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## HIGHLY EFFICIENT FACILITATED MEMBRANE TRANSPORT OF PALLADIUM(II) IONS FROM HYDROCHLORIC ACID SOLUTIONS THROUGH PLASTICIZER MEMBRANES WITH CYANEX 471X

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**Abstract:** In this work the efficient recovery of palladium(II) ions from hydrochloric acid solutions by transport through polymer inclusion membranes (PIMs) was studied. The membrane consisted of cellulose triacetate (CTA) as the polymeric support, o-nitrophenyl octyl ether (ONPOE) as the plasticizer and Cyanex 471X (triisobutylphosphine sulphide) as the ion carrier. The effect of various parameters on the transport kinetics and the recovery factor of palladium(II) was studied, including concentration of Cyanex 471X in the membrane, hydrochloric acid concentration in the source phase and potassium thiocyanate (KSCN) concentration in the receiving phase.

**Keywords:** *palladium, platinum group metals (PGMs), Cyanex 471X, polymer inclusion membrane (PIM)*

### Introduction

Recently, we can observe growing interest in application of membrane processes for metal ions separation. Transport processes across liquid membranes, especially polymer inclusion membranes (PIMs) are a good alternative to classical separation methods, such as solvent extraction, ion exchange, precipitation etc. (De San Miguel et al., 2011). Liquid membrane processes have been suggested as a clean technology due to their characteristic of high specificity, high intensity and productivity as well as low energy requirements (O'Rourke et al., 2011). Moreover, in liquid membranes the extraction and stripping processes occur simultaneously, in a single stage. High selectivity, operational simplicity, use of small amount of solvents/extractants, as well as low cost of process belong to the most important advantages of transport through liquid membranes (De Agreda et al., 2011).

Polymer inclusion membranes contain polymeric support (i.e. CTA), plasticizer and ion carrier. The ion carrier is generally a complexing agent or an ion exchanger, which chemically interacts with the species from aqueous solutions and retains it on membrane (Pospiech and Walkowiak, 2010). Plasticizer improves membrane flexibility, retention and transport properties. It penetrates between the polymer chains and increases the distance between them, such that the plasticizing process reduces the intermolecular forces (hydrogen bonds or van der Waals forces) between the polymer chains (Gherasim et al., 2011). Polymer plays a crucial role in providing the mechanical resistance of the membranes. Despite of a great variety of solid polymers, which are used in many industrial application, only cellulose triacetate (CTA) or poly(vinyl chloride) (PVC) are used as the polymer support in PIMs (Gherasim et al., 2011; De San Miguel et al., 2011). This type of liquid membranes shows higher chemical stability and mechanical resistance comparing to the most commonly used liquid membranes, i.e. bulk liquid membranes (BLMs), emulsion liquid membranes (ELMs) and supported liquid membranes (SLMs). As an example Pospiech (2012a; 2013) showed neither loss of ion carriers (Cyanex 471X and Cyanex 301) nor any significant loss of performance of PIMs after repetitive cycles during the transport of Ag(I) and Co(II). In other work (Gardner et al., 2004) authors studied the resistance to hydrolysis of various PIMs under acidic and alkaline conditions. They prepared membranes using few cellulose derivatives and showed that durability increased when acetyl substituent on the cellulose polymer was replaced by propionyl or butyryl group. It was observed that transport of metal ions across PIM decreased as the alkyl chain lengths increased. Gherasim et al. (2011) reported the preparation of PIM containing only PVC polymer and bis(2-ethylhexyl) phosphoric acid (D2EHPA) as ion carrier. Their investigation revealed that the carrier is dispersed in the polymer matrix and confirmed its plasticizing role towards the PVC polymer matrix. These PIMs containing only PVC polymer and D2EHPA showed also higher chemical stability and mechanical resistance than other types of liquid membranes.

Natural resources of platinum group metals (PGMs) are limited. On the other hand, the demand for these metals increases due to their wide application (Fornalczyk and Saternus, 2013). Recycling of spent materials is appropriate for many important reasons, i.e. it is often beneficial to recover valuable materials, especially if their supply is limited (Chagnes and Pospiech, 2013). Spent catalysts contain a number of noble metals, such as platinum (Pt), palladium (Pd), rhodium (Rh) and are the potential source of these important metals (Saternus and Fornalczyk, 2013; Pospiech, 2012b). Palladium is used extensively in the electrical and electronics industry and as a catalyst in the chemical industry. Since this metal has a very high value, its efficient recovery from mainly acidic aqueous solutions is of considerable importance (Kolev et al., 2000).

