ORIGINAL PAPER

CROWN ETHERS AND *p-tert*-BUTYLCALIX[4]ARENE MIXTURES AT THE CHLOROFORM / WATER INTERFACE

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Abstract. *The study presents the effect of adding p-tert-butylcalix[4]arene, benzo ether crowns and their equimolecular mixture in the organic phase on the interfacial tension for the chloroform water interface. It was found that addition of macrocyclic ligands to the organic phase has different effects on the interfacial tension. The higher the number of oxygen atoms in the ethereal ring of the benzo crown ethers, the higher the values of interfacial tension, while same modification of the ethereal ring produces an opposite effect in the case of amino benzo ethers, indicating different arrangements of molecules in the interface.The simultaneous presence of p-tert-butylcalix[4]arene and benzo crown ethers in the interface leads, in some situations, to significant changes in the interfacial tension values, a phenomenon explained by the modification of the macrocyclic ligands assembly in the interface. Also, composition of the aqueous phase influences the value of measured interfacial tension, type of the alkaline cation from the aqueous solution leading to different behavior of macrocyclic ligands in the interface.*

Keywords: *calixarene, crown ethers, interface, macrocyclic ligands, self-assembling.*

1. INTRODUCTION

Calixarenes and crown ethers represent a class of intensively studied macrocyclic compounds [1, 2]. The molecules of these macromolecular species have practical utility due to the presence in the same structure of hydrophobic and hydrophilic areas. Besides this, the cavity of the macrocyclic ligand is easily modifiable if the working parameters are changed during the synthesis of the macrocyclic compounds [3].

Calixarenes and crown ethers have structures recommended for processes that involve molecular recognition for the purpose of forming molecular aggregates with practical utility as biosensors, catalysts, etc. [4-6]. Thus, a rapid development of the systems based on calixarene and ether crowns occurred, they have also proven usefulness in the field of nanotechnologies, being able to imitate very well the processes of self-recognition and self-assembly as in biological systems [7].

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The low acidity of the calixarenes is responsible for the ability to bind and transport metal cations [8, 9]. Together with this binding capacity, that is mainly due to electrostatic interaction, calixarenes act on the size-matching principle for guest-host molecular structures. Thus, the macroclyclic ligand of calixarenes (host molecules) will bind and transport metal cation (guest) whose size matches, and this is a selection criterion. This selected criterion for the complexation of the metal cations is also valid for the crown ethers; the complexation capacity being influenced by the type of functional groups grafted on the basic structure [10].

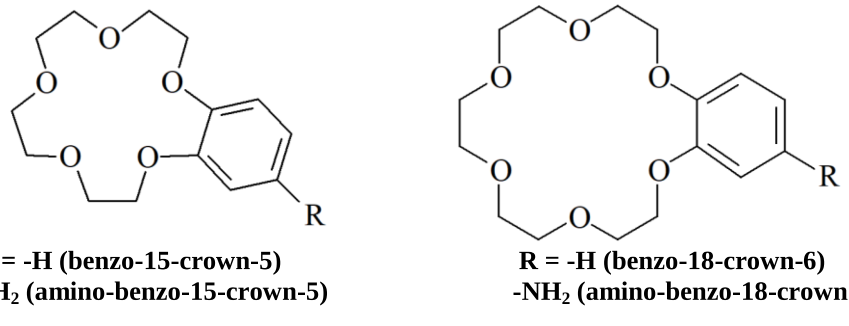
Due to complexation properties that take into account the size of the guest species, both the calixarenes and the crown ethers are considered good models for the host-guest supramolecular systems [11].

The purpose of present study is to assess whether there is a different way of assembling the calixarene molecules and crown ethers when the amino group is introduced into the crown ether molecule. The presence of the grafted amino group on the crown ether structure may induce basicity to macrocyclic ligand molecules. In this situation, it may interact to some extent with the calixarene molecules that are weakly acidic. This specific behaviour would lead to different packing of the macrocyclic ligands in the interface, and therefore leading to the modification of the interfacial tension and of the complexation capacity. This study aimed to evaluate the interfacial behaviour of *p-tert*–butylcalix[4]arene, benzo-15-crown-5, benzo-18-crown-6, 4’-NH_2-benzo-15- crown-5, 4’-NH_2-benzo-18-crown-6 and of the mixtures calixarene: crown ethers. These mixtures were indicated to have synergistic effect in the extraction processes at the chloroform-water interface [12-15].

