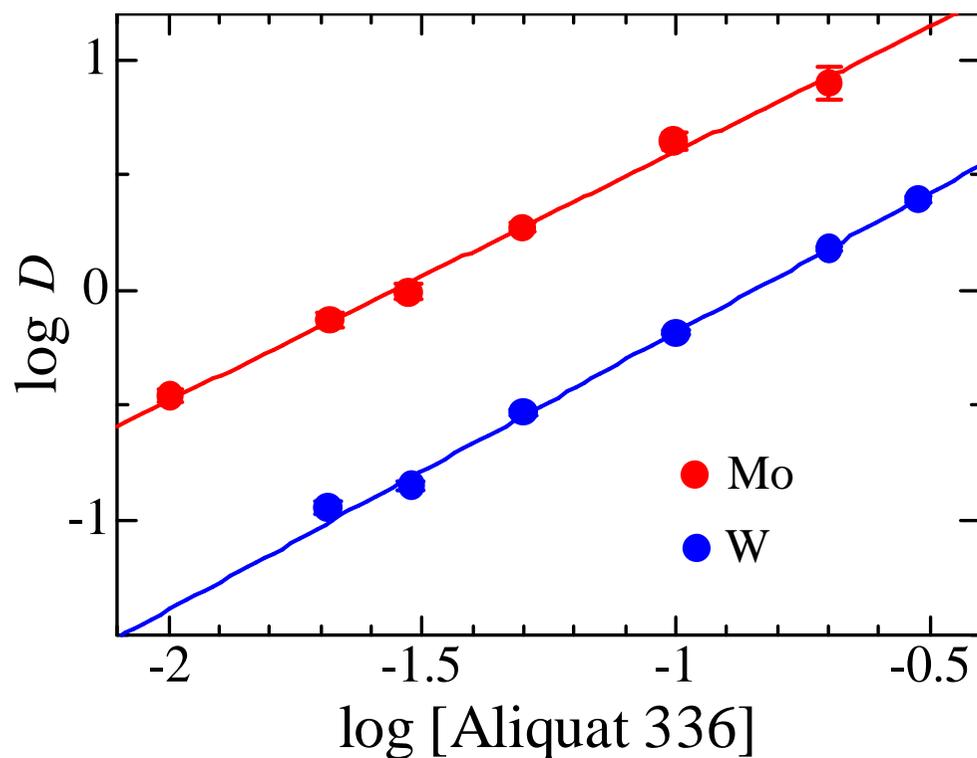
Organic phase: Aliquat 336-chloroform solution

Extractant concentration 0.01–0.2 M (Mo)
0.02–0.3 M (W)

Experimental procedure

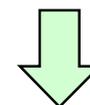
Nuclear reaction products were transported by He/KCl gas-jet system
and extracted by batch method

Result and discussion



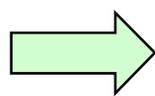
Slopes of the straight lines

Mo: 1.08 ± 0.04 W: 1.21 ± 0.02



The net charges of mainly extracted species are both -1

Expected extracted species Mo: $\text{MoO}_2\text{Cl}_3^-$
W: WO_2Cl_3^- , WOC_5^-

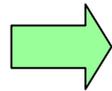


It is required to investigate the number of chloride ion related to extraction process

Summary

▪ Ion-pair extraction behavior of carrier-free Mo and W from 0.1–11 M HCl solution was investigated for the chemical experiment of Sg

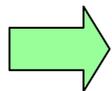
- The anionic chloride complexes of Mo and W are formed



- W exist as cationic and/or neutral species in 0.1–4 M HCl

- The D value of Mo is greater than that of W under the studied conditions

▪ Dependence of D values of Mo and W on extractant concentration was studied to investigate the charge of extracted species



The net charges of mainly extracted species of Mo and W are both -1

Expected extracted species Mo: $\text{MoO}_2\text{Cl}_3^-$
W: WO_2Cl_3^- , WOC_5^-

