

# THE INTERFACIAL BEHAVIOR OF CALIXARENE AND CROWN ETHERS AT THE AIR/WATER AND CHLOROFORM/WATER INTERFACE

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**Abstract.** Presence of different chemical species at the liquid / liquid interface can facilitate or not the transfer of a compound from one phase to another. The process of transferring alkaline cations from the aqueous phase to the organic phase using calixarenes or crown ethers as macrocyclic carriers is influenced by the transfer of chemical species through interface. In this context, the interfacial tension value is important for assessing the cation transfer process through the interface. Present study investigates the interfacial tension variation at the chloroform / water interface when *p*-tert-butyl-calix[n]arenes (*n* = 4, 6, 8), benzo-15-crown-5, benzo-18-crown-6, 4'-NH<sub>2</sub>-benzo-15-crown-5, and 4'-NH<sub>2</sub>-benzo-18-crown-6 were added to the organic layer. The addition of sodium or potassium hydroxide to the aqueous phase has led to significant reduction of interfacial tension for the studied chloroform / water systems. Neutralization of basic solution was achieved by adding of hydrochloric acid solution to aqueous solution conducting to the increase of the interfacial tension value. Modification of the macrocyclic ligand present in the organic layer led to the modification of the shape of curve interfacial tension vs. pH indicating a possible contribution of macrocyclic ligand selectivity for a particular alkaline cation complexation.

**Keywords:** calixarene, crown ethers, interfacial tension, macrocyclic ligands.

## 1. INTRODUCTION

Interfacial tension is related to the expended work needed to increase the size of the interface between two adjacent phases which do not mix. Thus, the presence of different chemical species with various concentrations will change the interfacial tension of the heterogeneous system. This effect can be explained based on the concentration profile of different ions near the interface [1].

The mechanism of binding and transfer of ions in the organic phase is influenced by the experimental conditions, the efficient transport of ions through interface being related to the properties of interfacial region. This region plays a key role in the process [2, 3]. In most of the cases, the interface is represented by the overlapping of the two phases with a well-

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defined boundary or by a third phase, which contains the mixture of the two solvents [4]. The chemical and physical properties of the interface influence the reactivity and selectivity of the species placed at the interface. One certain chemical species behaves differently at the interface than it behaves in the bulk solution [6].

A valuable tool for many analytical applications is the permeation liquid membrane, consisting of two aqueous solutions in different compartments (the source phase and the strip phase) separated by an organic phase [10-14, 33]. The organic phase contains an organic carrier, which selectively transports the ions from the source phase to the strip phase. In the case of hydrophobic ligands (like calixarenes and crown ethers) two types of mechanisms were proposed for the ionic transfer: *transfer by interfacial complexation* and the *transfer of the ion followed by complexation* in the organic phase [6].

When macromolecular systems are used as permeation liquid membrane, organic molecules are present at the interface. The interactions that may occur at the interface are between ions and macromolecules on one hand, and between ions and water molecules directly contacting the macromolecules from the organic phase on the other hand [16]. The physicochemical properties of biological and colloidal systems such as macromolecular association, protein activity, denaturation etc. are affected by the presence of salt ions in the surrounding aqueous solution. Water molecules involved in the formation of chemical bonds with the chemical species present in the interface influence the way these species arrange at the interface. Interactions that influence interfacial tension, and therefore transfer of chemical species through the interface, are non-covalent interactions occurring between ions and molecules existing at the interface [15].

Yoshida and Freiser pointed out that the origins of many ion-specific effects are found in ion-binding to macromolecules rather than in water structuring effects [17]. The interaction forces involved in the formation of supramolecular compounds are electrostatic interactions and London dispersion forces (that are valid for all types of polar and non-polar chemical species). If a chemical species able to complex cations is present at the interface, then the resulted macromolecular ions are neutralized by the opposite sign ions existing at the interface. According to the traditional theory of the electrical double layer, the two electrically charged surfaces will interact so that the charge distribution will overlap [15].

