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## ORIGINAL ARTICLE

# Separation of nitrophenols. Equilibriums in bi- and tri-phasic systems

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## KEYWORDS

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2,4-Dinitrophenol;  
Extraction;  
Transport through bulk liquid membranes;  
Nitrophenols separation

**Abstract** The paper presents experimental data obtained in the study of liquid–liquid partition equilibriums in biphasic system in order to optimize the process of transport through bulk liquid membranes (triphasic partition systems). The partition equilibriums of some nitrophenols using chloroform as extraction solvent and membranary solvent, respectively, were studied. The influence of the pH on the partition equilibriums was investigated. The repartition constants and the  $pK_a$  values of the studied nitrophenols were calculated. Nitrophenols were transferred in triphasic system from a feed phase with pH 2, through a chloroform liquid membrane, into a receiving phase with pH 12, with efficiencies over 90%.

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## 1. Introduction

During the simultaneous separation of several chemical species, it is sometimes necessary to carry out concentration of

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the target species in order to apply a more efficient and reliable analytical separation. Various methods such as solvent extraction and membranary methods are two modalities that are used to separate compounds in a mixture. The solvent extraction permits obtaining efficient separations through simple experimental procedures. Consequently solvent extraction was a topic of several researches aimed to improve the experimental techniques. Improvement of the solvent extraction methods permitted the enrichment of the separation techniques with new techniques that use the transport through membranes (Luca et al., 1991; Ruse et al., 1999; Serban et al., 2000; Gheorghe et al., 2006; Kim et al., 2008). Nitrophenols are contaminants with high toxic potential level, frequently encountered in the environment due to some industrial activities, such as pharmaceuticals and dyes industries (Luan and

Plaisier, 2004). A review related to this point of view has been published by Busca et al. (2008). Due to the economic and environmental impact it is important to separate and develop efficient separation methods for these nitrophenols. The separation procedure based on liquid emulsion membranes (Terry et al., 1982; Teramoto et al., 1983; Gadekar et al., 1992; Kakoi et al., 1996; Correia and Carvalho, 2000, 2001) and supported liquid membranes techniques were applied (Abed-Ali et al., 1998; Brisdon and Watts, 1985; Yahaya et al., 2000a,b; Yahaya et al., 2001; Peretti et al., 2001; Jaber et al., 2005). The main objectives of this study is the separation of nitrophenols (mono- and di-substituted) in biphasic system (solvent extraction) and triphasic system (transport through bulk liquid membranes) and the possibility of recuperative separation of nitrophenols through the technique of bulk liquid membranes.

## 2. Experimental

### 2.1. Reagents

All the reagents used are of analytical grade. *p*-Nitrophenol, *o*-nitrophenol, 2,4-dinitrophenol were supplied by Merck (Germany). Chloroform, previously saturated with distilled water, is used as an organic solvent in the partition equilibriums was purchased from Merck (Germany). Hydrochloric acid and sodium hydroxide were used for the variation of the pH between 2 and 12. The distilled water used in this study was also saturated with chloroform and was used for the preparation of the feed phase and of the receiving phase.

### 2.2. Apparatus

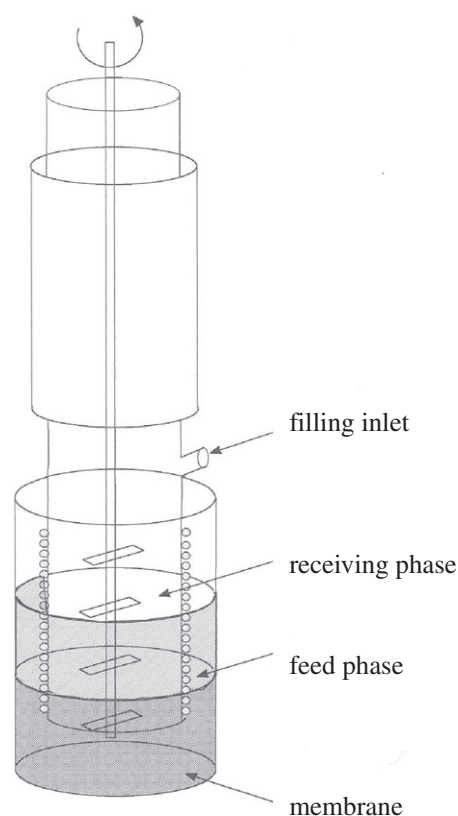
The pH was measured with a glass/AgCl, Ag combined electrode using SevenMulti Metler Toledo pH-meter. The nitrophenols content from the aqueous phases was measured using a LAMBDA 750 spectrophotometer (Perkin Elmer Co).