2. MATERIALS AND METHODS

2.1. MATERIALS

The macrocyclic ligands used in these experiments were *p-tert*–butylcalix[4]arene (Sigma Aldrich) with 95 % purity, and 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. Solutions of 10^{-4} M of each macrocyclic ligand were prepared using as solvent chloroform (Merck Millipore) stabilized with 0.6-1% ethanol (99% purity). Sodium hydroxide pellets (purity 98 %, carbonate < 0.5%), potassium hydroxide pellets (purity > 85%, carbonate < 1%) and hydrochloric acid (37% solution) were purchased from a local producer (Chimopar). Redistilled water (conductivity below 0.10 $\mu S \cdot cm^{-1}$ at 25 °C) was used for all experiments.



R = -H (benzo-15-crown-5)
-NH_2 (amino-benzo-15-crown-5)

R = -H (benzo-18-crown-6)
-NH_2 (amino-benzo-18-crown-6)

Figure 1. Crown ethers structures.

For the determination of interfacial tension at the air-water and chloroform-water interfaces, a Willhelmy device was used, while maintaining a constant temperature of the mixture by using a water circulator; this setup ensured 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 (π-A) for the air-water interface were measured using a Wilhelmy device with a platinum plate. Redistilled water was added in a rectangular tray made of glass, then 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. The interfacial tension was calculated considering the recorded force that pulls out the platinum plate.

The water – chloroform interface was characterized at 25 °C using a device with a general operation scheme presented elsewhere [16]. The concentration of the macrocyclic ligands added to the organic phase was calculated using data from the air-water interface measurements. The area of the tray was divided to that of area of one molecule as calculated in the air-water interface experiment that had the purpose to obtain a thin compact layer of macrocyclic ligands at the liquid-liquid 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 50% solution were added to the aqueous phase in order to reach the 0.1 M concentration for NaOH . Once the stability of the phase was obtained (interfacial tension reaches a constant value) a HCl 37% solution is added with a micropipette, to neutralize the NaOH solution and reproduce the liquid-liquid experiment calixarene: crown ethers described elsewhere. Same setup and procedure were followed, but using KOH solution instead of NaOH, so that various cation sizes influences may be studied during experiments.

To asses the variation of interface tension with pH, the value of pH of aqueous solution was measured.

3. RESULTS AND DISCUSSION

The added volumes of calixarene and crown ethers from prepared stock solutions have been established so that a fine compact layer of macrocyclic ligands was formed at the interface. For this purpose, the area of the tray in which the experiment is carried out was divided into the area of the molecules as established in a previously published study [16].

Table 1. Area/molecule for studied macrocyclic ligands at the air/water interface [16].

Macromolecular compound	Area/molecule (Å^2)
p-tert–butylcalix[4]arene	100 ± 5
benzo-15-crown-5	85 ± 5
benzo-18- crown -6	100 ± 5
4’-NH_2-benzo-15- crown -5	110 ± 5
4’-NH_2-benzo-18- crown -6	120 ± 5

Water / chloroform interface study

The area/molecule values at the air/water interface were used to calculate the volume of macrocyclic ligands solution that was added to the organic phase. In the aqueous phase alkaline hydoroxide was added (either NaOH, or KOH). After the system reaches equilibrium, HCl was gradually added, so that interface tension variation with pH of aqueous phase may me recorded. Consequently, hidroxy groups are replaced by chloride ions and, in this situation, the cation concentration remains constant. The ionic species that changes during this experiment are hydroxyl, chloride and hydronium.

Fig. 2 shows the variations of the interfacial tension for the situation when the alkali hydroxides are neutralized with hydrochloric acid in the aqueous phase. It can be observed that the curves are different, indicating different influences of the ion type present in the interface.