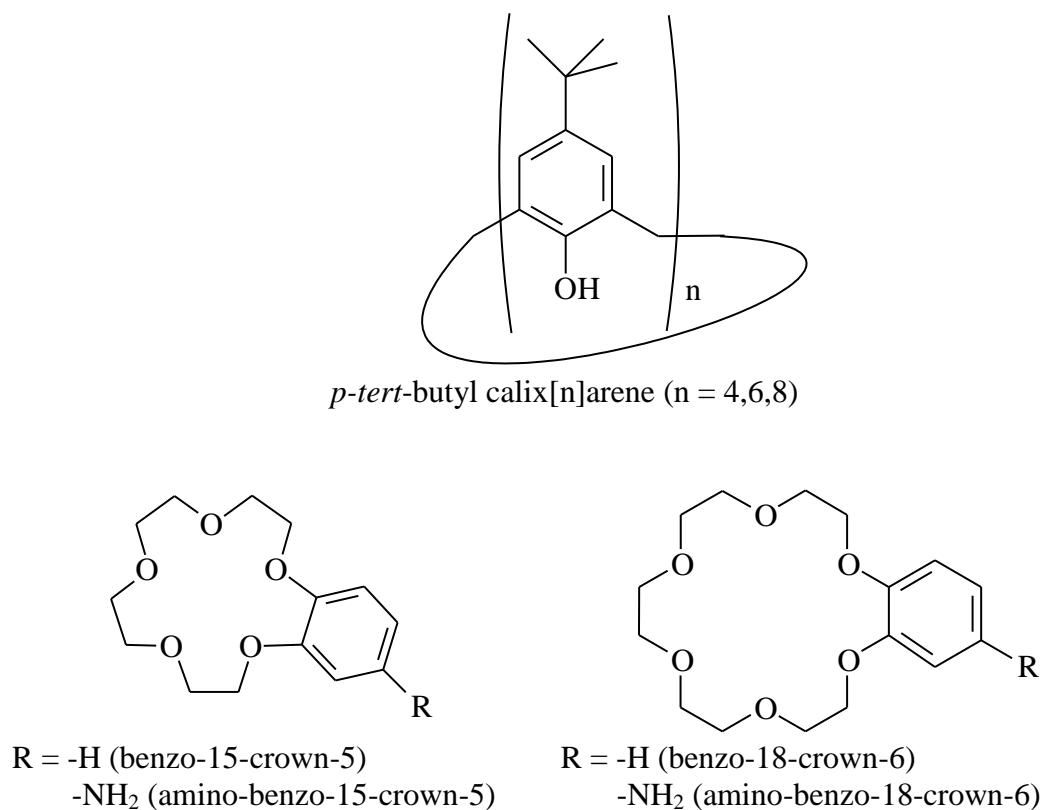
The electrochemical study performed by Yoshida and Freiser with with valinomycin (a natural neutral ionophore used in the transport of potassium and as antibiotic) explains the potential shift by the movement of the ligands in the aqueous phase, complexation, and the transfer of the formed complex back in the organic phase [17]. Koryta et al. explained, on the other hand, that the cation is first transferred in the organic phase and then complexed with the ligand in the organic phase [18, 19]. Another study proposed that the macrocyclic ligand lies in the region between the phases and binds the cation in this zone [20].

Although the macrocyclic ligands, like calixarenes and crown ethers, are more soluble in chloroform than in water, the molecular dynamic simulations indicated their high affinity for the interface. Thus, the dissolved ligands in chloroform prefer the interface instead of bulk organic solvent [21, 22]. Due to their amphiphilic nature, the macrocyclic ligands could self-assemble in the interface. The formation of self-assembled structures is not desirable in the extraction or transport applications because the efficiency of the process decreases. Shinkai and co. established that the lower rim esterified *p-tert-butyl-calix[4]-*, *p-tert-butyl calix[5]-* and *p-tert-butyl calix[6]-*arenes can form monolayer with the coordination "atmosphere" for the alkali ions in the air-water interface [23].

Markowitz et al. found that *p-tert-butyl calix[6]arene* produces stable monolayers of 10Å thickness, and the complete removal of the *tert-butyl* groups leads to the calix[6]arene, which forms membranes with an apparent thickness of  $\sim 20 \pm 5$  Å, this result indicating the formation of the bilayer membrane [24].

Troxler and Wipf studied an ionophoric system with uncomplexed 18-crown-6 and their complex with potassium picrate at the water-chloroform interface. The authors presented the fact that 18-crown-6 has a higher affinity for the interface, which is consistent with the experimental data indicating the high interfacial activity of this ionophore in the interface. This behavior is similar to that of alcohols and esters [25].

