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摘要： (microemulsion) 、， 。，，(reversed micelle)。， 。 (W/O) 。：(1) 、， W/O ；(2) ，，，。，。、。，，。， 。

关键词： ；；；；
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Research Progress on Extraction of Metal Ions by Reversed Micelles and Microemulsions

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Abstract: Microemulsion systems have been widely studied in the field of extraction and separation due to their advantages of large specific surface area, convenient separation and good solubilization. In the extraction process, the extractants combine with metal ions to form complexes, which further aggregate to form reversed micelles. With an increase in the concentration of metal ion, the reversed micelles might undergo a structural change or even secondary assembly. Considering that the extraction process can be also based on the

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designed water-in-oil (W/O) microemulsion, the extraction mechanism is divided into two types: (1) A typical extractant, which is saponified or protonated, or a conventional surfactant act as the main component constructing the W/O microemulsion to extract metal ions; (2) Together with a conventional surfactant, a typical extractant serves as the cosurfactant constructing the W/O microemulsion to extract metal ions, in which the former is the structural component and the latter the functional component. The mechanisms of the synergism and the formation of third phase in extraction have always been important scientific issues in the field of extraction chemistry. In this review, the mechanism of synergistic extraction and the formation of third phase in terms of reversed micelles and W/O microemulsions is clarified. In addition, the application of ionic liquid based microemulsions on extraction as well as several new separation techniques with microemulsions are introduced. In the end, the perspective of extraction concerning reversed micelles and W/O microemulsions is presented.

Key words: reversed micelles; microemulsions; extraction and separation; aggregates; the third phase

(microemulsion) 、 、 。

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、 ，

[1-5]。Winsor[6] 。 ，Neuman[11] Osseoasare[12]

， Winsor □、□、□、□(1(a))， 。Neuman

(1(b))。Jain [11] " "， -

[7] [8] ， ， -

， ： ( ) ， 。Osseoasare[12]

(bound water)、 (bulk water) (TBP) ，TBP

(trapped water)。 ，

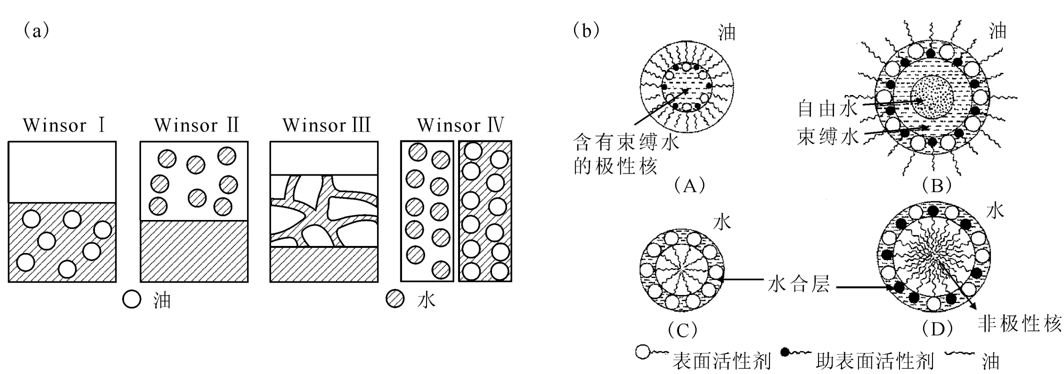
、 ， 。 ，TBP、NO_3^-、

。20 80 ，

， [9-10] [12]。 ，

。 、 、 、 、 、

， [13-14]。



(b)：(A)—— ，(B)——W/O ，(C)—— ，(D)——O/W

1 (a)、 、W/O 、 O/W (b)[6]

Fig. 1 Schematic diagrams of microemulsion phase behavior(a), reversed micelle, W/O microemulsion, micelle and O/W microemulsion(b)[6]

[12,15] Zhou[16]

Guilbaud[17]

CMC

[18]

[19]

W/O

[20-45] [27,30,36-38,46-54]

1

1 2-

1 萃取体系反相胶束的形成

1.1 金属-萃取剂配合物

-

1

Table 1 Reversed micelles formed by different extractants with lanthanides and actinides