Future work

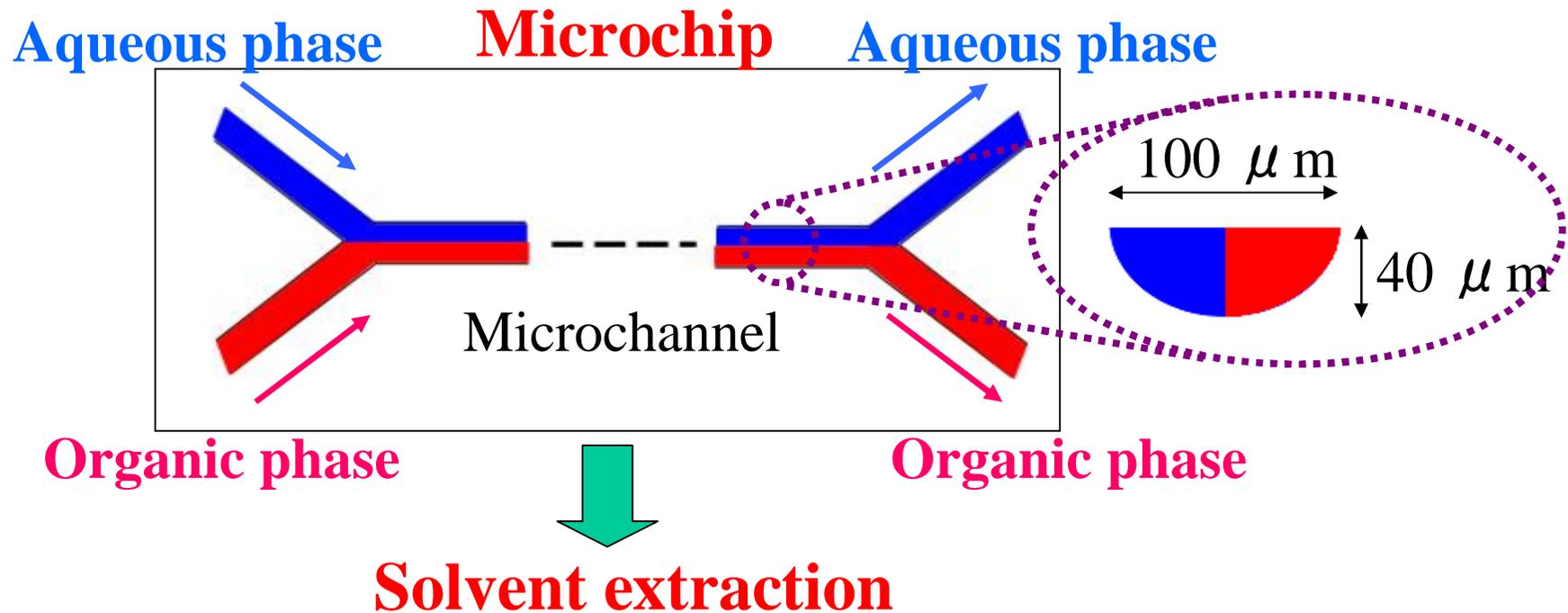
- Further speciation analysis of extracted species of Mo and W

→ *D* values will be studied as a function of chloride ion concentration under constant proton concentration

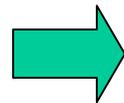
- Investigation of redox behavior of Mo and W in HCl solution for reduction experiment of Sg