The aim of the present study is to evaluate the behavior of the monolayer of *p*-*tert*-butyl-calix[n]arene ( $n = 4, 6, 8$ ), benzo-15-crown-5, benzo-18-crown-6, 4'-NH<sub>2</sub>-benzo-15-crown-5, 4'-NH<sub>2</sub>-benzo-18-crown-6 and of the mixture calixarene : crown ethers. These mixtures were indicated to have synergistic effect in the extraction process on the chloroform-water interface [5-8, 34 - 35].



**Figure 1. Macrocyclic ligands structures.**

## 2. MATERIALS AND METHODS

### 2.1. MATERIALS

Macrocyclic ligands *p*-*tert*-butyl calix[n]arene ( $n = 4, 6, 8$ ) (Sigma Aldrich) with 95 % purity were used to prepare  $10^{-5}$  M chloroform solutions. Crown ethers benzo-15-crown-5, 4'-amino-benzo-15-crown-5, benzo-18-crown-6, 4'-amino-benzo-18-crown-6 (98 % purity) were purchased from Sigma Aldrich. Chloroform (Merck Millipore) stabilized with 0.6 – 1 % ethanol, 99 % purity was used to prepare macrocyclic ligands solutions. Sodium hydroxide pellets (purity 98 %, carbonate < 0.5 %), potassium hydroxide pellets (purity > 85 %, carbonate < 0.5 %),

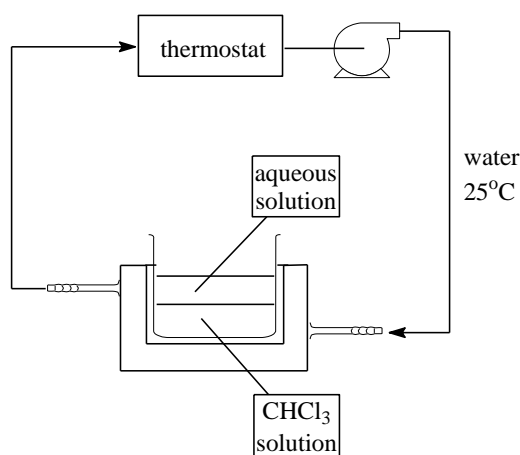
carbonate < 1 %) and hydrochloric acid (37 % solution) were purchased from Chimopar. Redistilled water (conductivity below  $0.10 \mu\text{S}\cdot\text{cm}^{-1}$  at  $25 \text{ }^\circ\text{C}$ ) was used in for all the experiments.

The air-water and chloroform water interface were examined with a Willhelmy device. The temperature of the mixture was maintained constant by using a water circulator, thus ensuring the reproducibility of the results.

The pH and conductivity of the aqueous solutions were measured using a WTW InoLAB Multi 9430 meter, equipped with an IDS SenTix 980 pH-sensor.

## 2.2. METHODS

The surface tension - area isotherms ( $\pi$ -A) at the air water interface were measured using a rectangular tray made of glass. The macrocyclic ligands were spread on the water surface using  $10^{-4}$  M chloroform solutions. After 10 minutes, the solvent evaporates and the layer is compressed with a teflon bar. Measurements of the surface tension at the air water interface were made with a Willhelmy device.



**Figure 2. Device used to measure chloroform-water interfacial tension**

The water – chloroform interface was characterized at  $25 \text{ }^\circ\text{C}$  using a device with general operation scheme presented in Fig. 2. The macrocyclic ligands were added to the organic phase to obtain a monolayer at the liquid-liquid interface, the surface occupied by one molecule considered being the one measured from surface tension - area isotherms ( $\pi$ -A) at the air-water interface.

The chloroform solution (80 mL) was mixed with redistilled water (80 mL) and the interfacial tension was measured after the equilibrium was reached. Afterwards, small amounts of NaOH (KOH) 50 % solution were added to the aqueous phase in order to reach the 0.1 M concentration for NaOH (KOH). Once the stability of the phase was obtained (interfacial tension reaches an equilibrium value) HCl 37 % solution is added, using a micropipette, to neutralize the NaOH solution and reproduce the liquid-liquid experiment calixarene: crown ethers.

The value of pH and conductivity of water were measured in order to assess the variation of interface tension with pH and conductivity.

The amount of the ligand solution added to the organic phase was calculated in order to obtain a compact monolayer of macrocyclic ligands in the interface, considering the area / molecule value calculated from the pressure – area per molecule isotherm for air / water interface.