Cyanex 301	Ln		[20-22]
DEHiBA	U		[48]
D2EHAA	Th, U		[54]
DMDOHEMA	Ln		[23-25,44]
DMDBTDMA	Ce		[26]
DNPPA	Eu, U		[27]
HDEHP	Th		[52-53]
HDEHP	Lu		[28]
HDEHP	Nd		[29]
HDEHP-DMDOHEMA	Ce, Nd, Eu, Am		[30]
HDEHP-DMDOHEMA	Nd, Eu		[31-32]
TBP	Ce		[33-34]
TEHDGA	Nd		[35]
TEHDGA	Eu		[36]
TODGA	Eu		[37-38]
TODGA	Nd		[39]
TODGA	Ln		[40-41]
TODGA	Ln		[42]
TODGA	Am		[37-38]
TODGA	Am		[51]
TBP	U		[50]
TBP-HDBP	Dy		[43,45]

2,4,4- (Cyanex 301) N,N-2- (DEHiBA) 2- (D2EHAA) N,N′- -N,N′- (DMDOHEMA) N,N′- -N,N′- (DMDBTDMA) (DNPPA) - 2- (TEHDGA)

(HDEHP)、 (TBP)、N,N,N',N'- -3- (TODGA)
。 - ,
。
。[20-21]
(2,4,4-)
(Cyanex 301) ,
($c(NaOH)/c(\text{Cyanex 301})\leqslant 10\%$)
。 ,
Nd(□) Cyanex 301 S 。
,Nd(□) ,
Nd(□) S , O
。
S ,
O ,
。Marie[55] TALSPEAK
HDEHP
。 ,
$Ln(DEHP\cdot HDEHP)_3$ $Ln_2(L)_2(HDEHP)_4$
(L)。Ellis[44]
DMDOHEMA
。
, ,NO_3^- Ln(□)
; ,
,NO_3^- Ln(□) 。 ,Ellis
[23,26,28,33-34,40-42,45]
,
。

, (
Am^{3+}、Th^{4+}、UO_2^{2+})
[27,30,36-38,46-54]。 [52]
HDEHP Th^{4+} ,NO_3^-
H_2O 。
,Th^{4+} $Th(DEHP)_3NO_3$,
NO_3^- ,H_2O NO_3^-
$Th(DEHP)_3NO_3$ 。 Th^{4+}
, L、 X
$M(X)_n\cdot yL$ [30,37-38,47]。

1.2 聚集体状态

、
、 、
。HDEHP
$(HDEHP)_2$, 。
HDEHP ,
。
, Neuman[11]
, [56]
。 Ş

,2 nm

,

2 nm

。 [38,54],

Am(□)、U(□)

, Am(□)、U(□)

。 ,

HNO_3

[27,38], ,

HNO_3 ,

。

。

。 1987 Thiy-

agarajan [57] X (SANS)