### 2.3. Procedures

Liquid-liquid extraction experiments were carried out in the range pH 2–12 range. The pH variation was obtained by adding to a solution on nitrophenol ( $10^{-4}$ – $10^{-3}$  mol/L) in HCl 0.01 mol/L, a solution with the same concentration of nitrophenol in NaOH 0.01 mol/L. Ten millilitre of nitrophenol at different pH values were extracted with the same volume of chloroform. After an agitation of 15 min the two phases were let to rest for 5–10 min and then were separated.

Transport experiments were carried out in a transport cell wall in wall type showed in Fig. 1. The feed phase (FP) consisted in 20 mL of aqueous or acid solution of nitrophenol of  $10^{-4}$ – $10^{-3}$  mol/L. The receiving phase (RP) was 7 mL of NaOH solution  $10^{-2}$ – $10^{-4}$  mol/L. The two aqueous phases are separated through 50 mL chloroform membrane. All the experiments were carried out at  $25 \pm 1$  °C and the transport time was 3 h.

The content of nitrophenol was analyzed in the UV region, at the characteristic wavelength for each compound: *p*-nitrophenol at 317 nm (acid, neutral medium) and 404 nm (alkaline medium), *o*-nitrophenol at 363 nm (acid, neutral medium) and 417 nm (alkaline medium), while 2,4-dinitrophenol at 358 nm (acid, neutral medium) and 361 nm (alkaline medium). The



**Figure 1** Experimental device for the transport experiments.

nitrophenol content in the organic phase was determined from the mass balance of the three phases of the partition system.

## 3. Results and discussions

### 3.1. Partition equilibriums in biphasic system

Partition equilibriums in biphasic system were studied in order to determine the optimum conditions of the extraction of the nitrophenols from aqueous solution in the organic solvent.

Nitrophenols (Ar-OH) are organic compounds with acid character distribute in a liquid-liquid biphasic system according to the partition equilibrium:



where, w = aqueous phase, s = solvent depending how much its repartition constant *R* permits:

$$R_{\text{Ar-OH}} = \frac{[\text{Ar-OH}]_s}{[\text{Ar-OH}]_w} \quad (2)$$

In the aqueous phase the equilibrium with proton transfer is established:



Equilibrium (3), controlled by pH, is characterized by the acid dissociation constant  $K_a$ :

$$K_a = \frac{[\text{Ar-O}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{Ar-OH}]} \quad (4)$$

At  $\text{pH} < \text{pK}_a$  Ar-OH molecular species extractable in the organic phase predominates, while at  $\text{pH} > \text{pK}_a$  Ar-O<sup>-</sup> hydrophilic ionic species, non-extractable predominates.

For a global quantitative assessment of the process is defined as the distribution ratio  $r$ :

$$r_{\text{Ar-OH}} = \frac{(\text{Ar-OH})_{\text{total in s}}}{(\text{Ar-OH})_{\text{total in w}}} = \frac{(\text{Ar-OH})_s}{(\text{Ar-OH})_w + (\text{Ar-O}^-)_w} \quad (5)$$

or:

$$r_{\text{Ar-OH}} = \frac{R_{\text{Ar-OH}}}{1 + 10^{\text{pH}-\text{pK}_a}} \quad (6)$$

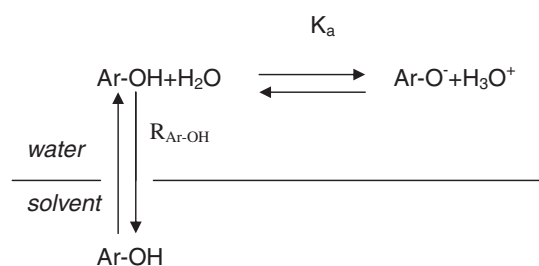
The equilibria mentioned above are summarized in Fig. 2.

Accordingly, the results indicate that the pH of the aqueous phase is an operational parameter that can influence the repartition of the nitrophenols as shown by the experimental data presented in Fig. 3.

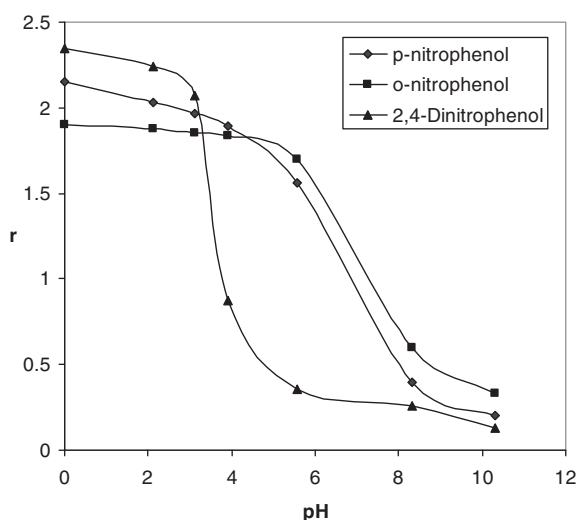
The repartition constants and the values of the  $\text{pK}_a$  in the system water–chloroform for the studied nitrophenols were evaluated from the extraction curve shown in Table 1.