### 3. RESULTS AND DISCUSSION

#### 3.1. RESULTS

##### Air / water interface study

Fig. 3 presents the  $\pi$ -A isotherms for *p-tert*-butyl-calix[n]arene (n = 4, 6, 8). From the variation of interfacial tension ( $\pi$ ) with area / molecule it can be set the maximum area available in the interface for one molecule once the compact monolayer was formed at the air / water interface. The experimental values established for calixarenes are presented in table 1.

An interesting behavior presents the *p-tert*-butyl-calix[8]arene monolayer, which it doesn't break at value of pressure higher than 20 dyne/cm. The curve tendency (Fig. 3 - (c)) indicates a rearrangement of the molecules when the monolayer is compressed.

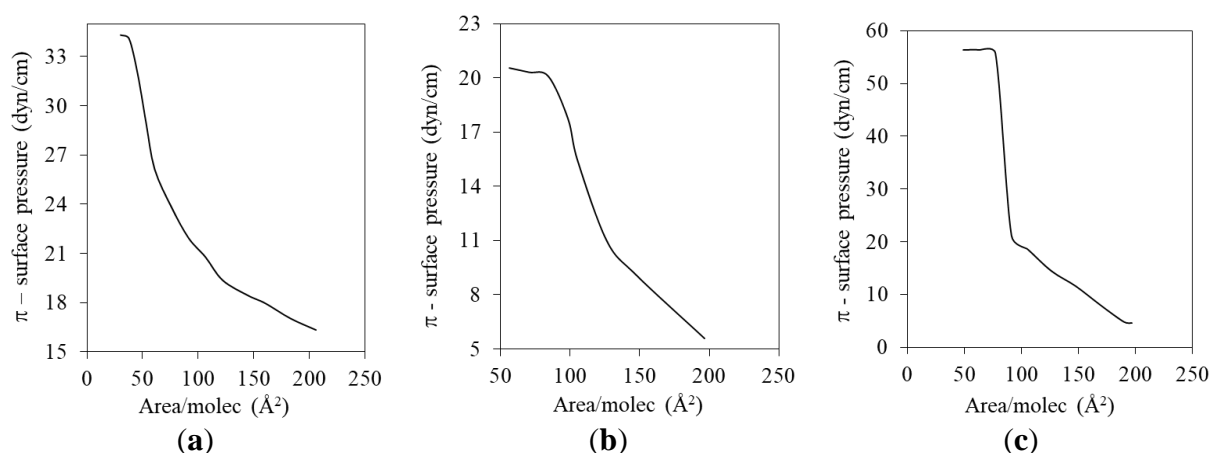


Figure 3. The  $\pi$ -A isotherms at air/water interface for (a) *p-tert*-butyl-calix[4]arene, (b) *p-tert*-butyl-calix[6]arene and (c) *p-tert*-butyl-calix[8]arene.

Table 1. Area/molecule for calix[n]arene at the air water interface (n=4,6,8).

Macromolecular compound	<i>p-tert</i> -butyl-calix[4]arene	<i>p-tert</i> -butyl-calix[6]arene	<i>p-tert</i> -butyl-calix[8]arene
Area/molecule ( $\text{\AA}^2$ )	$100 \pm 5$	$160 \pm 5$	$220 \pm 10$

From the  $\pi$ -A isotherms of the four crown ethers studied the area / molecule was calculated the and the values are presented in table 2. The values of area / molecule obtained for benzo-15-crown-5 and benzo-18-crown-6 and their 4'-NH<sub>2</sub>-derivatives presented in the table are similar with values reported in the literature [17, 18].

Table 2. Area/molecule for benzo-15-crown-5, benzo-18-crown-6, 4'-NH<sub>2</sub>-benzo-15-crown-5 and 4'-NH<sub>2</sub>-benzo-18-crown-6 at the air/water interface .

Macromolecular compound	benzo-15-crown-5	benzo-18- crown -6	4'-NH <sub>2</sub> -benzo-15-crown -5	4'-NH <sub>2</sub> -benzo-18-crown -6
Area/molecule ( $\text{\AA}^2$ )	$85 \pm 5$	$100 \pm 5$	$110 \pm 5$	$120 \pm 5$

### Water / chloroform interface study

The area / molecule values at the air/water interface were used to set the concentration of the ligand in the organic phase. The addition of HCl in the system leads to neutralization of the hydroxy group, as well as to its replacement by the chloride ions. In this situation the sodium cation concentration remains constant.