$Co(DEHP)_2$ 。

Pr^{3+} -*N*,*N*-

(CMPO) ,

CMPO 。Chiarizia

, [58] (2-) (H_2DEH

[MDP]) Fe^{3+}

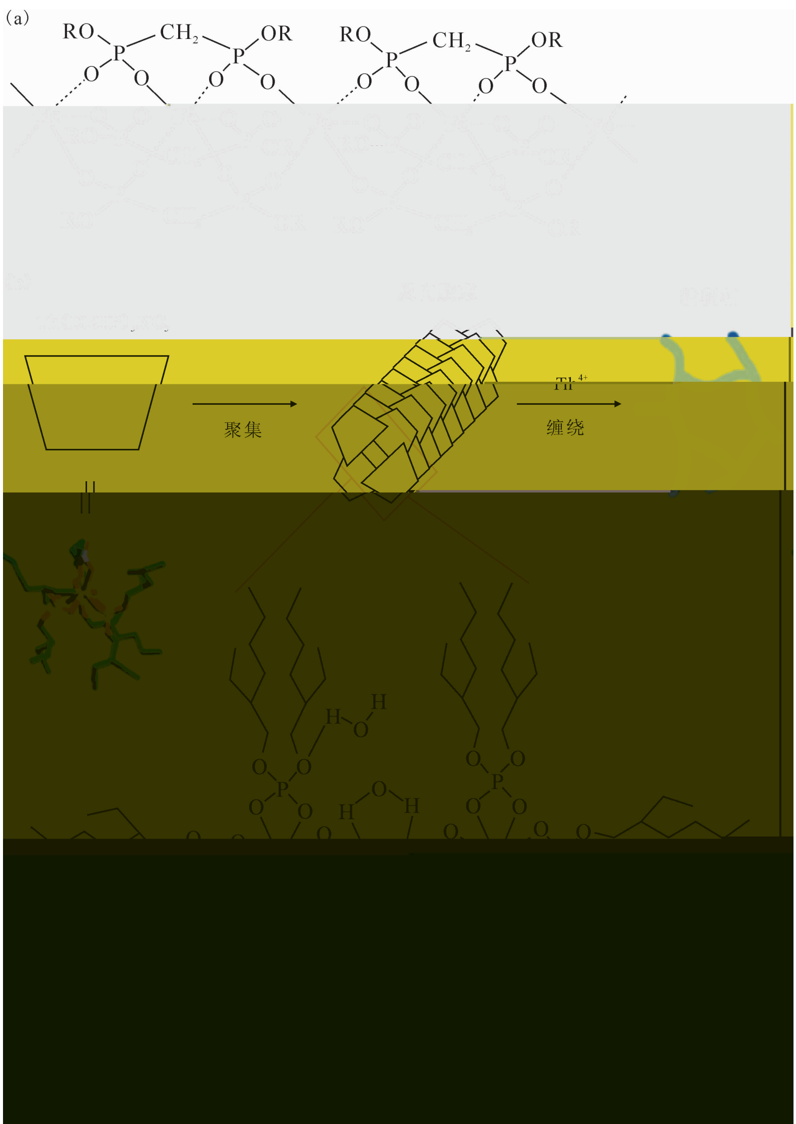
,H_2DEH[MDP] ,

P ═ O Fe^{3+}

,Fe^{3+} ,

H_2DEH[MDP] , (3

(a)), 。



3 H_2DEH[MDP] Fe^{3+} (a)[58]、HDEHP Th^{4+} (b)[52]

Fig. 3 Schematic diagrams of rod-like micelles formed by H_2DEH[MDP] and Fe^{3+} (a)[58], rod-like micelles and worm-like micelles formed after extraction of Th^{4+} by HDEHP(b)[52]

[52] Th^{4+} (HDEHP) (HDEHP , TBP) 。 Th^{4+} ,$Th(DEHP)_3NO_3$, 。 Th^{4+} , W/O 。 , (3(b))。 ((2-) “ (AOT)) 。 ” [59]。 -*N*, W/O , *N*- (CMPO) 。 UO_2^{2+} , 。 ,

