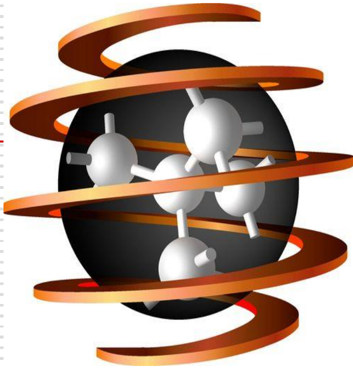
2nd World Congress and Expo on Recycling



Ionic liquids as effective carriers of precious metal ions in membrane processes from leach liquors of metal waste

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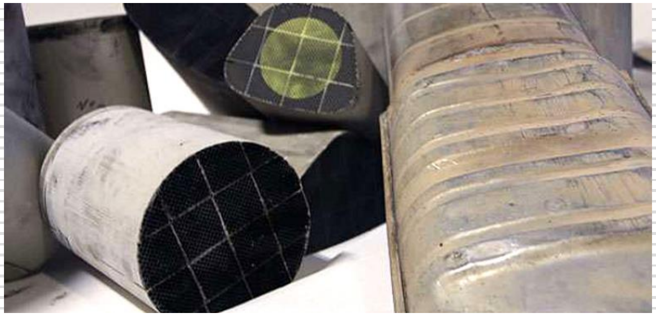
APPLICATION OF PRECIOUS METAL

- Spent catalysts contain many metals and can be important source of precious metals.



- The spent catalyst can be treat by hydrometallurgical processes. This technology is a good way to treat and recycle of the metals.

Metallic waste

LEACHING

SEPARATION OF PHASES → Waste

SOLUTION

SEPARATION OF METAL IONS

RECOVERY OF **METAL** OR **METAL COMPOUND**

SEPARATION METHODS

- adsorption
- ion exchange
- solvent extraction
- membrane processes

Liquid membranes

- bulk liquid membranes
- emulsion liquid membranes
- supported liquid membranes
- **polymer inclusion membranes**

PIM

- ✓ **transparaent, flexible and mechanically strong**
- ✓ **longer lifetime than others liquid membranes due to the reduced loss of the membrane liquid phase**

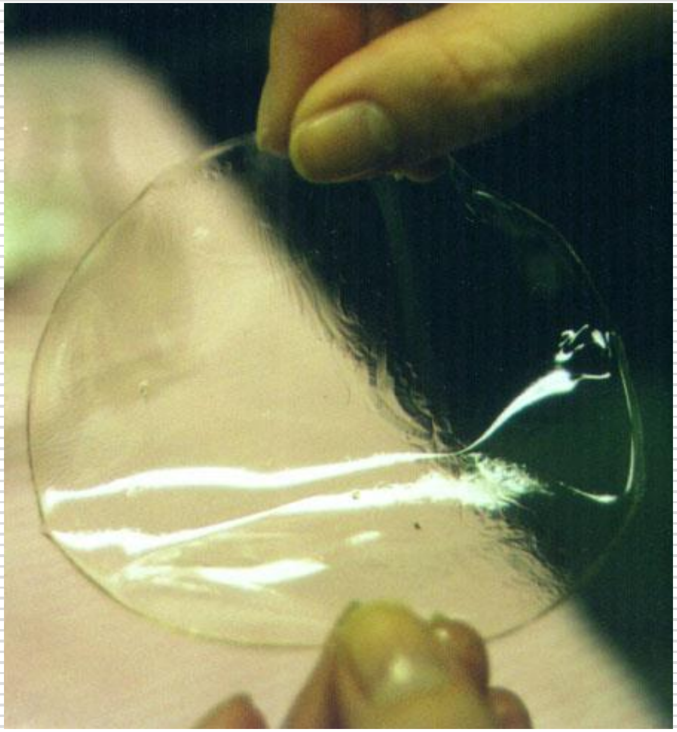


Fig. 1. Visualisation of PIM

SYNTHESIS
of polymer inclusion membranes (PIM)

- **polymer** support (cellulose triacetate, CTA)
- **plasticizer** (nitrophenyl alkyl ether)
- **ion carrier**