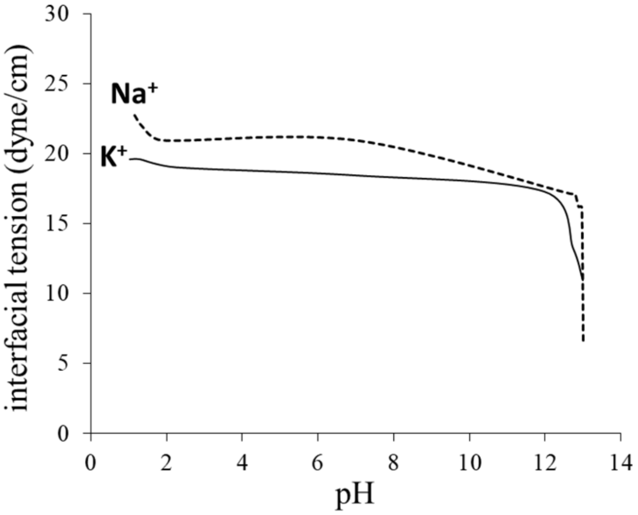


Figure 2. Interfacial tension vs. pH for water/chloroform interface when the organic phase contains no macrocyclic ligands.

In the same time calixarenes, which are slightly acidic are deprotonated in basic medium and aminocrown ethers are protonated in basic medium.

p-tert–butylcalix[4]arene / benzo-15-crown-5 mixture at the liquid interface

Table 2 presents the interfacial tensions of the chloroform/water interface recorded in the absence and in the presence of alkaline cations. When only the macrocyclic ligands are found in the interface, small differences are observed between the interfacial tensions, whether we speak of the *p-tert*–butylcalix[4]arena, benzo-15-crown-5, or of their equimolecular mixture. When sodium and potassium chlorides are present in the interface, the interfacial tension decreases, no matter the macrocyclic ligand structure in the interface.

When the organic phase contains calixarene only, it is observed that the decrease of interfacial tension is somewhat similar for the interfaces that contain sodium and potassium. This may indicate that calixarene forms complexes at the interface with alkaline cations, without having a preference for any of the studied cations. However, when benzo-15-crown-5 is present in the interface, a more pronounced decrease of the interfacial tension is recorded when 0.1M potassium chloride was added to the aqueous solution.

Table 2. The interfacial tension (dyne/cm) at pH=7 when *p-tert*–butylcalix[4]arene and / or benzo-15-crown-5 are present in the organic phase.

Organic phase		no macrocyclic ligand	*p-tert*–butylcalix[4]arene	benzo-15-crown-5	equimolecular mixture calixarene-crown ether
Aqueous phase (pH=7)	no alkaline cation	32.80	25.20	23.00	27.60
	Na^+	25.10	19.20	22.60	21.00
	K^+	18.40	20.10	16.90	15.53

Fig. 3 shows the variation of the interfacial tensions for the situations when in the aqueous solution, a titration of a hard base (0.1 M NaOH / KOH) with a strong acid (HCl) was performed. In all cases it may be observed that the interfacial tension decreases with the decrease of pH, the appearance of the curves being different for the two situations (either sodium, or potassium in the aqueous phase), regardless of the content of the organic phase. This can be explained by the replacement of the hydronium ion with hydroxyl from the aqueous phase following the neutralization of the alkaline bases with hydrochloric acid. Also, the change of the organic phase component leads to different variations of the interfacial tensions, at different pH. This different behaviour is explained by the way the chemical species interact and the way the structures formed in the interface are packed.