2 W/O 型微乳液萃取机理

, 。 。 4。 , , 。

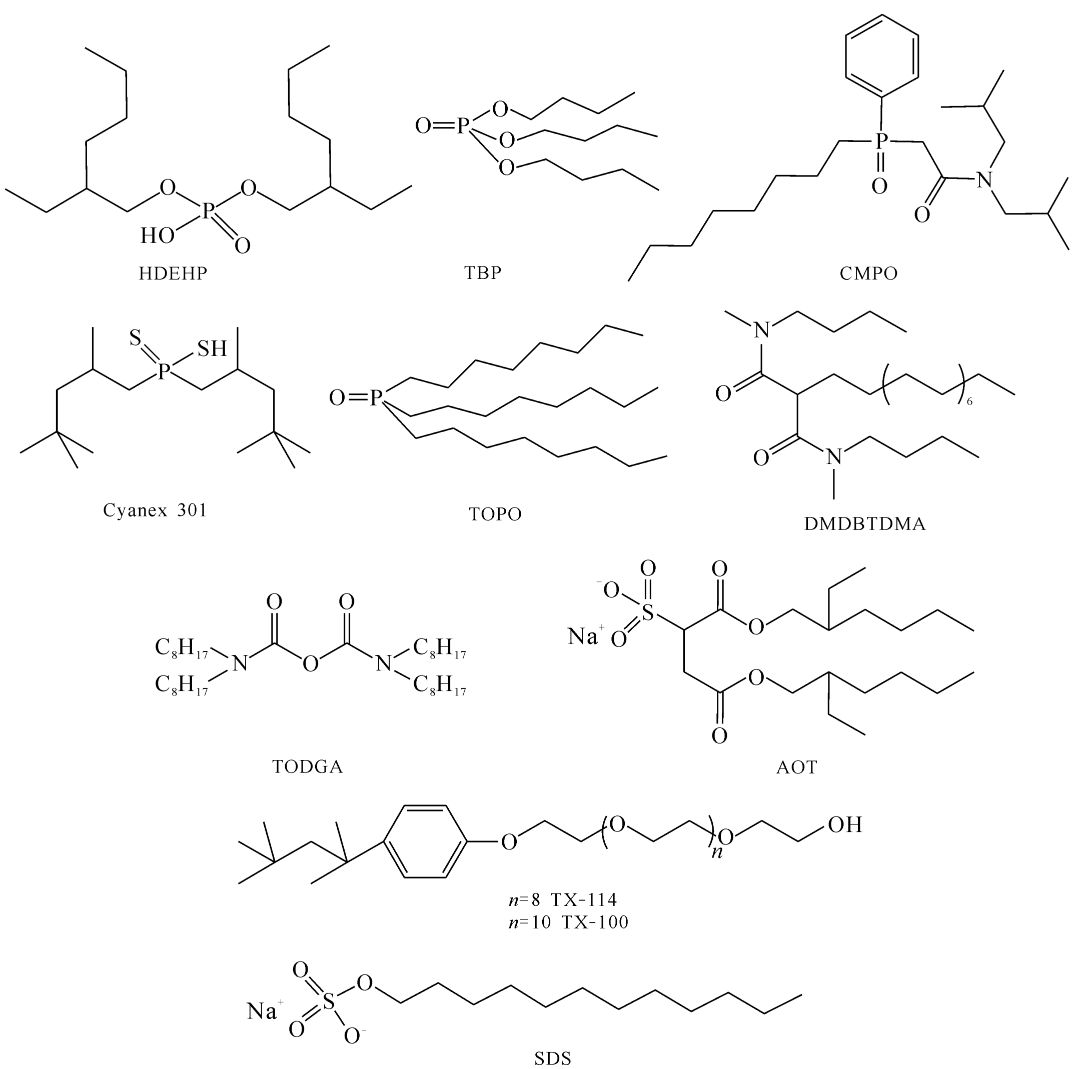


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Fig. 4 Schematic representation of typical extractants and conventional surfactants used in microemulsion based extraction

2.1 微乳液萃取机理一

20 80 , [9-10] 、

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NH_4^+

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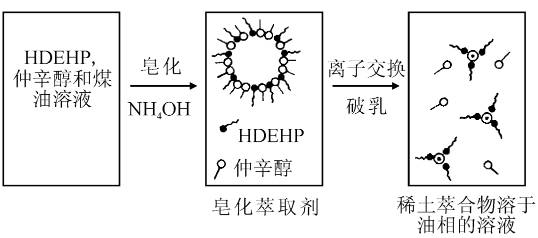
。 ,

, ,

, 5[9]。



5 HDEHP [9]

Fig. 5 Schematic diagram of rare earth ions extraction by HDEHP after saponification[9]

W/O

。 ,

。Pal [60]

AOT Li^+ 、

Na^+、K^+、Cs^+ 。 ,

Cs^+ Na^+

。

(CTAB)

, Au(□)、

Mo(□)、Re(□) [61-62]。

,

。

2.2 微乳液萃取机理二

W/O

(CTAB[61,63])、

(AOT[64-65])、 (

(Brij 30)[66]、

(TX-100)[67])。 ,

、

[45,61,68-69]。Naganawa [64]

AOT W/O ,CMPO 。

Ln^{3+} , AOT,

AOT H^+ 、

。 CMPO ,H^+ AOT

CMPO , H^+-CMPO

,

(6[64])。CMPO

, Ln^{3+}-CMPO

AOT

, ,

, (6[64])。 [53]