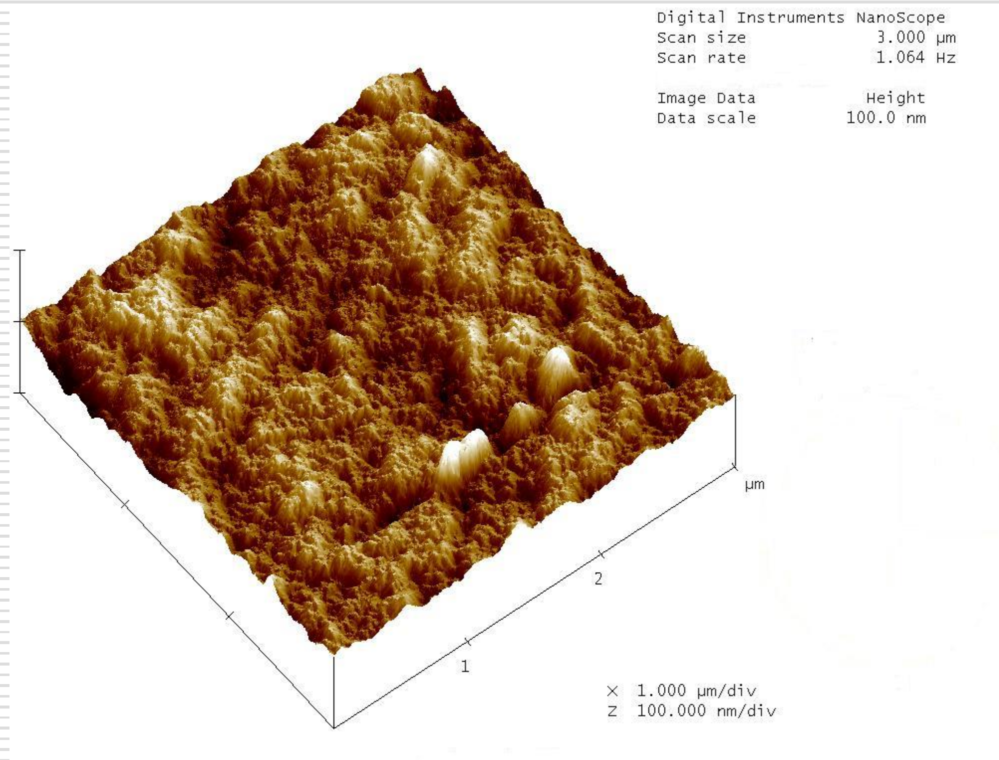


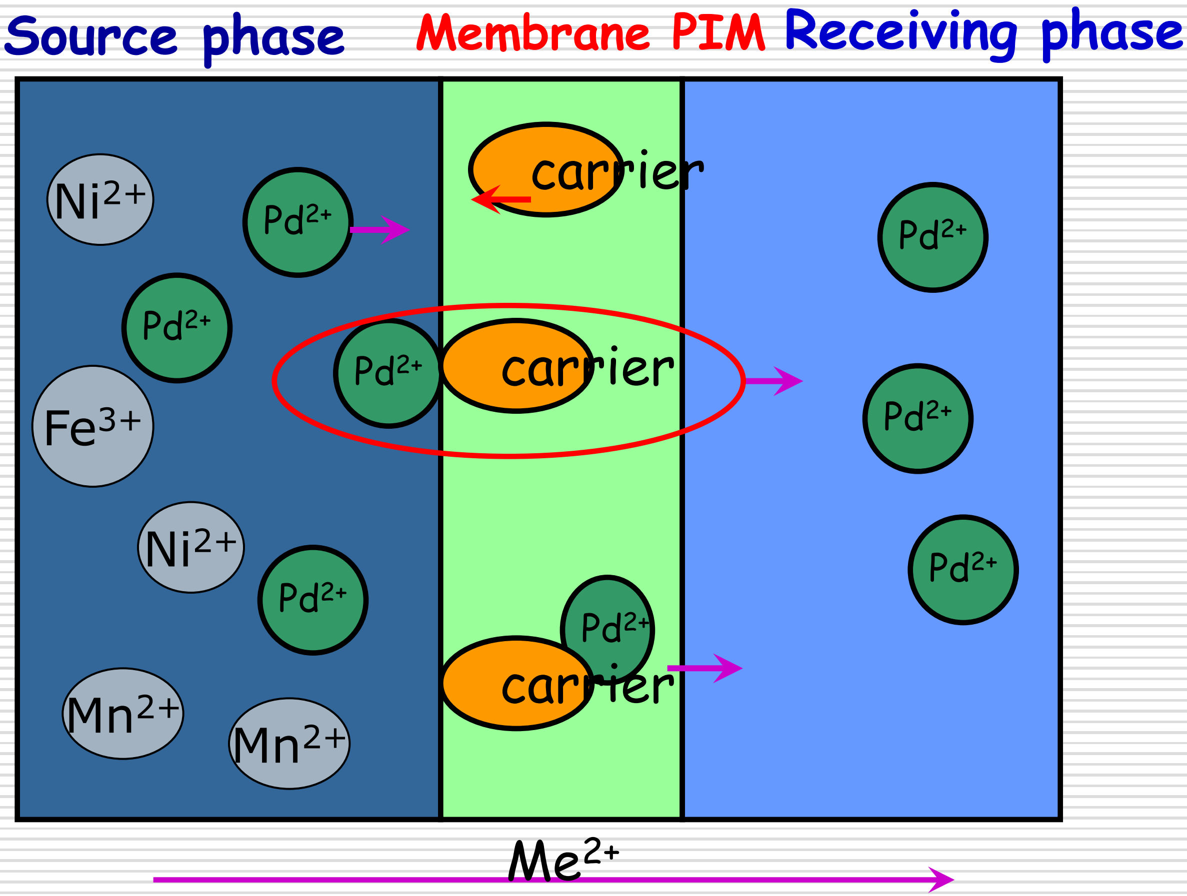
Fig. 2. Visualisation of PIM
by *Atomic Force Microscope (AFM)*