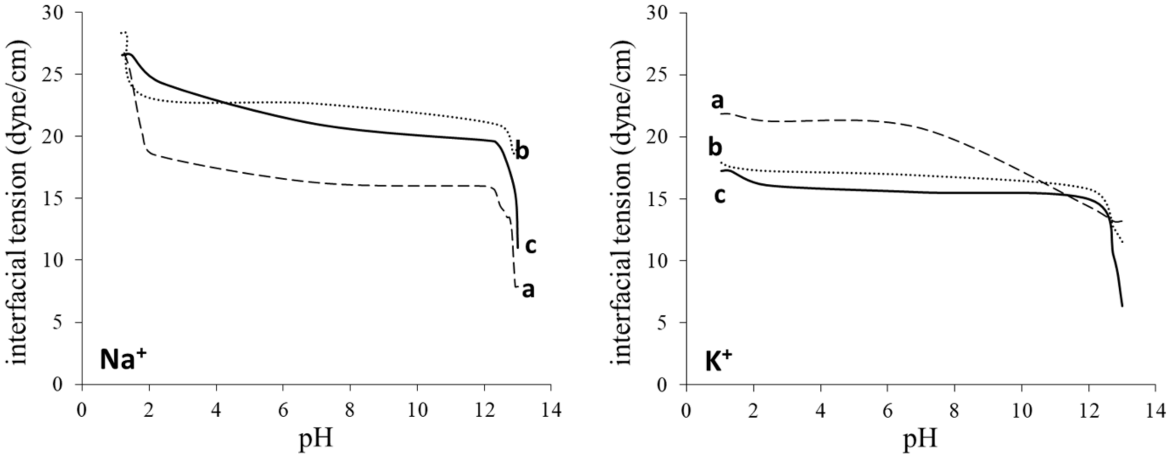


Figure 3. Interfacial tension *vs.* pH for water/chloroform interface when the organic phase contains: a. *p-tert*–butylcalix[4]arene, b. benzo-15-crown-5, c. equimolecular mixture *p-tert*–butylcalix[4]arene / benzo-15-crown-5, when sodium or potassium is added in the aqueous medium.

At pH<12, the mixture behaves differently depending on the type of the cation from the aqueous phase. When in the water phase is sodium (Na^+), below are mentioned the interfacial tension (γ) variations in different ranges:

- at $pH \in (4,12)$ $\gamma_{\text{mixture}} \in (\gamma_{\text{calixarene}}, \gamma_{\text{crown ether}})$
- at $pH<4$ $\gamma_{\text{mixture}} > \gamma_{\text{crown ether}} > \gamma_{\text{calixarene}}$
- at $pH \in (4,12)$ $\gamma \in (\gamma_{\text{calixarene}}, \gamma_{\text{crown ether}})$
- at $pH<4$ $\gamma_{\text{mixture}} > \gamma_{\text{crown ether}} > \gamma_{\text{calixarene}}$

If the aqueous phase contains potassium the mixture presents synergism by lowering the interfacial tension at any pH value.

p-tert–butylcalix[4]arene / benzo-18-crown-6 mixture at the liquid interface

The values of the interfacial tensions at neutral pH, if the crown ether is replaced in the organic phase with benzo-18-crown-6, are presented in Table 3. It is observed that the presence of benzo-18-crown-6 in the organic phase causes the decrease of interfacial tension compared with the situation when the crown ether with five oxygen atoms is present in the organic phase. It is possible that increase of the number of oxygen atoms leads to an increase of the number of macrocyclic ligands crowded in the interface.

The addition of sodium in the aqueous phase leads to a decrease in the interfacial tension, while the addition of potassium in the aqueous phase determines a constant, unchanged interfacial tension. On the other hand, addition of an equimolecular mixture of macrocyclic ligands in the organic phase leads to increase of the interfacial tension compared to the situation when the ligands are not mixed in the organic phase, for aqueous solutions with no cations. The same variation is registred when the aqueous solution contains sodium.

Table 3. The interfacial tension (dyne/cm) at pH=7 when *p-tert*–butylcalix[4]arene and / or benzo-18-crown-6 are present in the organic phase.

Organic phase		no macrocyclic ligand	*p-tert*–butylcalix[4]arene	benzo-18-crown-6	equimolecular mixture calixarene-crown ether
Aqueous phase (pH=7)	no alkaline cation	32.80	25.20	17.80	28.70
	Na^+	25.10	19.20	12.40	24.30
	K^+	18.40	20.10	17.30	19.80