The hydrometallurgical recovery of platinum group metals (PGMs) is based on the solvent extraction processes because the noble metal ions are easily extractable into the organic phase with various reagents (Cieszynska and Wisniewski, 2011).

Palladium(II) ions were extracted from different solutions with commercial extractants, i.e. Cyanex 471X (Ahmed et al., 2011), LIX 84I and Alamine 336 (Reddy et al., 2010), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) (Bandekar and Dhadke, 1998) and ionic liquids Cyphos 101 and Cyphos 104 (Cieszynska and Wisniewski, 2011).

Literature survey revealed that the transport process of Pd(II) ions through liquid membranes have been reported extensively by many researchers, employing ion carriers, such as tricaprilmethylammonium chloride (Aliquat 336) in PIMs (Kolev et al., 2000), Cyanex 471X in SLMs (Fontas et al., 2003), di(2-ethylhexyl)phosphoric acid (D2EHPA) and tri-*n*-octylamine (TOA) in SLMs (Sadyrbaeva, 2013) and calixarenes in PIMs (Fontas et al., 2007).

Cyanex 471X have not been used yet as an ion carrier of Pd(II) ions in transport process through polymer inclusion membranes. The results of the solvent extraction of Pd(II) with Cyanex 471X in kerosene were reported by Ahmed et al. (2011). The stripping of the loaded organic phase was performed using thiosulphate solution. The method was developed for the recovery of Pd(II) from a synthetic chloride solution similar in composition to that expected from the leaching of spent automotive catalyst and the recovery of Pd(II) was found to be 75%. This study confirms that Cyanex 471X can be used as the ion carrier of Pd(II) from chloride aqueous solutions. Therefore, the main aim of present work is to study the transport process of Pd(II) ions from hydrochloric solutions using PIMs based on cellulose triacetate with a commercial carrier (Cyanex 471 X). The effect of ion carrier concentration in the membrane, hydrochloric acid concentration in the source phase and the stripping agent concentration in the receiving phase was studied in order to determine the optimal conditions of transport process, maximum initial flux and recovery factor of Pd(II) ions from hydrochloric acid solutions across PIM.

## Experimental

Inorganic chemicals, i.e. palladium(II) chloride ( $\text{PdCl}_2$ ), potassium thiocyanate (KSCN), hydrochloric acid (HCl), were of analytical grade and were purchased from POCh (Gliwice, Poland). Aqueous solutions were prepared with deionized water (conductivity of  $0.1 \mu\text{S}/\text{cm}$  at  $25^\circ\text{C}$ ). The initial concentration of Pd(II) in the source phase was  $0.001\text{M}$ .

Organic reagents, i.e. triisobutylphosphine sulphide (Cyanex 471X), cellulose triacetate (CTA), *o*-nitrophenyl octyl ether (ONPOE), dichloromethane were of analytical reagent grade (Fluka) and were used without further purification. The density of plasticizer ONPOE was  $1.041 \text{ gcm}^{-3}$ .

### Synthesis of polymer inclusion membrane

A solutions of cellulose triacetate (CTA), the ion carrier (Cyanex 471X), and the plasticizer (ONPOE) in dichloromethane were prepared. A portion of this solution was

poured on a flat-bottom glass Petri dish which was kept on a leveled surface. The organic solvent was allowed to evaporate over a 12 h period. The resultant membrane was peeled off from the Petri dish and this membrane was washed with water and equilibrated in distilled water before use. The thickness of the PIM samples was measured 10 times using a digital micrometer and was shown as average value of these measurements.

