# Interfacial Activity of Pyridine Extractants in Model Extraction System

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Interfacial tension and surface excess isotherms as well as adsorption parameters for selected pyridine extractants and their chloride and bromide salts in model extraction system were determined and interpreted. Despite their high hydrophobicity, all extractants studied adsorb at the hydrocarbon/water interfaces and decreases effectively the interfacial tension. The interfacial activity of pyridine extractants in model extraction system was affected mainly by the structure of compounds. The highest ability to reduce interfacial tension at the hydrocarbon/water interface was observed for quaternary salts of pyridine extractants.

## 1. Introduction

Solvent extraction is one of the essential methods used to purify, concentrate, and separate various metals from different aqueous solutions. It is already a mature technology today, though still developing and improving its performance. One of the proposals is to obtain novel, selective and efficient extractants. Interesting examples of such compounds are hydrophobic pyridine extractants and their chloride and bromide salts. These extractants have been studied in our group and proposed as ligands for copper(II), zinc(II), cadmium(II), lead (II) and iron(III) removal using a liquid−liquid extraction technique [1-6] and as carrier in membrane processes realized with the hollow fiber module [7-8].

The hydrophobic-hydrophilic structure of the extractant compounds and as a result their surface activity at the water/organic solvent interface, as well as their significant hydrophobicity (very low solubility in the aqueous phase) causes that the complexation reaction of metal ions in the extraction process probably occurs as a surface reaction [9]. Surface mechanism of the process is preceded by a transfer of extractant molecules from the bulk organic phase to the interfacial area by diffusion. The molecules of extractants form a packed monolayer at the interface or, at the latest literature reports, the bilayer [10]. Therefore, in the study of the mechanism and kinetics of the extraction of metal ions by hydrophobic extractants parameters analysis such as the molecular structure of the extractant, composition of the aqueous phase or the organic solvent type are also important. They affect both the adsorption, as well as diffusion of the extractants molecules between organic solvent and aqueous phase.

The purpose of the present work is to study the interfacial activity and estimate basic adsorption parameters of novel hydrophobic pyridine extractants (ketone and amidoxime derivatives) and their chloride and bromide salts in model extraction systems.

## 2. Experimental

### 2.1 Reagents

The novel hydrophobic pyridine extractants (1-(3-pyridyl)undecan-1-one, pyridine-3-carboximidamide, *N'*-alkyloxypyridine derivatives, Figure 1) were synthesized as were described earlier [11,12]. The mixture of toluene with 10% (v/v) of decan-1-ol was used as the organic phase, while the aqueous phase was water obtained from the PURELAB Classic, Elga with resistivity=18.2 MΩ·cm at 25°C. Toluene was supplied by POCh S.A., decan-1-ol was supplied by Merck, and all other reagents necessary to synthesizes were analytical-grade reagents.
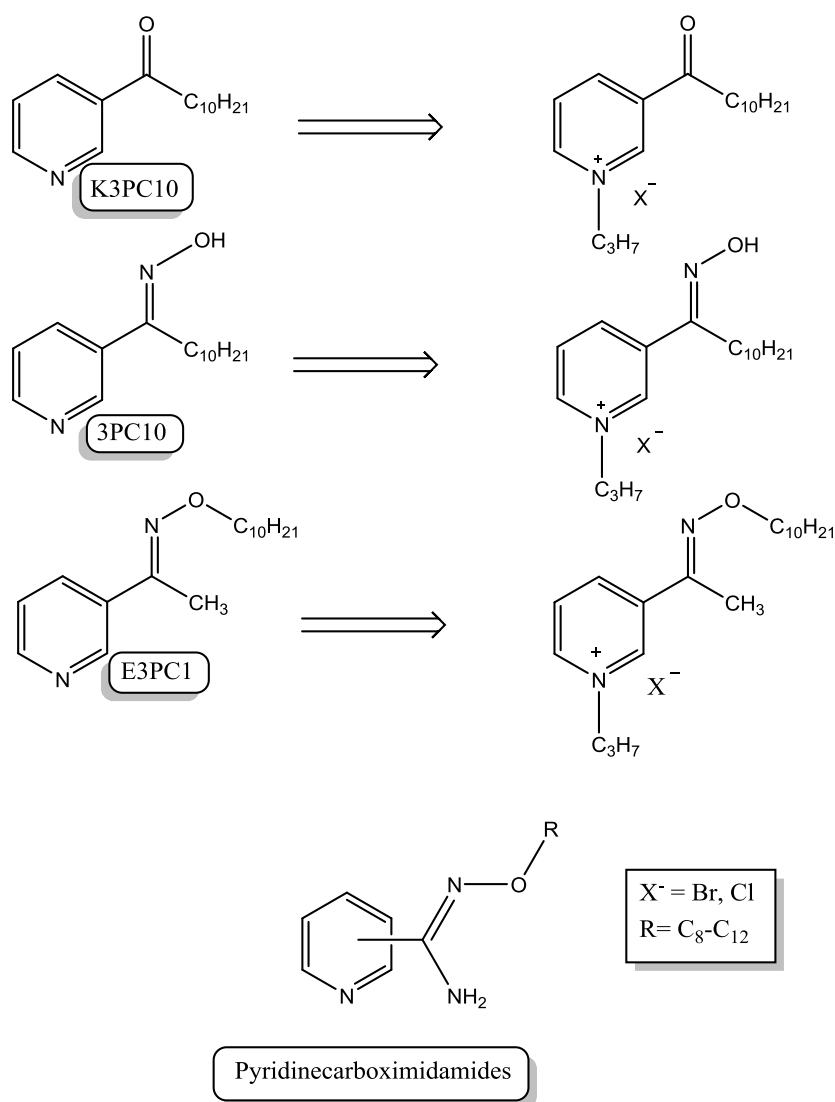