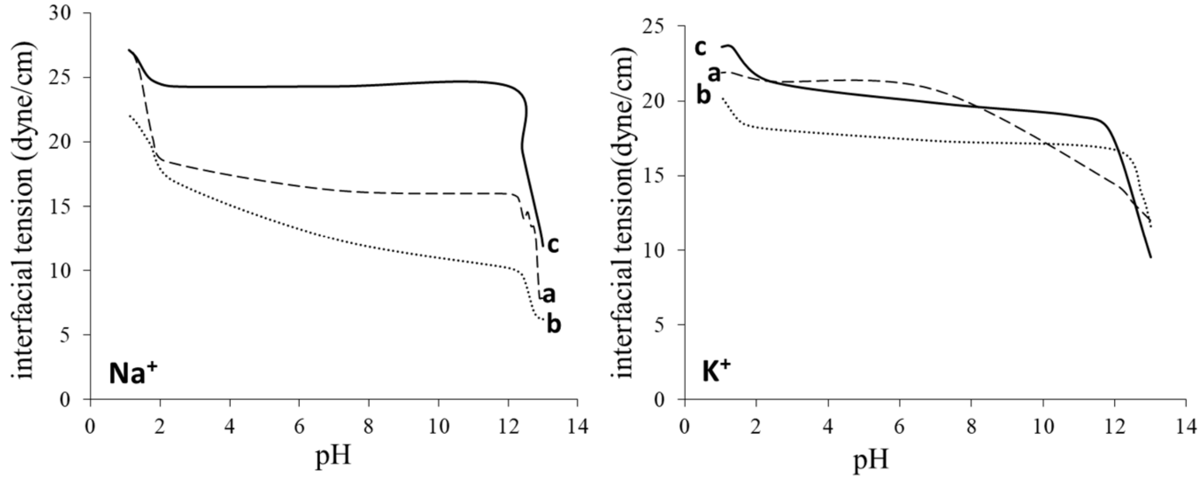


Figure 4. Interfacial tension *vs.* pH for water/chloroform interface when the organic phase contains: a. *p-tert*–butylcalix[4]arene, b. benzo-18-crown-6, c. equimolecular mixture *p-tert*–butylcalix[4]arene / benzo-18-crown-6, when sodium or potassium is added in the aqueous medium.

If the water phase contains only sodium, the mixture calixarene – crown ether from the organic phase (Fig. 4), the interfacial tension increases for all the pH domain, except the very acidic and very basic medium (pH>12 and pH<2). By observing the values of the interfacial tension and the allure of the curve in Fig. 4, it may be also underlined that, when the potassium cation is present in the water, certain differences were recorded.

p-tert–butylcalix[4]arene / 4'-amino-benzo-15-crown-5 mixture at the liquid interface

Addition of 4'-amino-benzo-crown-5 to the organic phase leads to a value of 23.6 dyne/cm when in the aqueous phase there is no alkaline cation (Table 4), a value which is close to the interfacial tension of the system containing calixarene in the organic phase. Addition of equimolecular calixarene/amino crown ether mixture leads to significant increase of interfacial tension, a tendency that is more pronounced if there is no alkaline cation or if potassium is present in the aqueous solution (Table 4).

The results presented in the Fig. 5 show that the equimolar mixture of 4'-NH_2-benzo-15-crown-5: *p-tert*–butylcalix[4]arene has the effect of increasing the value of interfacial tension at pH lower than 12, regardless of the contents of the aqueous phase, if either with sodium or potassium. This effect is probably due to the aromatic amino group from the crown ether structure. The most probable mechanism that could explain this behaviour involves formation of supramolecular assemblies with higher areas compared with the sum of both macrocyclic ligands. This way, some of the macrocyclic ligands from the interface re-enter in the organic phase and outdistance themselves from the interface.

Table 4. The interfacial tension (dyne/cm) at pH=7 when *p- tert* – butylcalix[4]arene and / or 4'-amino-benzo-15-crown-5 are present in the organic phase.

Organic phase		no macrocyclic ligand	*p-tert*–butylcalix[4]arene	4'-amino-benzo-15-crown-5	equimolecular mixture calixarene-crown ether
Aqueous phase (pH=7)	no alkaline cation	32.80	25.20	23.60	49.50
	Na^+	25.10	19.20	10.40	20.40
	K^+	18.40	20.10	23.40	39.90