Microchip extraction

We are developing a solvent extraction apparatus with microchips

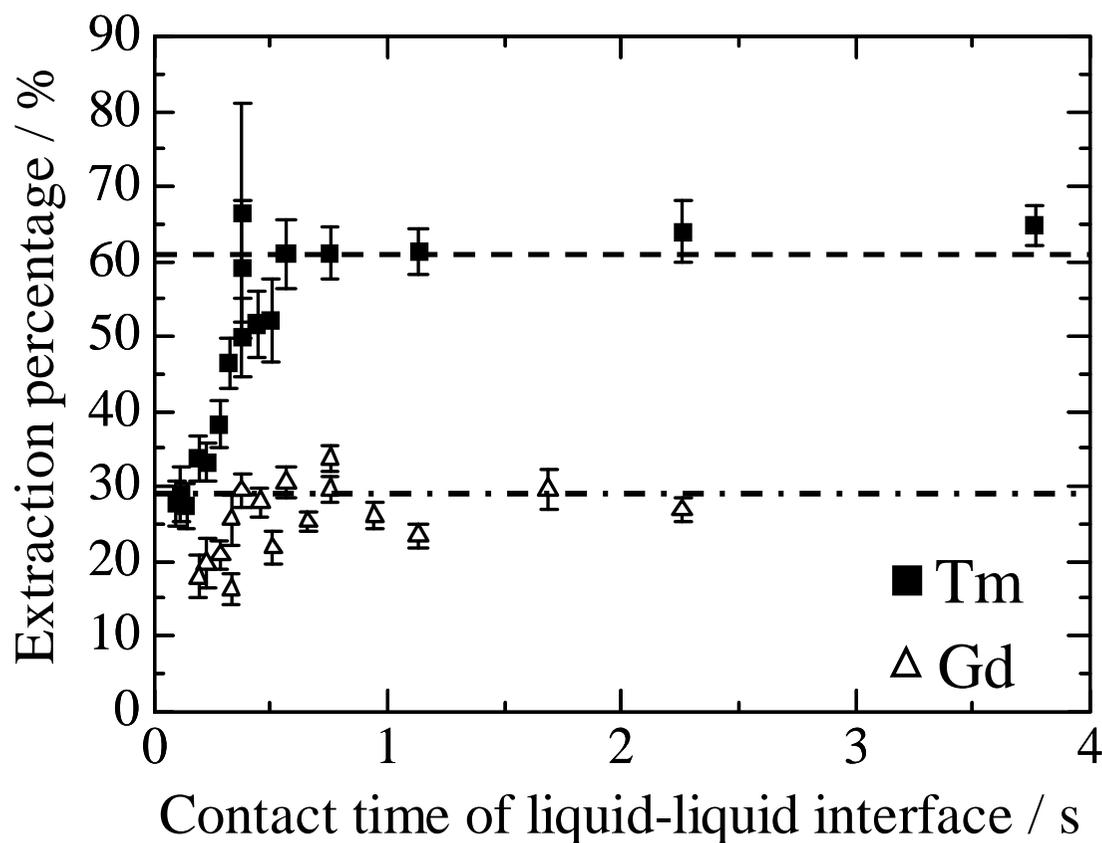


Short diffusion length
Large specific interfacial area



Solvent extraction equilibrium
is rapidly achieved.

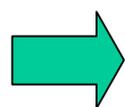
Microchip extraction



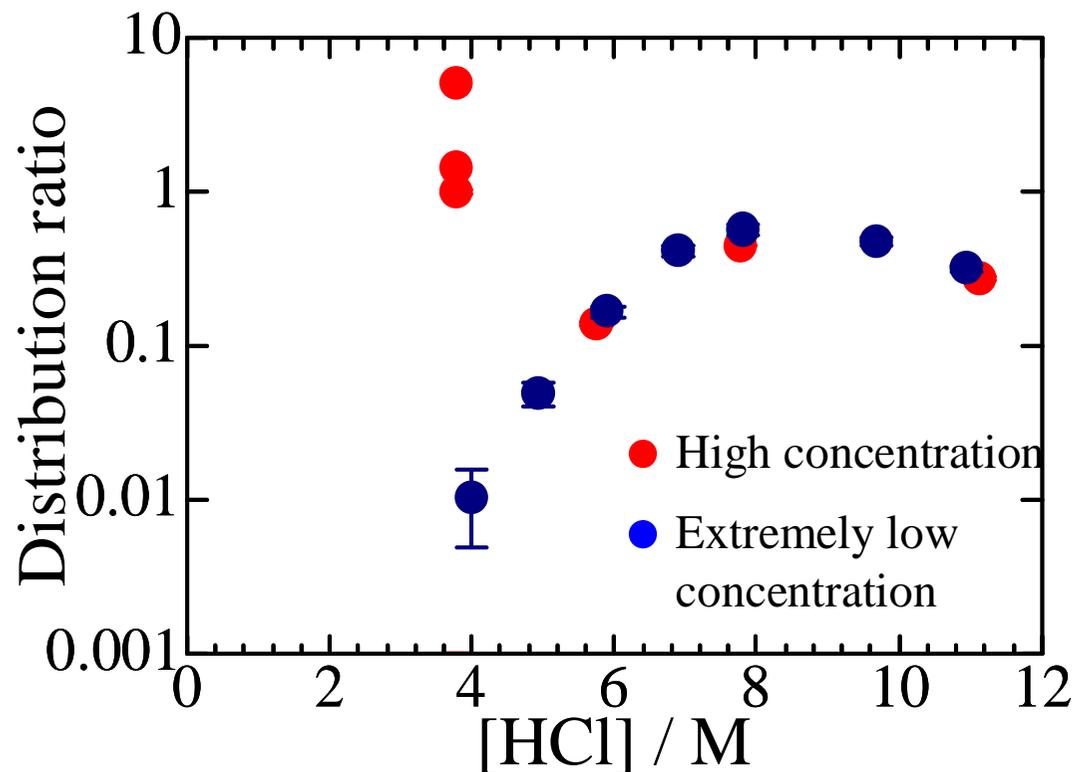
Aqueous phase: acetic acid-sodium acetate buffer solution (pH 4.5)

Organic phase: 0.04 M 2-thenoyltrifluoroacetone-toluene solution

Extraction equilibria of lanthanides were attained **within about 1 s**.