### Transport experiments

To transport of Pd(II) ions across PIM, a membrane module was used, to which both aqueous phases were pumped with a peristaltic pump (PP1B-05A type, Zalimp, Poland) working at a speed of  $100 \text{ cm}^3 \text{ min}^{-1}$  from tanks containing source and receiving phases, respectively. The volume of source and receiving phases was  $100 \text{ cm}^3$ . The effective membrane area, which was exposed to both phases was  $12.56 \text{ cm}^2$ . Figure 1 shows the schematic diagram of the experimental setup of PIM system. Both, the source and receiving aqueous phases were stirred by a magnetic stirrer. The permeation of metal ions was monitored by sampling of the source phase and the receiving phase. The concentration of metal ions in aqueous phases was analyzed by an atomic absorption spectrophotometer (Solaar 939, Unicam). The source phase pH was controlled by pH meter (pH meter CX-731, Elmetron with combine pH electrode (Hydromet, Poland)). The changes of the solution acidity were negligible. It can be explained by the mechanism of the transport and chemical character of the ion carrier, which belong to solvating reagents. The PIM transport experiments were conducted at room temperature ( $23\text{-}25^\circ\text{C}$ ).

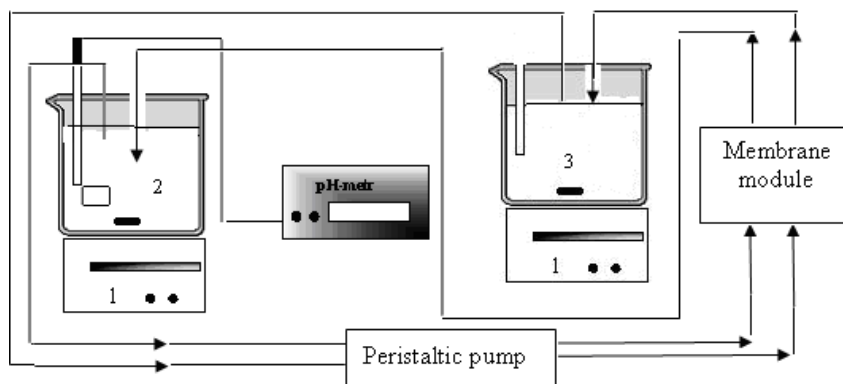


Fig. 1. Diagram of the transport experiments through PIM:  
1 – magnetic stirrer, 2 – source phase, 3 – receiving phase

The kinetics of PIM transport process was described by a first-order reaction in metal ion concentration (Danesi, 1984):

$$\ln\left(\frac{c}{c_i}\right) = -kt, \quad (1)$$

where  $c$  is the metal ion concentration (M) in the source phase at some given time,  $c_i$  is the initial metal ion concentration in the source phase,  $k$  is the rate constant ( $s^{-1}$ ), and  $t$  is the time of transport (s).

To calculate the  $k$  value, a plot of  $\ln(c/c_i)$  versus time was generated. The obtained linear dependence of  $\ln(c/c_i)$  versus time allowed to calculate permeability coefficient  $P$  ( $\mu\text{m}\cdot\text{s}^{-1}$ ) as:

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

where  $V$  is volume of the aqueous source phase ( $\text{m}^3$ ), and  $A$  is an effective area of membrane ( $\text{m}^2$ ). The initial flux  $J_i$  ( $\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ) was determined as:

$$J_i = P \cdot c_i. \quad (3)$$

The recovery factor  $RF$  (%) of metal ions from the source phase into receiving phase was calculated as:

$$\ln RF = \frac{c_i - c}{c_i} \cdot 100\%. \quad (4)$$

## Results and discussion

### Effect of membrane composition on the transport of Pd(II)

The carrier concentration in the membrane phase plays a significant role during the permeation of metal ions in transport processes across PIM. In this stage the effect of Cyanex 471X concentration in the range from  $0.5 \text{ mol}\cdot\text{dm}^{-3}$  to  $3 \text{ mol}\cdot\text{dm}^{-3}$  (on volume of plasticizer), on the permeation of Pd(II) ions was investigated. The plasticizer concentration was  $2.7 \text{ cm}^3/1.0 \text{ g CTA}$ . The initial flux of Pd(II) was only  $4.7 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  at  $0.5 \text{ mol}\cdot\text{dm}^{-3}$  concentration of the ion carrier in membrane. The permeability coefficient  $P$  increases with increasing carrier concentration up to  $2.0 \text{ mol}\cdot\text{dm}^{-3}$ , and then decreases for higher Cyanex 471X concentration (Fig. 2.). This concentration of Cyanex 471X represents probably a critical value above which the permeability of PIM decreases. The highest efficiency and the initial flux of Pd(II) transport was obtained by using the membrane containing  $0.094 \text{ g}$  of Cyanex 471X ( $2.0 \text{ mol}\cdot\text{dm}^{-3}$  on volume of plasticizer). The highest permeability coefficient  $P$  of Pd(II) was  $5.38 \mu\text{m}^{-1}$ .