Figure 1 Structure of studied reagents.

### 2.2 Interfacial tension measurements

The interfacial tension was measured by the Du Noüy ring method with a Krüss tensiometer, with resolution 0.01 mN/m, at a constant temperature 21°C. Measurements were made for the aqueous

solution/organic phase system at the initial concentration of extractants equal 0.1 M, other solutions were obtained by serial dilution method with concentration in the range from 0.1 to $10^{-6}$ M. The measurements were carried out with presaturated phases, which means that both phases (equal volumes ~10 cm$^3$) were together mechanically shaken at room temperature for 4 hrs then left for 24 hrs for the complete separation. They were separated directly before measurements. This procedure allows to avoid any transfer of the solvent during the adsorption process.



Figure 2 Interfacial tension isotherms for *N*-decyloxy-1-(3-pyridyl)ethanoimine (E3PC1) ■ and its chloride ● or bromide salts ▲ in model extraction sysytem.

**2.3 Calculation of adsorption parameters**

The interfacial tension data were fitted by the Szyszkowski equation [13]:

$$\gamma^{Sz} = \gamma_0 \left[ 1 - B_{Sz} \ln\left( \frac{c}{A_{Sz}} + 1 \right) \right]$$

(1)

Adsorption coefficients of the Szyszkowski isotherm (Eq. [1]) can be used to estimate the surface excess at the saturated interface ($\Gamma_\infty$), the minimum molecular area in the adsorption layer at the saturated interface ($A_{min}$) and the Gibbs free energy of adsorption ($\Delta G_{ads}$). The following equations are used for these estimations:

$$\Gamma_\infty = \frac{B\gamma_0}{RT}$$

(2)

$$A_{min} = \frac{1}{\Gamma_\infty \cdot N_A}$$

(3)

$$\Delta G_{ads}^{Sz} = RT \ln(A_{min})$$

(4)

In the equations (1)-(4) $A_{Sz}$ and $B_{Sz}$, $\gamma_0$, $c$, $N_A$, $R$, $T$ stand for Szyszkowski adsorption coefficients, interfacial tension for concentration c=0, Avogadro constant, gas constant and temperature, respectively.