TRANSPORT PROCESS ACROSS LIQUID MEMBRANES

Polymer inclusion membrane (PIM)

separates two aqueous phases –
source phase and receiving phase.

Metal ions are transported from
-source phase (donor phase) into
-receiving phase (acceptor phase).

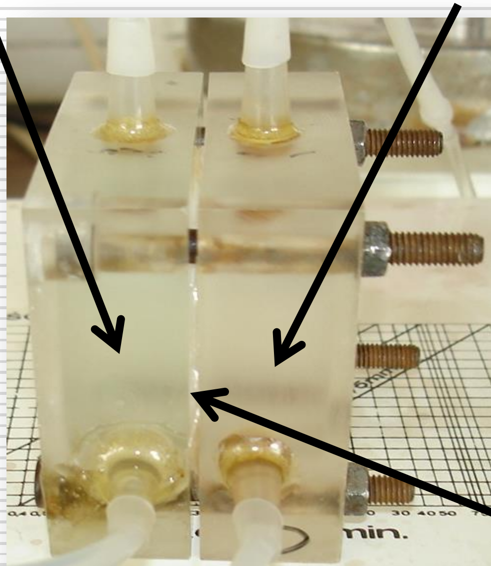


Experimental part

PIM system
for transport of metal ions

donor phase

acceptor phase



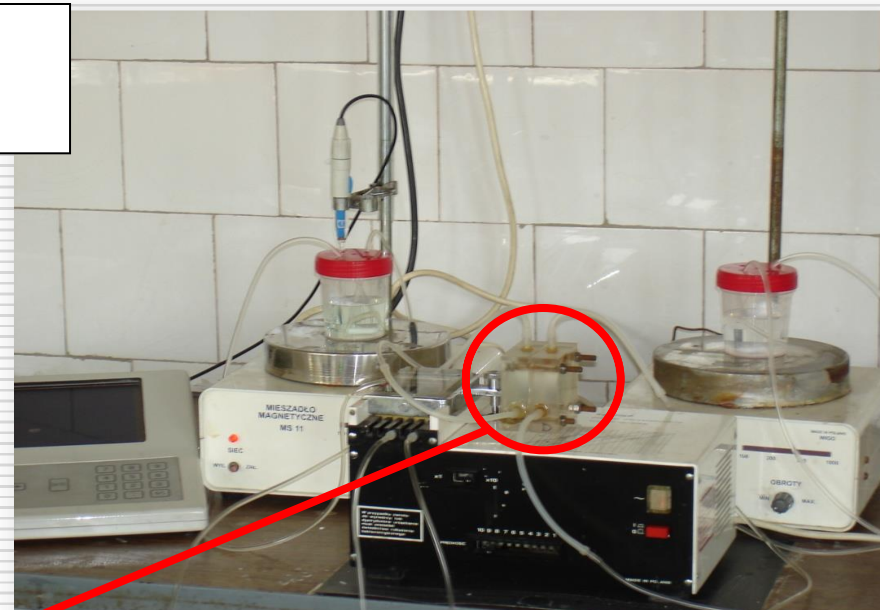


Fig.3. Set of equipment to membrane transport.

membrane

The volumes of source and receiving phases were 100 cm^3, each.
Membrane area = 12.56 cm^2

PIM

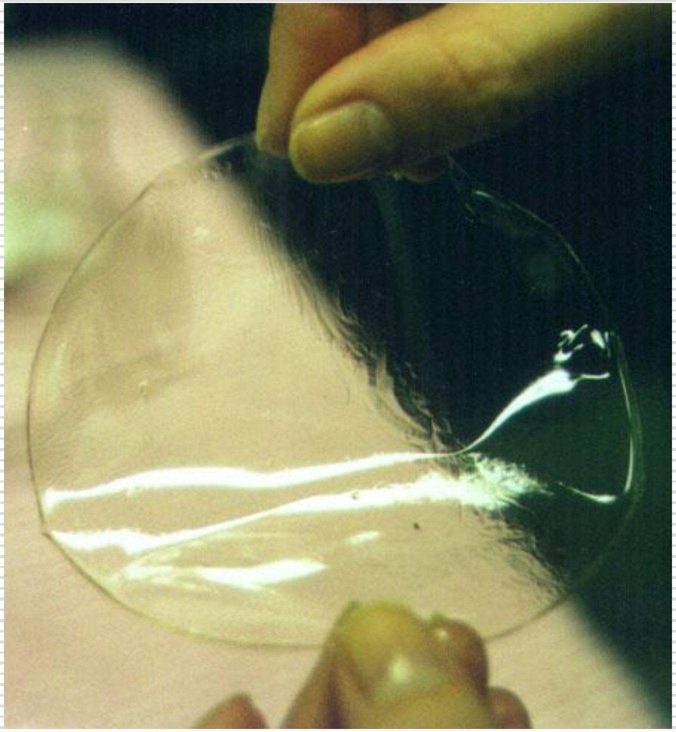
- CTA
- ONPOE
- ILs:

a) tricaprylmethylammonium thiosalicylate

- **TOMATS**

a) tetradecyl(trihexyl)phosphonium chloride

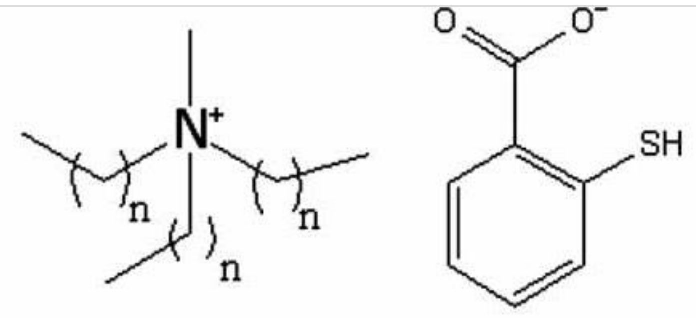
- **Cyphos IL 101**



STRUCTURE AND PROPERTIES **IONIC LIQUIDS**

Molecule of IL contains:

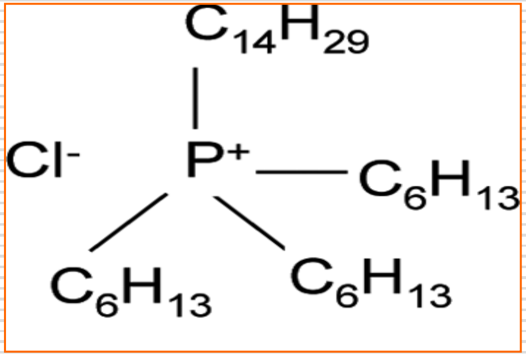
- **organic cation.**
- **anion:** organic or inorganic.



TOMATS
trioctylmethylammonium thiosalicylate

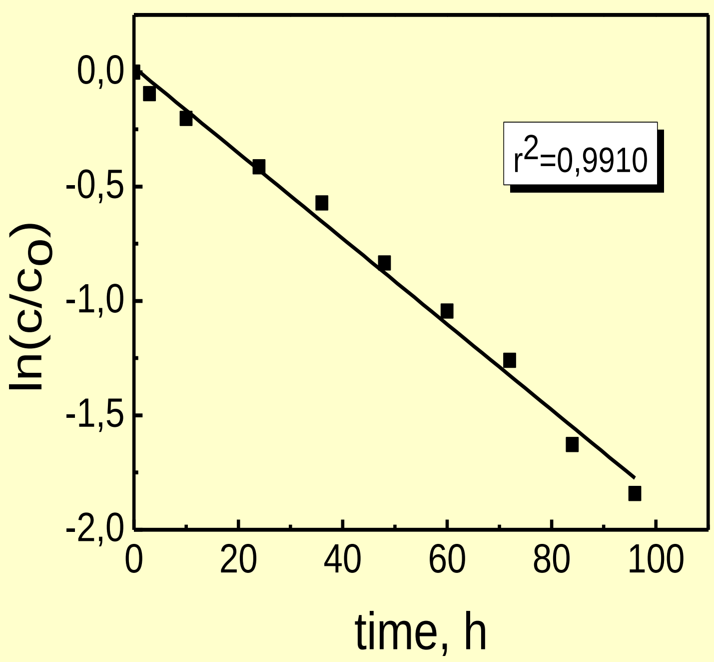
ILs have many attractive properties:

- **immeasurably low vapor pressure**
- **chemical and thermal stability**
- **nonflammability**
- **good extractability of many metal ions**



Cyphos IL 101
trihexyl(tetradecyl)-phosphonium chloride

Kinetics of transport through PIM



$$\ln\left(\frac{c}{c_0}\right) = -kt \qquad (1)$$

k – rate constant [h^{-1}]

Fig. 4. Relationship of $\ln(c/c_0)$ vs. time for metal ions transport across PIM