The  $\text{pK}_a$  values determined in biphasic system differ from the values presented in literature for homogeneous systems (Lars et al., 1964).

From the extraction diagram of the three nitrophenols some useful observation can be made regarding the possibility of separation the monosubstitute nitrophenols (*p*-nitrophenol



**Figure 2** Scheme of the partition equilibria in biphasic system.



**Figure 3** Extraction curve of nitrophenols in chloroform.

**Table 1** The extraction parameters determined through liquid–liquid extraction in the system water–chloroform.

Substrate	$\text{pK}_{a,\text{water-chloroform}}$	$\text{pK}_{a,\text{water}}$	$R$
<i>p</i> -Nitrophenol	6.85	7.018	2.15
<i>o</i> -Nitrophenol	6.90	7.15	1.90
2,4-Dinitrophenol	3.87	4.114	2.35

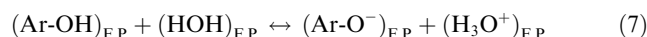
and *o*-nitrophenol) from the disubstituted one, 2,4-dinitrophenol respectively. At  $\text{pH} < 4$  all the three nitrophenols are extractable in chloroform; at  $\text{pH} > 7$  all the three nitrophenols are in the aqueous phase in the form of phenolates (Ar-O<sup>-</sup>). A possible separation can take place at the pH 5.5–6 when the 2,4-dinitrophenol is the aqueous phase as phenolate (Ar-O<sup>-</sup>) while the monosubstituted derivatives (*p*-nitrophenol and *o*-nitrophenol) are mainly in the organic phase.

### 3.2. Partition equilibria in triphasic system

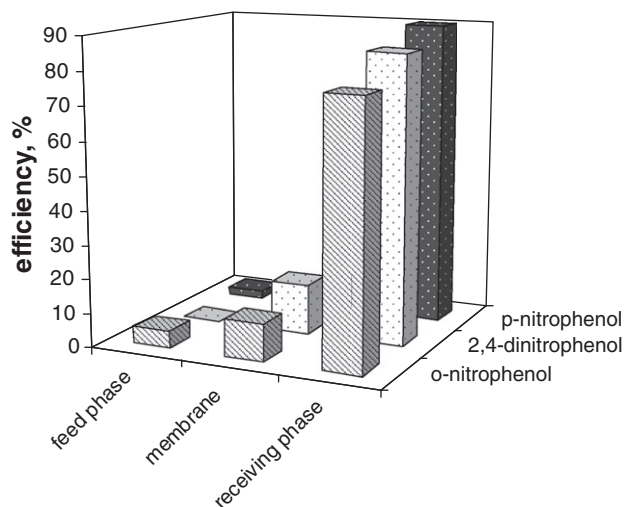
Phenols in the form of neutral molecules can be transferred through an aqueous phase (named feed phase) through a liquid membrane (organic solvent) in another aqueous phase (named receiving phase). Thus the studied nitrophenols (*p*-nitrophenol, *o*-nitrophenol and 2,4-dinitrophenol) have been transferred from an aqueous phase through a chloroform membrane into an alkaline receiving phase (NaOH solution with pH 12) with efficiencies ranging between 70–90% as it can be observed from Fig. 4.

The process is based on a succession of diffusion–extraction equilibria that take place at the two interfaces of the membrane.

In the feed phase (F.P) the phenolic compound having an acid character is in equilibrium involving proton transfer which is controlled by pH.



At acidic pH the undissociated form of the phenolic compound predominates and this is distributed between the feed

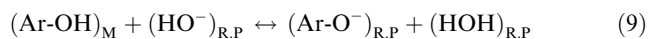


**Figure 4** Distribution of the phenolic compounds in the membranary phases at the end of the transport process.

phase and the membrane (M) according to the partition equilibrium:



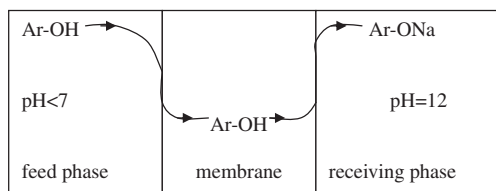
The molecules of the phenolic compound get through the membrane and at the interface membrane-receiving phase the proton transfer equilibrium takes place.