# 3. Results and Discussion

## 3.1 Interfacial tension isotherms

In Figure 1 exemplary interfacial tension isotherms for *N*-decyloxy-1-(3-pyridyl)ethano- imine and its chloride and bromide salts were presented. Both pyridine extractant and their quaternary salts adsorbed at the liquid/liquid interface and reduced the interfacial tension in model extraction system. However, the obtained results showed a higher interfacial activity of bromide and chloride pyridinium salts compared with pyridine extractants. The values of surface pressure ($\pi = \gamma_0 - \gamma_{min}$) in the model extraction system were comparable for the chloride and bromide salts, equal to 16 and 17 mN/m,
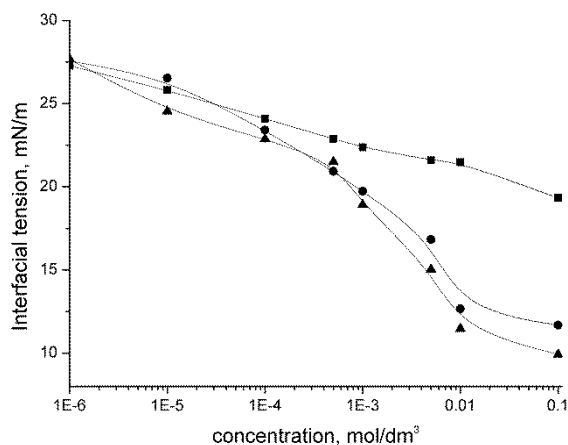
respectively, while for pyridine extractant the value of this parameter was twice time smaller. Thus the molecules of the pyridine extractants indicate the lower ability to reduce the interfacial tension. The same relationship was observed for other pyridine extractants as 1-(3-pyridyl)undecan-1-one and 1-(3-pyridyl)undecan-1-one oxime.

## 3.2 Adsorption properties

The interfacial tension data can be well fitted by various adsorption equations of theoretical, empirical or semiempirical origin. From the physicochemical point of view it is suitable to use the Szyszkowski equation, described in section 2.3. Based on these calculations the exemplary surface excess isotherms for ketone derivates of pyridine extractant and its salt are presented in Figure 2. The interfacial concentration of 1-(3-pyridyl)undecan-1-one at the saturated hydrocarbon/aqueous solution interface was lower in comparison to its chloride and bromide salts. The results obtained suggest that the structures of adsorbed monolayers formed at interfaces considered were different. The molecules of quaternary salts were more densely populated at the saturated interface than those of pyridine extractant. As a result, it may affect the overall rate of the extraction.
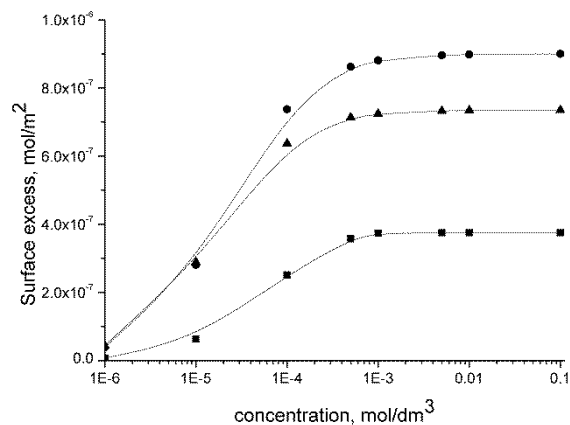


Figure 3 Surface excess isotherms for 1-(3-pyridyl)undecan-1-one (K3PC10) ■ and its chloride ● or bromide salts ▲ in model extraction sysytem.

For all considered extractants and their salt the negative values of free energy of adsorption were estimated, according to equation (4), in the range from -26 to -34 kJ/mol. These results suggest that adsorption process of extractants studied occurs spontaneously.

## 4. Conclusion

Pyridine extractants exhibits high interfacial activity at the hydrocarbon/water interface. The adsorption properties of extractants studied are significantly dependent on their type. The highest ability to reduce interfacial tension at the hydrocarbon/water interface is observed for quaternary salts of pyridine extractants.

Estimated values of surface excess indicated that structures of adsorbed monolayers formed at model extraction interfaces were different and depended of the extractant used. The negative values of free energy of adsorption for all considered extractants suggested that adsorption process occurs spontaneously.

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