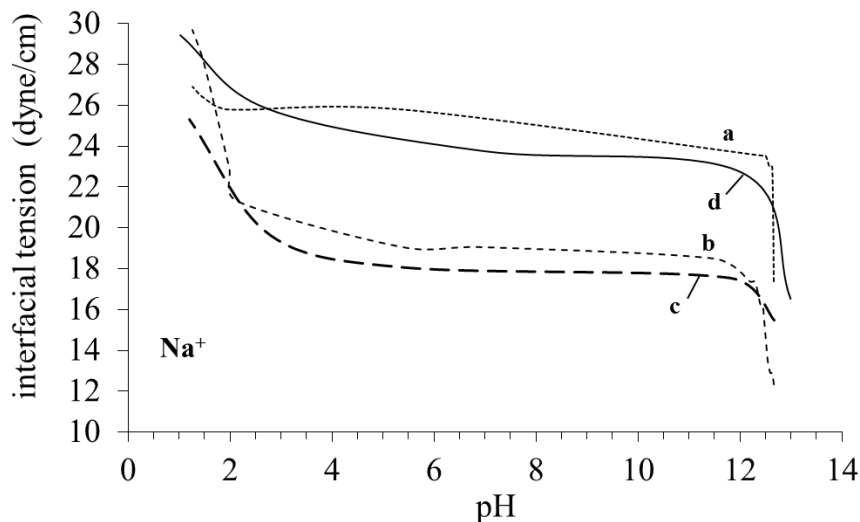


Figure 4. Interfacial tension vs. pH for water / chloroform interface when the organic phase contains: a. no calixarene, b. *p-tBu-calix[4]arene*, c. *p-tBu-calix[6]arene*, d. *p-tBu-calix[8]arene*.

Fig. 4 shows the variation of the interfacial tension at the water / chloroform interface when the content of the organic phase is varied by adding different calixarenes and when the sodium hydroxide solution is neutralized with hydrochloric acid.

Graphical representations indicate that the interfacial tension decreases when calixarenes are added to the organic phase (Fig. 4 curves b.-d.) compared with the pure chloroform (Fig. 4 curve a.) when the pH of aqueous solution is higher than 12. The deprotonation of calixarenes and the complexation of alkali cations may be the explanation for this interfacial behavior.

Fig. 5 shows the variation of the interfacial tension of water / chloroform interface, when the aqueous phase contained potassium ions in contact with solutions of different calixarenes in chloroform.

When sodium, chloride, hydroxide ions are present in the aqueous phase, the interfacial tension decreases at  $\text{pH} > 12$  when calix[4]arene is in the interface and when the sodium is replaced by potassium in the aqueous solution the interfacial tension decreases at  $\text{pH} > 12$  when calix[6]arene is the macrocyclic ligand from the organic phase. This behavior is consistent with the complexation tendency of calixarenes. The size of  $\text{Na}^+$  fits better with the four-ring ligand and  $\text{K}^+$  is better accommodate in the calix[6]arene structure.

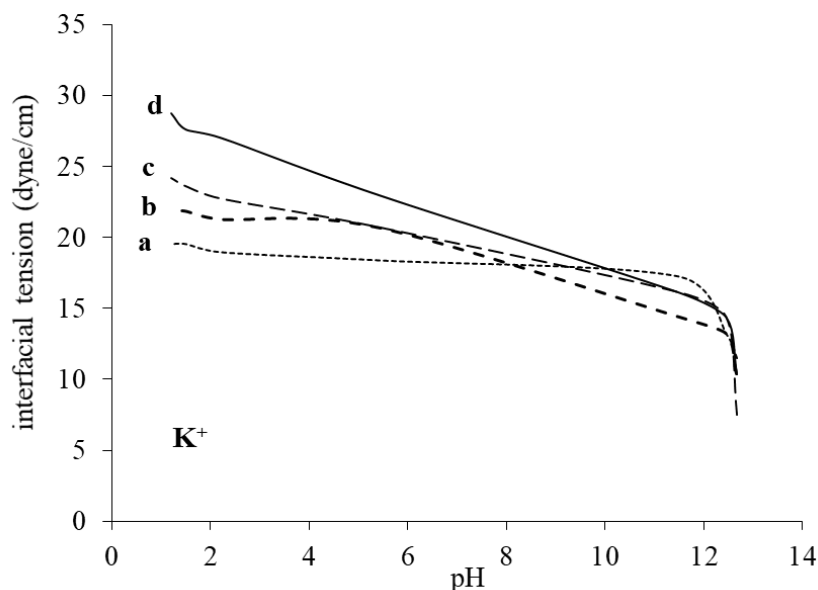


Figure 5. Interfacial tension vs. pH for water / chloroform interface when the organic phase contains: a. no calixarene, b. *p-tBu*-calix[4]arene, c. *p-tBu*-calix[6]arene, d. *p-tBu*-calix[8]arene.