Extraction of Mo and W with Aliquat 336 using microchips will be performed for future Sg experiment



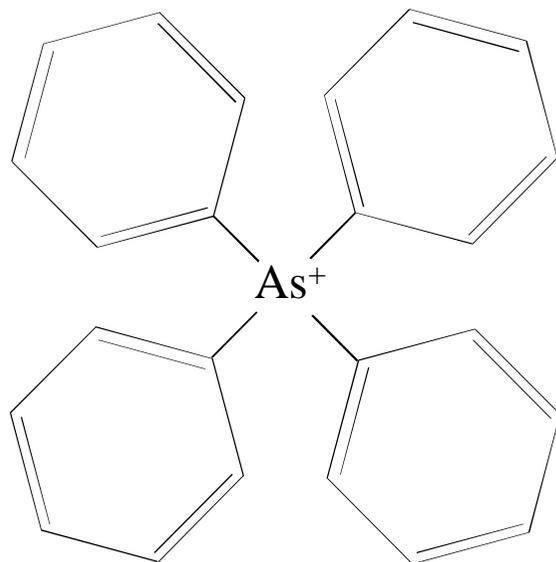
Extractions of W under high and extremely low concentration with 0.05 M Aliquat 336-chloroform

W concentration (extremely low concentration): 10^{-13} M

W concentration (high concentration)

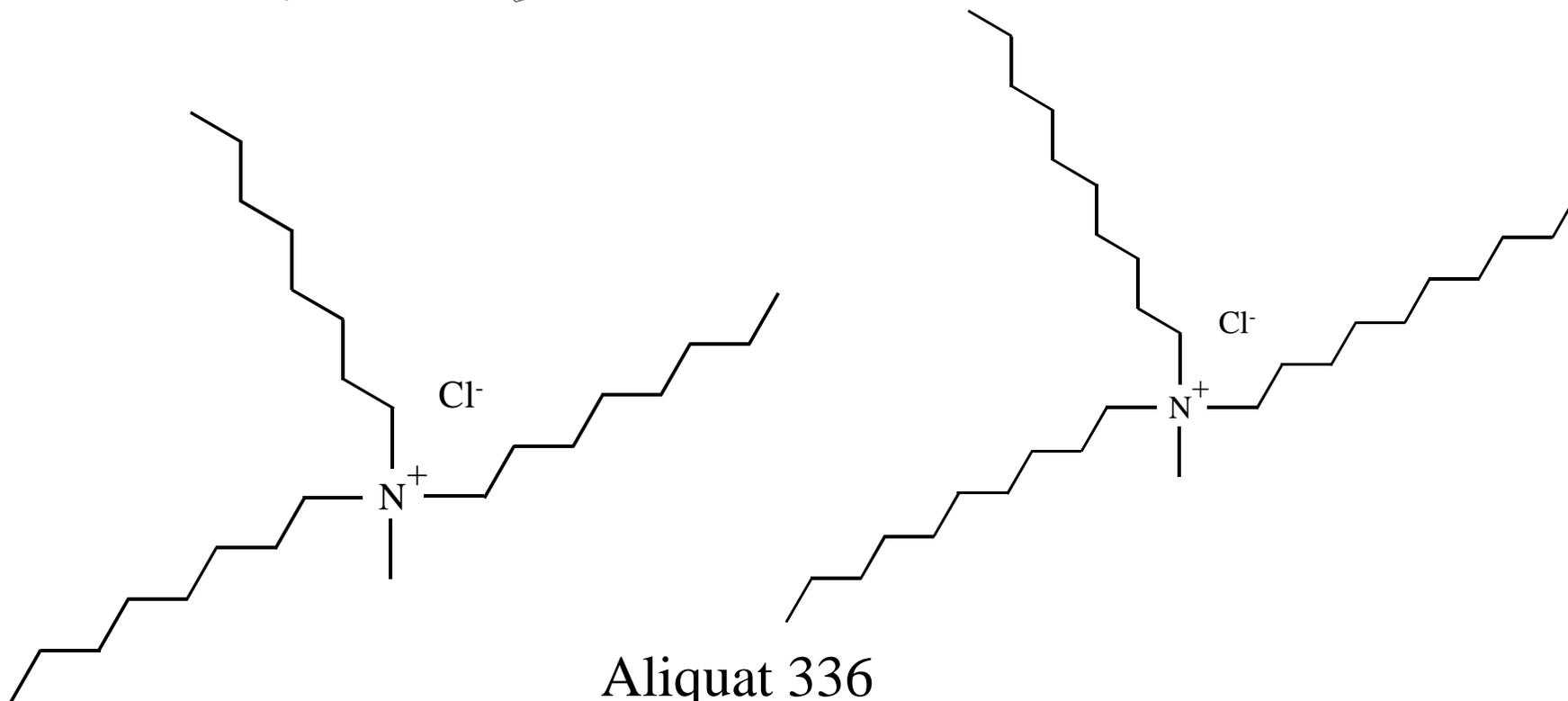
8×10^{-3} M (11.14 M HCl) 1×10^{-3} M (7.77 M HCl)

1×10^{-4} M (5.74 M HCl) 7×10^{-5} M (3.78 M HCl)



Tetraphenylarsonium chloride

Cl⁻



Aliquat 336

$$D = \frac{A_o V_a}{A_a V_o}$$

A_o ... Radioactivity in organic phase

A_a ... Radioactivity in aqueous phase

V_o ... Volume of organic phase

V_a ... Volume of aqueous phase