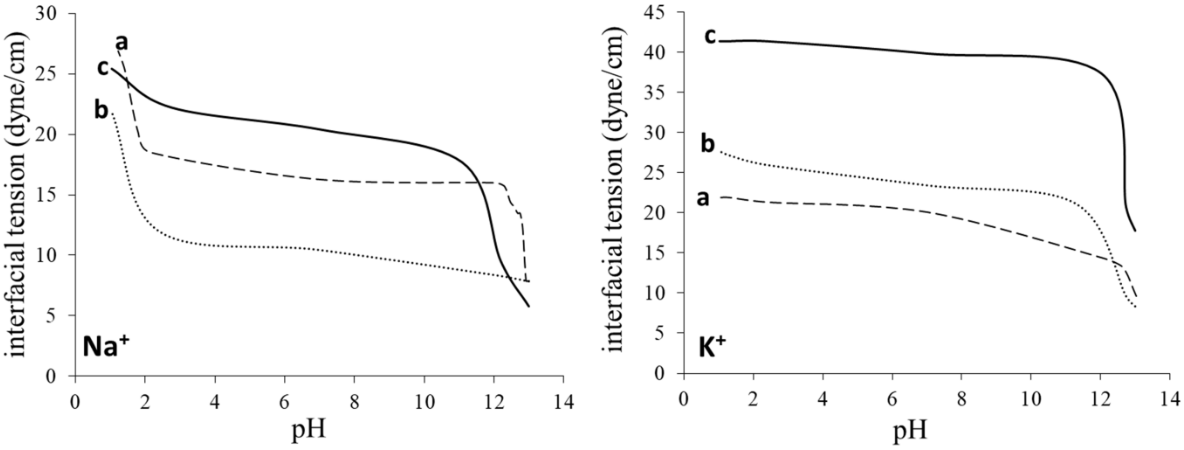


Figure 5. Interfacial tension *vs.* pH for water / chloroform interface when the organic phase contains: a. *p-tert*–butylcalix[4]arene, b. 4'-amino-benzo-15-crown-5, c. equimolecular mixture *p-tert*–butylcalix[4]arene / 4'-amino-benzo-15-crown-5, when sodium or potassium is added in the aqueous medium.

p - tert–butylcalix[4]arene / 4’-amino-benzo-18-crown-6 mixture at the liquid interface

Table 5. The interfacial tension (dyne/cm) at pH=7 when *p- tert*–butylcalix[4]arene and / or 4’-amino-benzo-18-crown-6 are present in the organic phase.

Organic phase		no macrocyclic ligand	*p- tert*–butylcalix[4]arene	4’-amino-benzo-18-crown-6	equimolecular mixture calixarene-crown ether
Aqueous phase (pH=7)	no alkaline cation	32.80	25.20	31.20	44.90
	Na^+	25.10	19.20	17.20	23.80
	K^+	18.40	20.10	26.80	25.90

Tables 5 and 6 show higher interfacial values for the situations where in the organic phase there are amino benzo ethers crown as compared to mixtures containing benzo ethers crown ethers (Tables 3 and 4) showing that the addition of the amino group to the basic structure significantly modifies the arrangement of the molecules in the interface.

The mixture 4’-amino-benzo-18-crown-6 + *p- tert*–butylcalix[4]arene (Fig. 6) shows similar interfacial behaviour with the mixture 4’-amino-benzo-15-crown-5 + *p-tert*–butylcalix[4]arene (Fig. 5), except the fact that the antagonist behaviour throughout the entire pH domain is observable when the sodium ion is present in the aqueous phase.

This variation in the interfacial activity, when sodium is in the interface for the mixture 4’-amino-benzo-18-crown-6 + *p- tert*–butylcalix[4]arene, is analogous to the variation of the interfacial tension when potassium is in water and the organic phase contains 4’-amino-benzo-15-crown-5 + *p-tert*–butylcalix[4]arene.