The permeability coefficient (P), m/s

$$P = \frac{V}{A}k \qquad (2)$$

The initial flux (J_0), mol/m²s

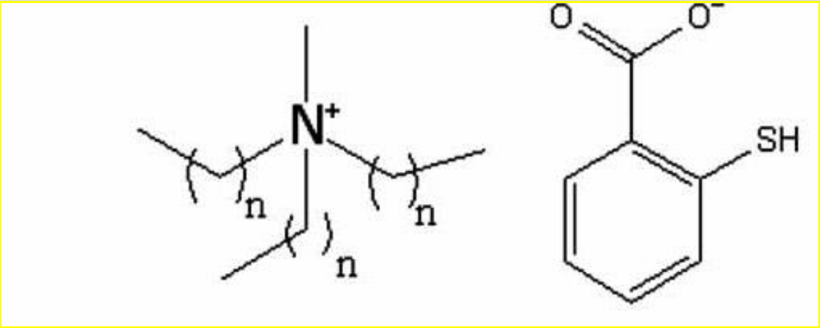
$$J_o = P \cdot c_o \qquad (3)$$

The recovery factor (RF), %

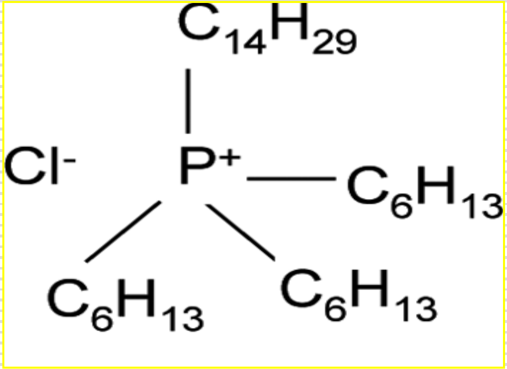
$$RF = \frac{c_o - c}{c_o} \cdot 100\% \qquad (4)$$

Aim of investigations

- Application of TOMATS and CYPHOS IL 101 as the ion carriers of Pd and Pt by transport across PIM.
- Selective recovery of **Pd** and **Pt** from synthetic leach liquor of spent automobile catalysts containing Fe, Cr, Ni and Mn.



tricaprylmethylammonium thiosalicylate - TOMATS



tetradecyl(trihexyl)phosphonium chloride - Cyphos IL 101

Table 2. Composition of the model leach liquor of spent catalysts

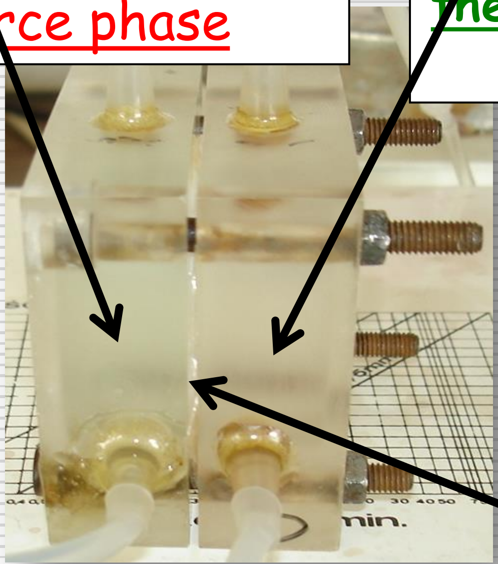
Metal	**Concentration, mol/l**
Pd(II)	0.001
Pt(IV)	0.002
Fe(III)	0.010
Ni(II)	0.010
Mn(II)	0.010
Cr(VI)	0.001

[HCl]= 3 mol/dm^3

PIM system
for transport of metal ions

Synthetic leach liquor of spent catalyst – as the source phase

0.5 M HCl + 0.3 M thiourea as the receiving phase



membrane

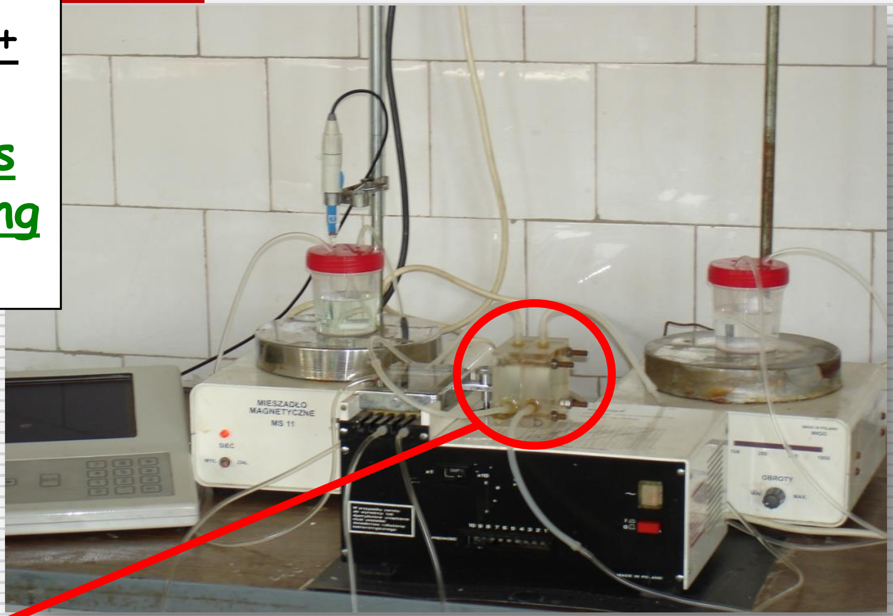


Fig.3. Set of equipment to membrane transport.