The resulting membrane contained 19.9 wt.% CTA and 24.9 wt.% Cyanex 471X and 55.2 wt.% ONPOE. Further increase of carrier concentration in membrane phase caused decrease of metal ion flux, probably due to limited solubility of carrier in ONPOE. This effect can be also attributed to the membrane saturation by the metal – ion carrier complex. The increase of the carrier ion concentration in membrane phase resulted also in increased thickness of the membrane, which affected the transport rates. The resulting membranes had different thickness, i.e. 61, 64, 68, 71, 73 and 78  $\mu\text{m}$ , respectively. The permeability coefficient  $P$  of Pd(II) ions transport was the highest for 68  $\mu\text{m}$  thick membrane. Similar results were obtained by Kolev et al. (2000), who investigated palladium(II) ions transport from hydrochloric acid solutions through PIMs for three different concentrations of Aliquat 336, i.e. 30%, 40% and 50%. They found that permeability coefficient  $P$  increases with carrier concentration increase until the critical value above which the permeability of PIM decreases.

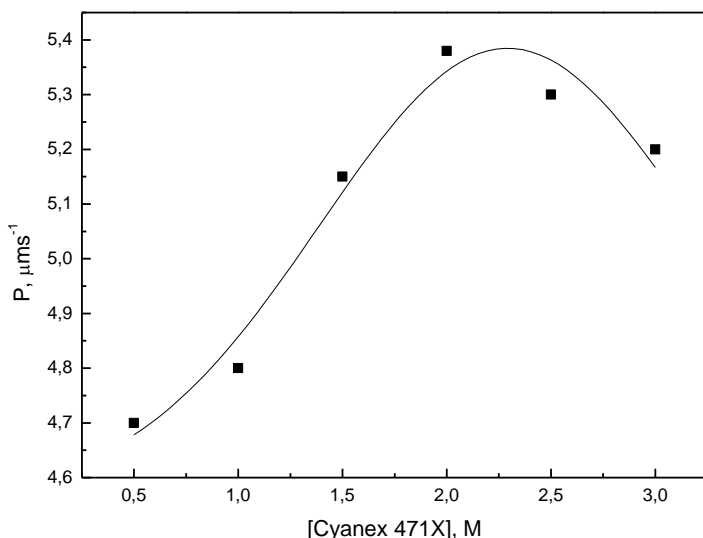
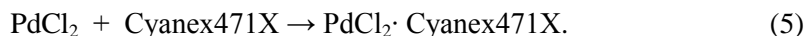


Fig. 2. Effect of Cyanex 471X concentration in PIM on the permeability of Pd(II); PIM: 0.075 g CTA, 2.7  $\text{cm}^3$  ONPOE/1 g CTA; the source phase: 0.001 M Pd(II) in 0.1 M HCl, the receiving phase: 0.5 M KSCN

### Effect of hydrochloric acid concentration in the source phase

In next experiments the effect of hydrochloric acid concentration in the source phase on the transport of Pd(II) was studied. The concentration of hydrochloric acid varied in the range 0.1-1.0 M. In this stage the composition of polymer inclusion membranes