Table 3. Interfacial tension at pH=7.

Compound present in the organic phase		no calixarene	<i>p-tBu</i> -calix[4]arene	<i>p-tBu</i> -calix[6]arene	<i>p-tBu</i> -calix[8]arene
Interfacial tension at pH=7 $\gamma$ (dyne/cm)	no alkaline cations	32.8	27.6	28.3	30.9
	Na <sup>+</sup>	25.1	19.2	18.1	23.8
	K <sup>+</sup>	18.4	20.1	20.6	22.9

At pH<12 the interfacial tension increases, and the order became

$$\gamma_{p\text{-tert-butyl-calix[4]arene}} < \gamma_{p\text{-tert-butyl-calix[6]arene}} < \gamma_{p\text{-tert-butyl-calix[8]arene}}$$

The modification of the water phase explains the continuous increase of the interfacial tension, with the decrease of pH. As is well known the anions have a higher interfacial activity compared with the cations of the same size or smaller in diameter. Hoffmeister established an anion classification on the basis of their effect on the stability of proteins in solution, behavior related to the interfacial activity of these species [28-31].

Thus, the chloride ion is less active in the interface compared with HO<sup>-</sup>. We assume that the interfacial behavior of the systems presented above could be presented as a two stage process:

- pH > 12 – the interfacial tension curve has a sudden drop, the decrease being more pronounced when calixarene were added to the organic phase,
- pH < 12 – the interfacial tension increases again, mainly due to the neutralization of the HO<sup>-</sup> and its gradual replacement from at the interface with Cl<sup>-</sup>. In the same time, the calixarenes begins to protonate the phenolat ions, which are replaced with aromatic OH in the interface.

The differences between the presented graphics in the two situations (fig. 4 and fig. 5) could be the result of the different complexation behavior of calixarenes with the alkaline

cations or the difference of the cationic volume, which can be responsible for different interfacial activity.

The value of interfacial tension for chloroform / redistilled water was higher than the interfacial tension for the calixarene solution / redistilled water systems (table 3). These results indicate the agglomeration of the studied calixarenes at the interface,

If the only specie present in the interface is the calixarene the value of the interfacial tension respects the sequence:

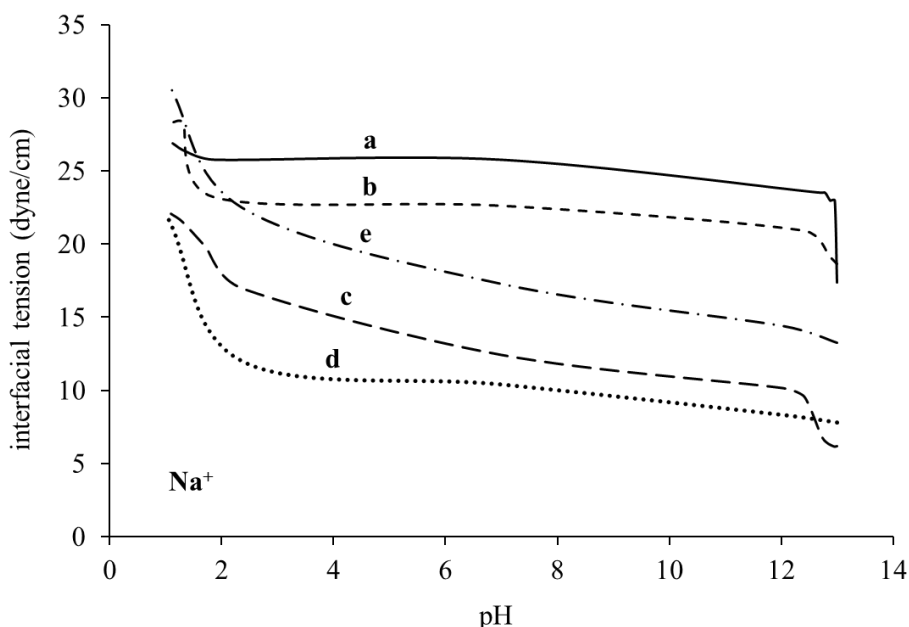
$$\gamma_{p\text{-tert-butyl-calix[4]arene}} < \gamma_{p\text{-tert-butyl-calix[6]arene}} < \gamma_{p\text{-tert-butyl-calix[8]arene}}$$

However, this sequence was not respected when cationic and anionic species were not present in the water phase.