The volumes of source and receiving phases were 100 cm^3, each.
Membrane area = 12.56 cm^2

Tab. 3. Composition (% wt.) of PIMs

No of PIM	CTA, % wt.	ONPOE, % wt.	Ion carrier , % wt.
1	21.5	44.8	33.7 % of tricaprylmethylammonium thiosalicylate **(TOMATS)**
2	21.6	44.9	33.5 % of tetradecyl(trihexyl)phospho-nium chloride **(Cyphos IL 101)**

Results and discussion

Fig. 5. Relationship of $\ln(c/c_0)$ vs. time for metal ions transport across PIM with ILs depending on the kind of the ion carrier

a) TOMATS

b) Cyphos IL 101

PIM: 0.0625 g CTA, 3.2 cm^3 ONPOE/1 g CTA.

Receiving phase: 0.5 HCl + 0.3 M thiourea

a) tricaprylmethylammonium thiosalicylate (TOMATS)

b) tetradecyl(trihexyl)phosphonium chloride (Cyphos IL 101)

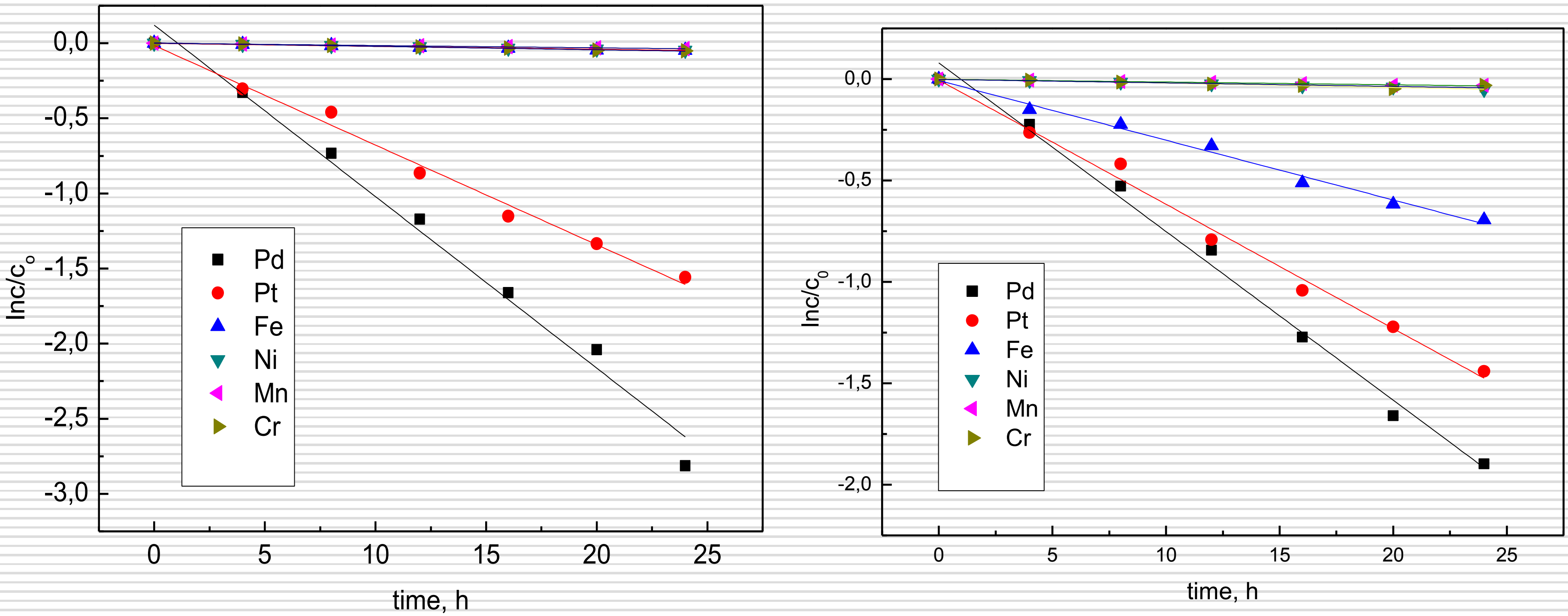
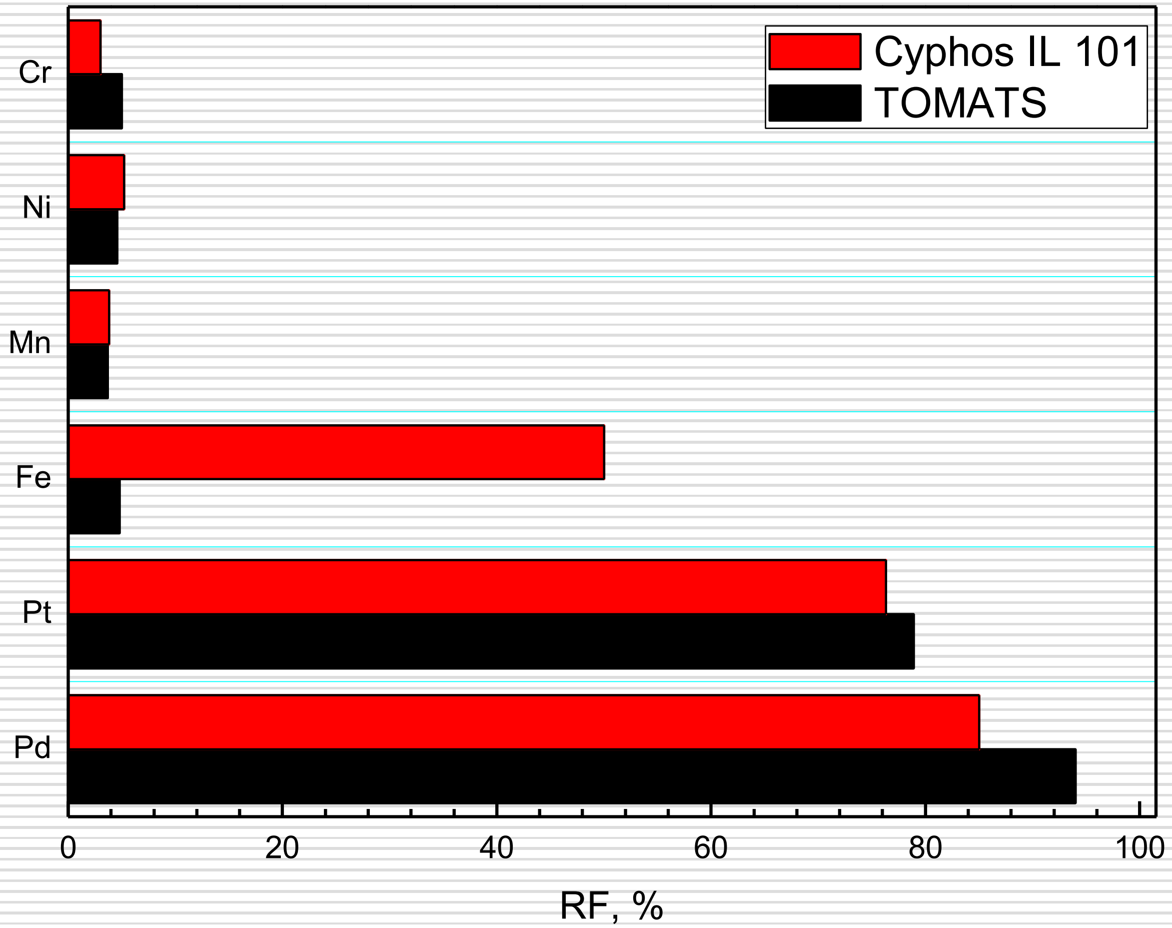


Table 3. Kinetic parameters of the transport through PIM with TOMATS and CYPHOS IL 101 as ion carrier. Conditions as Fig. 5.

Metal ions	ION carrier	Rate constant, *k* (h^{-1})	Initial flux, *Jo* ($\mu molm^{-2}\ s^{-1}$)	Recovery factor after 24 h, *RF*, %
Pd (II)	TOMATS	0.107	2.233	94.2
Pt(IV)		0.067	1.451	78.9
Fe(III)		0.002	0.042	4.8
Ni(II)		0.002	0.045	4.6
Mn(II)		0.001	0.068	3.7
Cr(VI)		0.002	0.092	5.0
Pd (II)	CYPHOS 101	0.079	1.632	85.1
Pt(IV)		0.062	1.323	76.3
Fe(III)		0.029	0.591	52.5
Ni(II)		0.002	0.046	4.7
Mn(II)		0.001	0.063	3.8
Cr(VI)		0.002	0.077	3.4