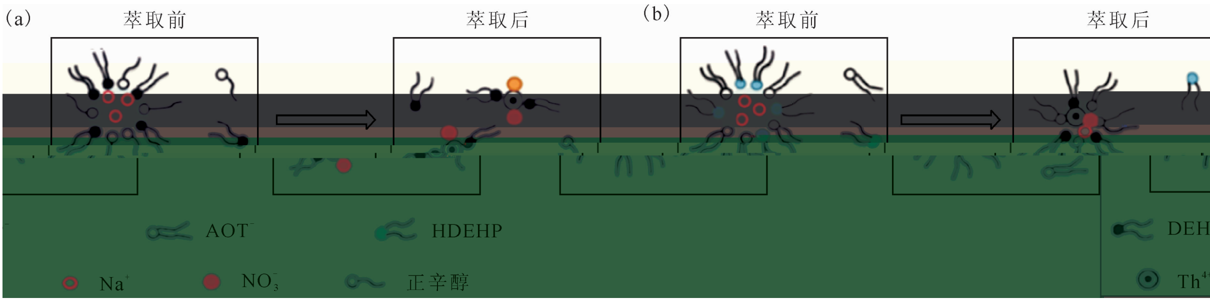
AOT

Th^{4+} , AOT

NaDEHP Th^{4+} ,

AOT AOT-HDEHP Th^{4+}

,



7 NaDEHP(a) AOT-HDEHP(b) Th^{4+} [

，

，

。 PUREX ，

TBP

。 ，

， PUREX

。 ，Plaue [71] TBP/

HNO_3/

，

“ ” 。

， ，

。

4.1 第三相形成的机理

，

， [12,19,72]。

，Osseoasare[12] TBP

，

。Erlinger [73] ，

SANS N，N′- -N，N′-

(DMDBTDMA)

。 ， (HNO_3、

H_2SO_4、HCl)

[74-75]。Ellis [76] ：

；

，

，

(9(a))。

HNO_3-

TBP- ，

[77-78]， 9(b) ，60% TBP -

。

4.2 微乳液及第三相的表征手段

， 、 、

、 、

。Gradzielski[18]

。

， 。

，

[79]、DLS[80]、 (SANS)[81-82]、

X (SAXS)[45]、 [83-85]、

[86]、 [32,87]、 (、

)[83,88-89] 。DLS、 、

。DLS

。 ，

，

(κ)

。

， (Cryo-TEM)

(FF-TEM)， ，

，

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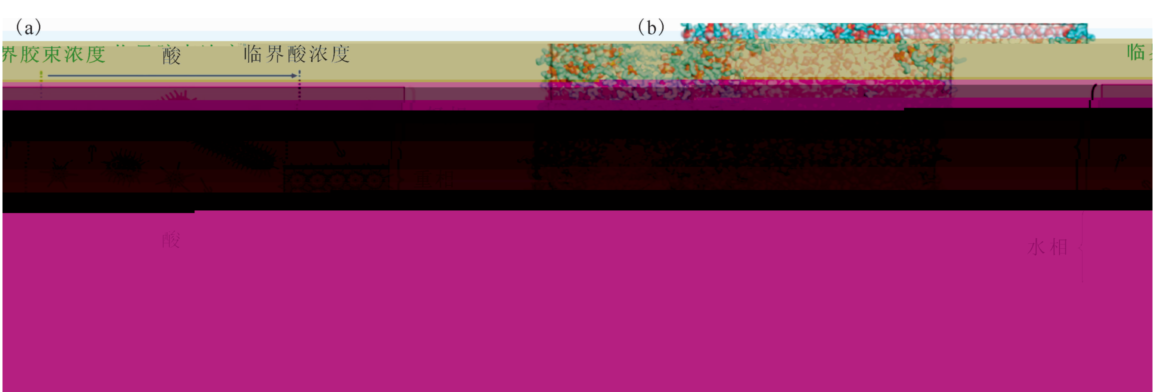


9 TBP/CMPO- (a)[76] TBP- (b)[78]

Fig. 9 Formation procedure of the third phase in TBP/CMPO-*n*-dodecane system(a)[76] and molecular dynamic simulation of bicontinuous phases in TBP-*n*-dodecane system(b)[78]

[19]

Subbuthai[90] TBP UO_2^{2+}

100 □ 300

percolation phenomenon

4.3 影响第三相形成的因素

LOC

LOC

Pathak[91]

TBP

TiBP Th^{4+} TiBP

LOC TBP LOC

TsAP Th^{4+} LOC

TAP LOC

TBP

TOPO

TOPO TBP

[92]

TOPO TBPO

$C_n mimNTf_2$ ($n=2, 4, 6, 8$) UO_2^{2+}

TOPO UO_2^{2+}

$n=2, 4$

$n=6, 8$

[82]

Berthon[93]