### *The interface water-chloroform+crown ethers study*

The graphical representations of the interfacial tension chloroform – crown ether / H<sub>2</sub>O + Na<sup>+</sup> (K<sup>+</sup>) + HO<sup>-</sup> + Cl<sup>-</sup> (Figs. 6-7) presents similar tendency as in the case of calixarenes. Thus, the  $\gamma$  values are lower when crown ethers are added, compared with the interfacial system containing no macrocyclic ligand.

This tendency is reported in all situations when macrocyclic ligands are used (Figs. 4-7) in the organic phase. This decrease of the interfacial tension at values of pH > 12 can explain the better extractibilities of the alkaline cations with macrocyclic ligands when the basic medium is used for the water phase. The low interfacial tension enables an easier transition of the hydrated anions and cations from water in the interface where they can easily dehydrate to form the complex, which crosses the interface and is then transferred in the organic phase.



**Figure 6. Interfacial tension vs. pH for water with sodium / chloroform interface when the organic phase contains: a. no crown ether, b. benzo-15-crown-5, c. benzo-18-crown-6, d. NH<sub>2</sub>-benzo-15-crown-5, e. NH<sub>2</sub>-benzo-18-crown-6.**

When Na<sup>+</sup> is present in the aqueous solution the interfacial tension decreases to values lower than interfacial tension values measured for mixtures that don't contain crown ethers in the organic phase (Fig. 6.) if the at pH values higher than 2.5.



The variation of interfacial tension with pH shows, also, that 4'-amino-benzo-crown ethers behave differently than the corresponding crown ethers. The curve shape is different in the case of the system with 4'-amino-benzo-crown ethers compared with the system with the benzo crown ethers. The benzo crown ethers systems follow the shape of the curve that presents the interfacial tension in the system with no crown ethers.

The graphical representation  $\gamma = f(\text{pH})$  in the systems with 4'-amino-benzo-crown ethers is divided in two domains:

- at  $\text{pH} > 4$  the interfacial tension has a slow increase;
- at  $\text{pH} < 4$  the interfacial tension increases rapidly to reach the interfacial tension of the system with no crown ethers.

Obviously, the amino group causes the different behavior in the interface because of its tendency to protonate at pH smaller than 4. The macrocyclic cation formed in the interface can reject the  $\text{Na}^+$  and  $\text{H}_3\text{O}^+$  cations and attract the chloride anion. The electrostatic repulsion between the protonated ligands can lead to an increased value of area/molecule. Thus, some ligand molecules leave the interface, and this fact causes the increase of interfacial tension. This behavior is similar to that reported for the functionalized calix[4]resorcinarene with amino groups at air water interface [32].

The value of the interfacial tension increases as described bellow:

$$\gamma_{\text{benzo-18-crown-6}} < \gamma_{\text{benzo-15-crown-5}} \text{ and } \gamma_{4'\text{-amino-benzo-15-crown-5}} < \gamma_{4'\text{-amino-benzo-18-crown-6}},$$