was selected based on previous results (19.9 wt.% CTA, 24.9 wt.% Cyanex 471X and 55.2 wt.% ONPOE). The kinetics of Pd(II) transport from the source phase containing different concentration of hydrochloric acid solutions through PIMs was studied. 0.5 M KSCN was used as the stripping phase. Figure 3 shows the dependence of  $\ln(c/c_i)$  versus time for the transport processes at different hydrochloric acid concentration in the source phase. The highest rate constant of the transport process was obtained when 0.1 M HCl was used as the source phase. Figure 4 shows the variation of the initial flux of Pd(II) versus the hydrochloric acid concentration in the source phase. Table 1 shows the variation of the rate constants, the permeability coefficients of Pd(II) and recovery factors  $RF$  after 8 hours versus hydrochloric acid concentration in the source phase. Recovery factor of Pd(II) was the highest (above 87%) at 0.1 M hydrochloric acid concentration in the source phase. As it can be seen (Fig. 4, Table 1), the initial flux and permeability coefficient depend on the concentration of the acid in the source phase and decreases slightly with HCl concentration increase from 0.1 to 2.0 M. This behavior can be explained by co-transport of hydrochloric acid or the formation of non-extractable palladium(II) anionic species at high chloride concentrations or due to the combination of both factors. Transport in hydrochloric acid medium proceeds according to a coordination solvation mechanism. The equilibrium extraction reaction at the source phase-membrane interface may be represented by:



The observed high efficiency in removal of Pd(II) from acidic aqueous solutions across PIM with Cyanex 471X is due to the fact that triisobutylphosphine sulphide is a soft Lewis base and forms strong complexes with this metal, which is soft acid (Pospiech, 2012a). Pan et al. (2013) also observed that Pd(II) transferring from hydrochloric acid solutions depend on HCl concentration in the aqueous phase.

Table 1. Effect of hydrochloric acid concentration in the source phase on the kinetic parameters of palladium(II) transport. PIM: 0.075 g CTA, 2.7 cm<sup>3</sup> ONPOE/1 g CTA, 2 M Cyanex 471 X; the source phase: 0.001 M Pd(II) in HCl, the receiving phase: 0.5 M KSCN

Concentration of HCl, M	Rate constant, $k$ , h <sup>-1</sup>	R <sup>2</sup>	Permeability coefficient, $P$ , $\mu\text{ms}^{-1}$	Recovery factor after 8 h $RF$ , %
0.05	0.178	98.44	3.83	75.3
0.1	0.243	98.89	5.38	87.2
0.3	0.227	98.71	5.03	84.4
0.5	0.219	98.34	4.85	83.5
1.0	0.201	98.03	4.44	81.7
2.0	0.192	98.51	4.12	78.0

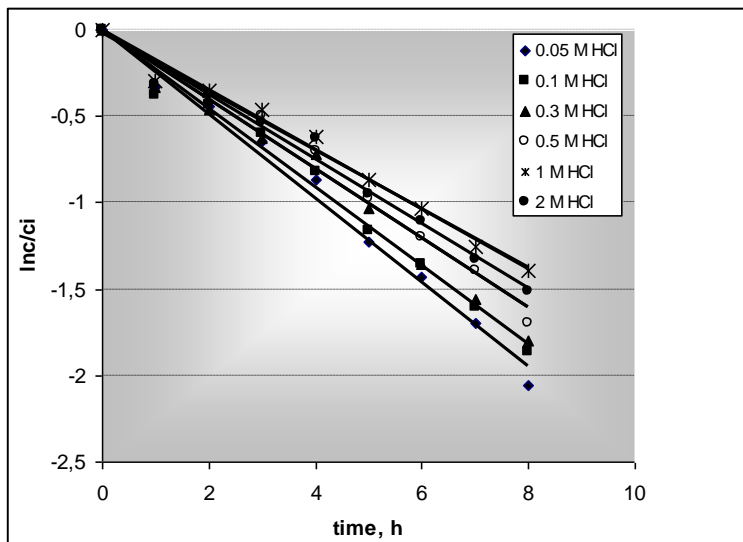


Fig. 3. Relationship of  $\ln(c/c_i)$  vs. time for Pd(II) transport across PIM; PIM: 0.075 g CTA, 2.7 cm<sup>3</sup> ONPOE/1 g CTA, 2 M Cyanex 471 X; the source phase: 0.001 M Pd(II) in HCl, the receiving phase: 0.5 M KSCN