Kedari[94] Cyanex 923 Ir □

HCl LOC

≈ > > > > >

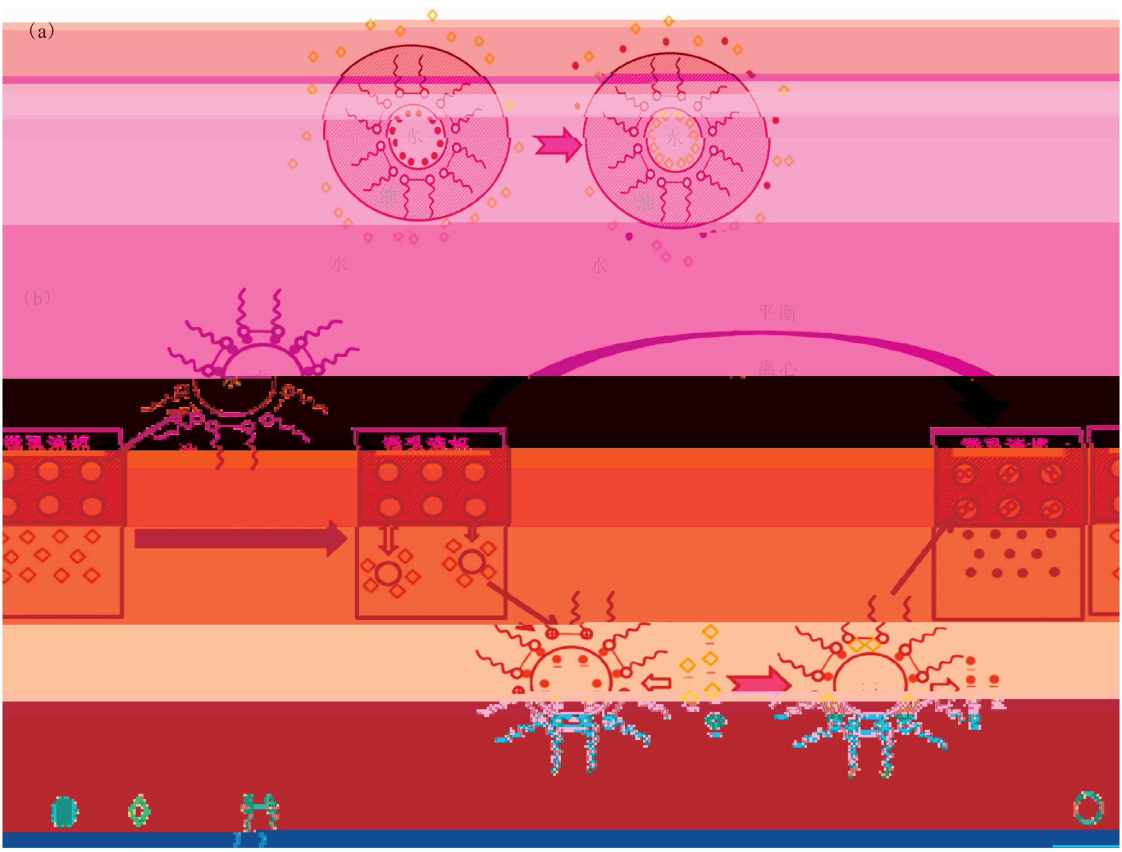
[$AuCl_4$]$^-$ ，，

Br^- （ 10(a))，，$BTMPP^-$ ，

，，$BTMPP^-$

10(b)。Dong [104] ，

[$P_{6,6,6,14}$][EHEHP] [$P_{6,6,6,14}$][BTMPP] 。



10 [C_{14}-*n*-C_{14}im]Br_2 Au(□) (a)[102]

Au(□) (b)[103]

Fig. 10 Schematic diagram of anion exchange mechanism in extraction of Au(□) by [C_{14}-*n*-C_{14}im]Br_2 microemulsion(a)[102] and extraction process of Au(□) by ionic liquid microemulsion system(b)[103]