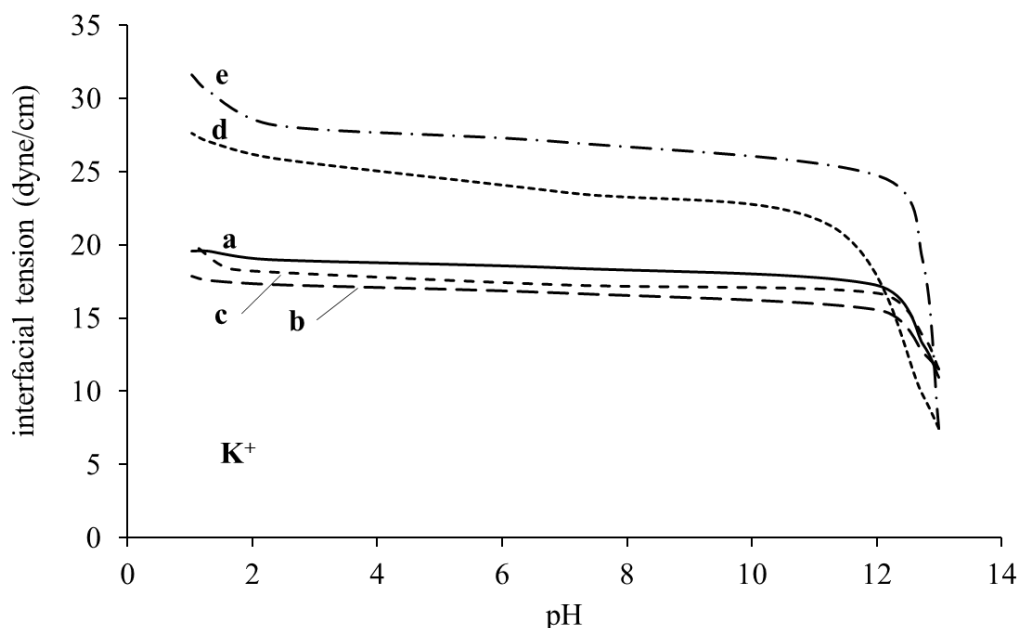
The behavior of amino-benzo-crown ethers is different from the behavior of the corresponding crown ethers.

The study of the systems containing potassium ions in the aqueous phase conducts to the graphical representation from Fig. 7, which presents different behavior of the amino-benzo-crown ethers with respect to the corresponding crown ethers.

**Table 4. Interfacial tension at pH=7.**

Compound present in the organic phase		no crown ethers	benzo-15-crown-5	benzo-18-crown-6	4'-NH <sub>2</sub> -benzo-15-crown-5	4'-NH <sub>2</sub> -benzo-18-crown-6
Interfacial tension at pH=7 $\gamma$ (dyne/cm)	no alkaline cations	32.8	23.0	17.8	23.6	31.2
	$\text{Na}^+$	25.1	22.6	12.4	10.4	17.2
	$\text{K}^+$	18.4	16.9	17.3	23.4	26.8

Table 4 presents the interfacial tension for the chloroform / water system when, only, crown ethers are added to the organic layer, which is in contact with the aqueous solution. The situation is similar to the system with calixarenes (Table 3), the  $\gamma$  values being higher when the alkali cations are not present in the aqueous phase.



**Figure 7. Interfacial tension vs. pH for water with potassium / chloroform interface when the organic phase contains: a. no crown ether, b. benzo-15-crown-5, c. benzo-18-crown-6, d. NH<sub>2</sub>-benzo-15-crown-5, e. NH<sub>2</sub>-benzo-18-crown-6**

#### 4. CONCLUSIONS

Interaction of cations with the chemical species in the interface is reflected by the variation of the interfacial tension for a liquid / liquid extraction system. The addition of the studied macrocyclic ligands (*p-tert*-butylcalixarenes ( $n = 4, 6, 8$ ), benzo-15-crown-5, benzo-18-crown-6, 4'-NH<sub>2</sub>- and 4'-NH<sub>2</sub>-benzo-18-crown-6) in the organic layer in contact with the redistilled water leads to the reduction of the interfacial tension, indicating the preference of the ligand molecules for the interface.

The evaluation of the area per molecule at the air / water interface indicated an increase in the area occupied by a calixarene molecule in the interface with the increase in the number of aromatic cycles in the structure of the macrocyclic compound. Crown ethers register the same type of variation, as the number of ethylene oxide units increases. The amino group added at the position 4' - of the aromatic ring makes the area occupied by the same crown ether larger than the non-derivatized crown ether.

The chloroform / water interface containing calixarenes or crown ethers was also, studied when the content of aqueous phase was varied by addition of alkaline hydroxide and subsequent neutralization of with hydrochloric acid. At pH higher than 12, the interfacial tension has the lowest values, these being lower when macrocyclic ligand is added in the organic layer. These data are useful for liquid extraction experiments that are more effective when the aqueous phase has basic pH values compared to cation extraction from acidic solutions.

Changing the cation in the aqueous phase (sodium instead of potassium) different forms of interfacial tension vs pH curves were recorded. The evolution of experimental results could be explained by the differentiated affinity of macrocyclic ligands for a certain type of cation, according to the lock and key principle.

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