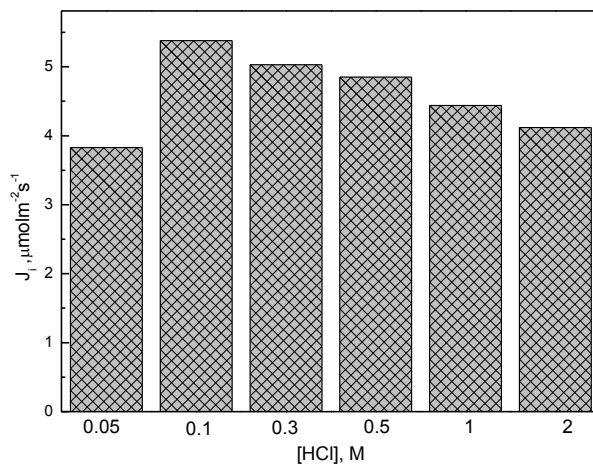


Fig. 4. Effect of HCl concentration in the source phase on the initial flux  $J_i$  of Pd(II); PIM: 0.075 g CTA, 2.7 cm<sup>3</sup> ONPOE/1 g CTA, 2 M Cyanex 471 X; the source phase: 0.001 M Pd(II) in HCl, the receiving phase: 0.5 M KSCN



### Effect of the potassium thiocyanate concentration in the receiving phase

In the next series of the experiments the influence of potassium thiocyanate concentration in the receiving phase on the transport and recovery factor of palladium(II) was studied. The stripping reaction at the membrane/strip interface plays a key role in the transport of metal ions. The transport of Pd(II) can be enhanced by the presence of thiocyanate, owing to formation of mixed-ligand Pd(II)-Cl<sup>-</sup>SCN<sup>-</sup> Cyanex 471X complexes. In order to analyze the effect of KSCN concentration on the transport of Pd(II), the aqueous solutions of KSCN with concentration ranged from 0.05 to 0.5 M were prepared and used as receiving phase. The polymer inclusion membranes contained Cyanex 471X (2.0 mol/dm<sup>3</sup> on the volume of plasticizer) and 2.7 cm<sup>3</sup> ONPOE/1 g CTA. Kinetic parameters of the transport of Pd(II) and the recovery factor after 8h are shown in Table 2. All parameters increases with increase of KSCN concentration in the receiving phase. The recovery factor of Pd(II) reaches maximum for 0.5 M KSCN in the receiving phase. As it can be observed, this process depends on thiocyanate concentration in the receiving phase due to the formation of different Pd-SCN-Cl<sup>-</sup> species which are transported in different extent with Cyanex 471X. Hidalgo et al. (1991) reported that analysis of the metal distribution suggests the formation of PdCl(SCN) Cyanex 471X, PdCl(SCN)<sub>2</sub>·2Cyanex 471X and Pd(SCN)<sub>2</sub>·Cyanex 471X in the organic phase. The ultraviolet absorption spectra of the organic phase support the hypothesis of formation of mixed-ligand complexes.

Table 2. Effect of KSCN concentration in the receiving phase on the kinetic parameters of Pd(II) transport and the recovery factor. PIM: 0.075 g CTA, 2.7 cm<sup>3</sup> ONPOE/1 g CTA, 2 M Cyanex 471 X; the source phase: 0.001 M Pd(II) in 0.1 M HCl

Concentration of KSCN, M	Rate constant, $k, \text{h}^{-1}$	Initial flux, $J_i, \mu\text{molm}^{-2}\text{s}^{-1}$	Recovery factor $RF, \%$
0.05	0.138	3.06	65.2
0.1	0.155	3.43	69.8
0.3	0.180	3.97	74.3
0.5	0.243	5.38	87.2

### Conclusions

The obtained results allow to conclude that transport process across polymer inclusion membranes with Cyanex 471X as the ion carrier can be used as the method for the recovery of palladium(II) from hydrochloric acid solutions in the studied conditions. The results show that the initial fluxes and recovery factors depend on the ion carrier concentration, as well as concentration of hydrochloric acid in the source phase and potassium thiocyanate concentration in the receiving phase. The obtained results show that transport process through PIM containing 19.9 wt.% CTA and 24.9 wt.% Cyanex 471X and 55.2 wt.% ONPOE enables extraction above 87% of Pd(II) from 0.1 M HCl

into 0.5 M KSCN after 8 h. Finally, the separation system developed can be successfully applied to the recovery of palladium(II) ions from chloride aqueous solutions in the studied conditions.

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