，、

Zheng [105] [Si_4mim]Cl 。

，

Pd(□)，

，

。

6 微乳液分离新技术

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，，，

，，。，

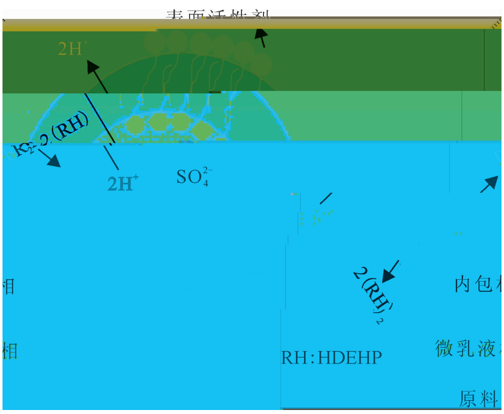
，，，

。“ ”。

、，[106]、[107]、[63] 。

，Yang [108] *N*- ，Na_2CO_3

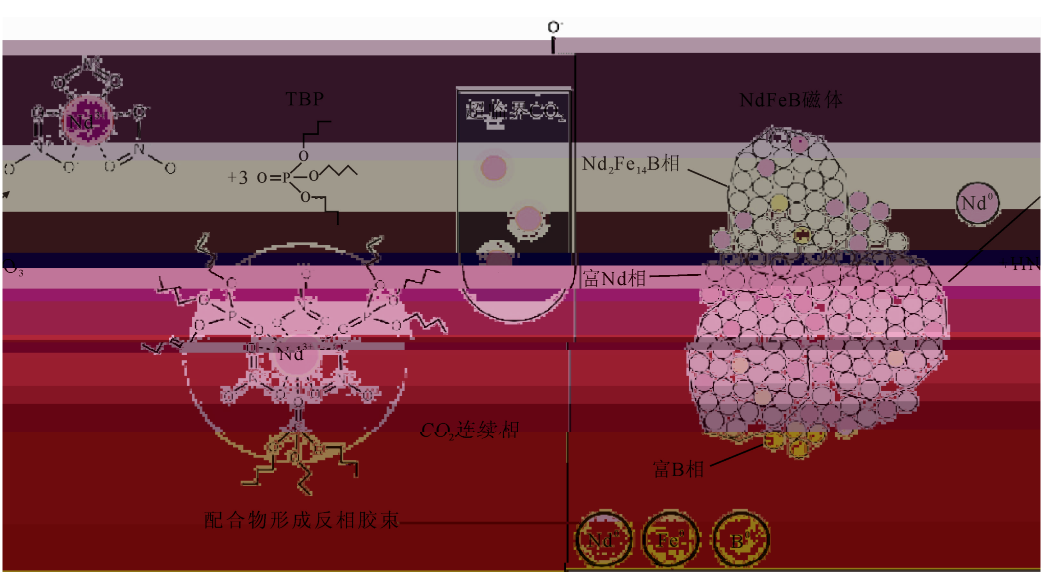
，
(Span-80)
UO_2^{2+} 。Mohammed [109] Span-
80 ， HDEHP
， Pb^{2+} ，
H_2SO_4 Pb^{2+}
（ 11）。Castro Dantas [110] /
/ ，
pH ，
Ni^{2+}、Cu^{2+}、Mn^{2+}
。 ，
、 ，
。



11 Pb^{2+} [109]

Fig. 11 Extraction mechanism of Pb^{2+} by microemulsion membrane[109]

，
， 、
，
。Nazari [111] 2-
-2- (2,4,4-)
(Cyanex 572) ，
(SDS)
(CTAB) ，
Tb^{3+}、Y^{3+}、Er^{3+}
Yb^{3+} 。
，
CO_2 CO_2
。 1987
Gale [112] AOT
， Johnston [113]
CO_2 “CO_2
” ，
[114-115]、 [114]
Sr^{2+} [116] 。Koh [117] 4-
(NP-4) CO_2
， (^{60}Co、
^{125}Sb、^{54}Mn、^{95}Zr) ， □
。Zhang [118] TBP ，
CO_2 NdFeB Nd Fe，
，NO_3^-、TBP Nd^{3+}
， CO_2
（ 12）。 ，



12 CO_2 Nd^{3+} [118]

Fig. 12 Extraction of Nd^{3+} and formation of reversed micelle in supercritical CO_2[118]

CO_2

，CO_2

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7 总结与展望

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(1) ，

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(2) W/O

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(3) ，

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(4)

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(1) ，

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(2)

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(3) ，

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FT-IR [J]. ，

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[J].

，1980，1(2)：14-22.

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