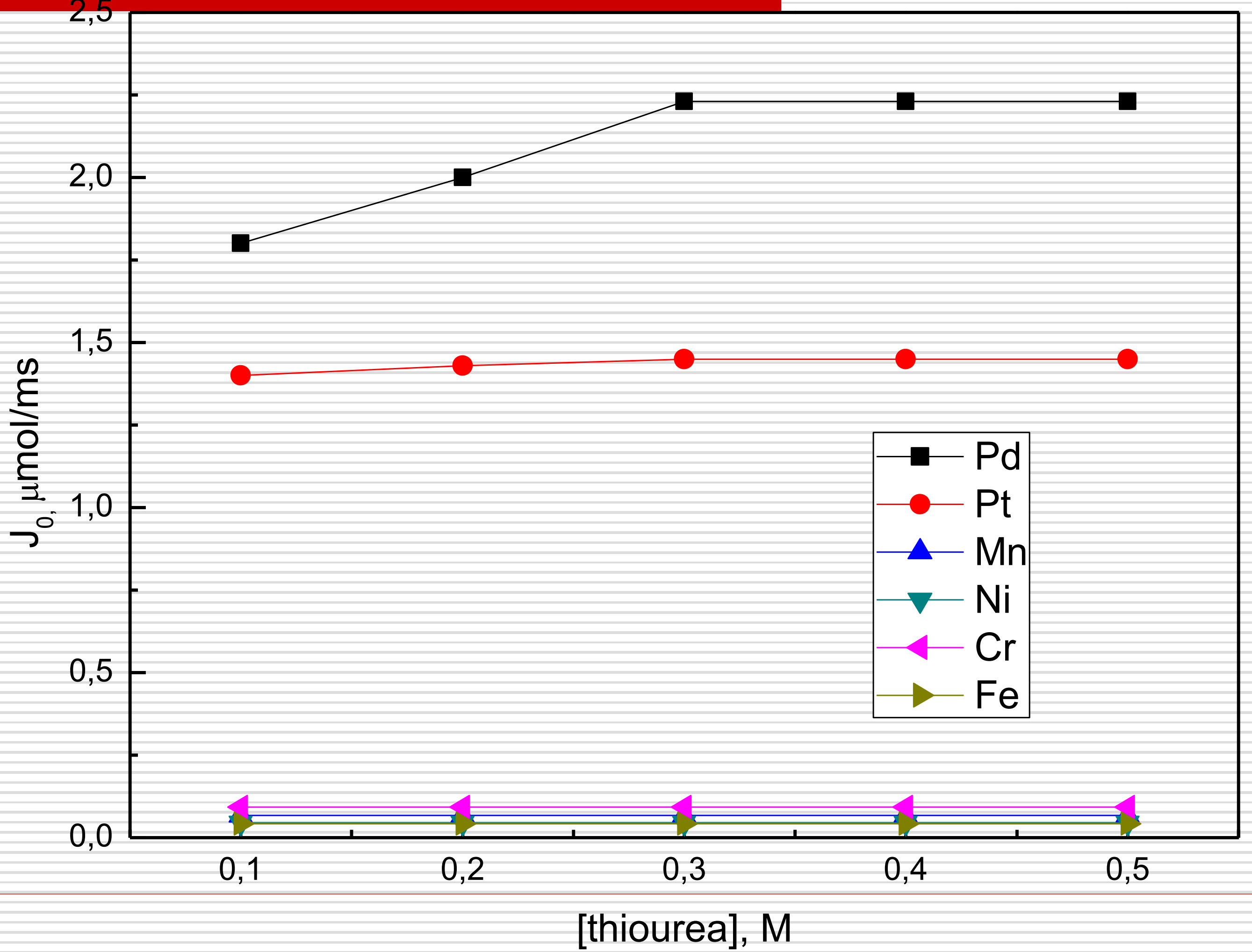
Fig. 6. Effect of the kind of the ion carrier on the recovery factor (RF, %) of metal ions from the source phase. Conditions as Fig. 5.



EFFECT OF THE RECEIVING PHASE

Fig. 7. Effect of thiourea concentration in 0.5 M hydrochloric acid as the receiving phase on the initial flux (J_0).

PIM: 1.5 M TOMATS, 0.0625 g CTA, 3.2 cm^3 ONPOE/1 g CTA



Conclusions

- Transport process across PIM with **tricaprylmethylammonium thiosalicylate** (TOMATS) and **tetradecyl(trihexyl)phosphonium chloride** (Cyphos IL 101) is effective method for recovery of Pd (RF about 90%) and Pt (RF about 80%) from aqueous chloride solutions in the presence of other metal ions.

- 0.5 M HCl solution containing 0.3 M thiourea was found to be effective receiving phase.

- Other metal ions present in the model leach liquor of spent catalyst (i.e. **Fe, Mn, Ni, Cr)** were not transported into the receiving phase across PIM with TOMATS (RF<5%).
- **Fe(III)** ions were also transported across PIM with Cyphos IL 101 (RF about 50%).

- The obtained results can be useful for the recovery of Pd and Pt in hydrometallurgical technologies of the metals recycling.

Thank you very much !