Formulas (7)–(9) summarize the transport mechanism equilibria which are schematically presented in Fig. 5.

The proposed mechanism was validated by the experimental results obtained in the conditions of the pH variation of the terminal phases of the membranary system. The efficiencies of the transport of *p*-nitrophenol, *o*-nitrophenol and 2,4-dinitrophenol at different values of the pH of the feed phase (pH 2–6) and of the receiving phase (pH 10–12) are shown in Table 2 indicating that the transport of the nitrophenols depend on the pH of the feed phase.

Therefore, it can be concluded that the pH of the receiving phase influences considerably the transport efficiencies of these compounds. The transport efficiencies exceed 90% when the nitrophenols transport takes place from a feed phase with the pH 2 through a chloroform membrane into a receiving phase with pH 12. The best results are obtained for *p*-nitrophenol where the transport recovery is 98%.



**Figure 5** Functional scheme of nitrophenols transport mechanism.

**Table 2** Transport recovery of the nitrophenols depending on the feed phase pH. (Feed phase-phenolic compound solution  $10^{-4}$ – $10^{-3}$  mol L $^{-1}$ , at pH 2–6; membrane – chloroform; receiving phase – NaOH,  $10^{-2}$  mol L $^{-1}$ ).

Substrate	pH	Phase composition (%mol)			Recovery (%)
		FP	M	RP	
<i>p</i> -Nitrophenol	2.01	1.48	0.76	97.7	97.7
	3.02	2.11	3.11	94.78	94.78
	3.99	2.86	4.35	92.79	92.79
	5.01	1.88	10.1	88.02	88.02
	6.02	1.05	15.43	83.52	83.52
<i>o</i> -Nitrophenol	2.02	2.1	2.6	95.3	95.3
	3.01	2.7	6.55	90.75	90.75
	4.03	1.78	9.87	88.35	88.35
	5.02	1.56	18.29	80.15	80.15
	6.03	1.23	26.35	72.42	72.42
2,4-Dinitrophenol	2.01	1.26	2.04	96.7	96.7
	3.02	4.71	5.17	90.12	90.12
	4.03	44.65	6.8	48.55	48.55
	5.02	80.74	7.01	12.25	12.25
	5.98	86.01	7.24	6.75	6.75

**Table 3** Transport recovery of nitrophenols derivatives depending on the receiving phase pH 10–12 (Feed phase-phenolic compound solution,  $10^{-4}$ – $10^{-3}$  mol L $^{-1}$ ; membrane – chloroform; receiving phase – NaOH solution,  $10^{-2}$ – $10^{-4}$  mol L $^{-1}$ ).

Substrate	pH	Phase composition (% mol)			Recovery (%)
		FP	M	RP	
<i>p</i> -Nitrophenol	10	19.5	75.62	4.88	4.88
	11.02	5.46	26.09	68.45	68.45
	12.01	2.25	7.75	90	90
<i>o</i> -Nitrophenol	10.01	18.35	77.35	4.3	4.3
	11.01	5.3	34.44	60.26	60.26
	12.02	2.15	20.85	77	77
2,4-Dinitrophenol	10	20.1	75.4	4.5	4.5
	11.03	5.75	28.8	65.45	65.45
	12.04	3.01	11.99	85	85

A significant difference in the transport recovery was observed upon the pH variation of the receiving phase. The experimental values obtained for the transport of the nitroderivatives depending on the pH of the receiving phase are shown in Table 3. The transport of the phenolic nitroderivatives takes place from a feed phase consisting of an aqueous solution of nitrophenol in distilled water through a chloroform membrane into a receiving phase with pH 10–12.

Variation of the pH value of the receiving phase causes a significant decrease of the recovery of the nitrophenols. Therefore, the pH gradient is considered the driving force of the transport of nitrophenols through the chloroform membrane that ensures a quantitative separation.

#### 4. Conclusions

The paper presents the results of the partition of nitrophenols in bi- and tri-phase system. The repartition data in biphasic system allowed the determination of some analytical constants in the water–chloroform system. The extraction curves obtained from experimental data provided the possibility of separating the mononitrophenols (*o*-nitrophenol and *p*-nitrophenol) from 2,4-dinitrophenol. The partition equilibria in triphase system is influenced by the pH gradient between the feed phase and the receiving phase through the chloroform membrane. The transport recovery is over 90% when the transport takes place from a feed phase (pH 2) through a chloroform membrane into an alkaline receiving phase (pH 12). This is a quantitative transport and it can be applied for the separation and extraction of nitrophenols from aqueous media.

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