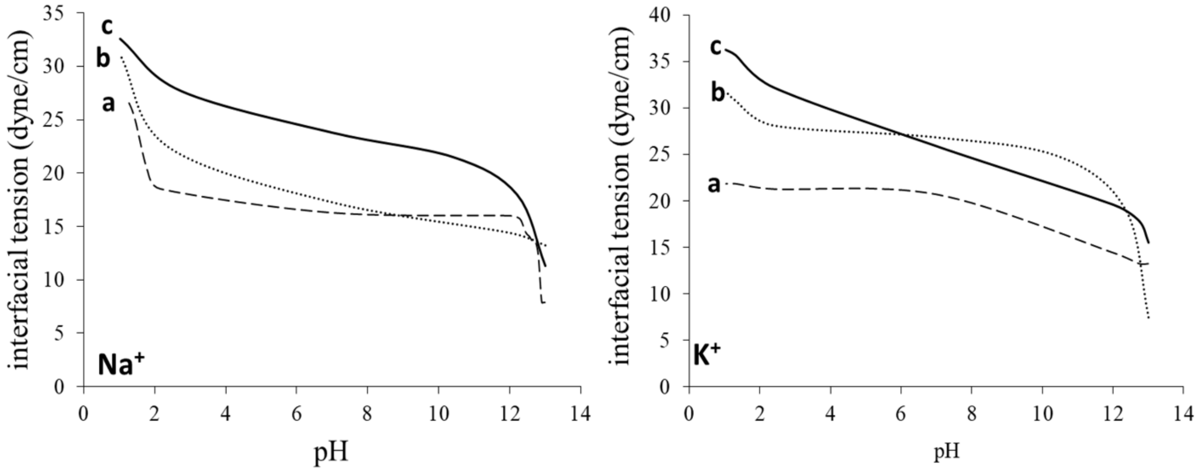


Figure 6. Interfacial tension *vs.* pH for water/chloroform interface when the organic phase contains: a. *p-tert*–butylcalix[4]arene, b. 4’-amino-benzo-18-crown-6, c. equimolecular mixture *p- tert*–butylcalix[4]arene / 4’-amino-benzo-18-crown-6, when sodium or potassium is added in the aqueous medium.

These results indicate that the amino aromatic group is very active in the formation process of the supramolecular assemblies in the interface. It was found that the amino group is able to increase the surface occupied by the supramolecular structure formed in the interface, compared with the sum of the areas of each type of molecule.

The evolution of the interfacial tension with the pH indicates also an important contribution of the amino group to the complexation process of the alkaline cation in the interface. The results presented in the Fig. 6 show a decrease of the interfacial tension, which can be assigned to the formation of supramolecular aggregates in the interface.

4. CONCLUSIONS

Calixarenes and crown ethers are macrocyclic ligands that can bind and transport metal cations, providing a hydrophilic cavity for complexing the guest species By studying the interfaces properties and processes, a significant contribution to explaining and anticipating the mechanisms followed by macrocyclic ligands when transferring metal cations from the aqueous phases to organic ones.

In the present study, the effect of adding two types of macrocyclic ligands in the organic phase, on the interfacial tension values, measured at the contact with aqueous phases with various compositions was studied. The organic phases studied were either mono-component, with one of the macrocyclic ligand, or bi-component, using a mixture of the two ligands. To study the effect of the metal cations from the aqueous phase, composition of the aqueous solution was varied by adding hydrochloric acid to the alkaline hydroxide solution. Composition of the aqueous phase varied from the mixture of alkaline cation and hydroxide under conditions of basic pH, to alkaline cation and chloride when the pH was neutral, and to alkaline cation, anion chloride and hydronium in acidic solution. In these conditions, the interfacial tension decreases with increasing pH for all the studied situations, regardless of the composition of the organic phase.

The addition of calixarene and of crown ether led to different values of interfacial tension showing that macrocyclic ligands were present at the interface and interacted with water molecules and other chemical species present in the aqueous phase. It is noteworthy that the modification of the ether ring from five to six oxygen atoms in the case of benzo crown ethers led to a decrease in interfacial tension regardless of the water phase composition, while the same modification of the ring produced the opposite effect in the case of amino benzo crown ethers.

If in the organic phase mixtures of calixarenes and crown ethers have been introduced, there have been modifications of interfacial tension. The type of cation from the aqueous solution influenced the measured values of the interfacial tension. It is noteworthy the large variation of the interfacial tension when mixtures of *p*- *tert*–butylcalix[4]arene and amino benzo ether crown are found in the organic phase.

The different results obtained with the amino-benzo-crown-ethers compared with the corresponding benzo-crown-ethers indicate the contribution of the amino group on the ordering of the crown ethers molecule at the chloroform-water interface. The different interfacial activity was assigned as related to formation of supramolecular assemblies calixarene-crown ethers where the molecules are bound by electrostatic forces, intermolecular hydrogen bonds and van der Walls forces.

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