Separation of *p*-Aminobenzoic Acid by Reactive Extraction in the Presence of 1-Octanol as Phase Modifier

A.-I. Galaction,[a] L. Kloetzer,[b] and D. Caşcaval[b,*]

[a]University of Medicine and Pharmacy "Gr. T. Popa" of Iasi, Faculty of Medical Bioengineering, Dept. of Biotechnologies, M. Kogalniceanu 9–13, 700454 Iasi, Romania

[b]Technical University "Gh. Asachi" of Iasi, Faculty of Chemical Engineering and Environmental Protection, Dept. of Biochemical Engineering, D. Mangeron 71, 700050 Iasi, Romania

Original scientific paper
Received: April 23, 2009
Accepted: December 18, 2009

The paper presents the studies on reactive extraction of *p*-aminobenzoic acid with two extractants (Amberlite LA-2 and D2EHPA) dissolved in two solvents with different dielectric constants (*n*-heptane, dichloromethane), at various 1-octanol concentrations in the solvent. The addition of 1-octanol induced the increase of the extraction efficiency, the most important influence being recorded for the solvent with lower polarity (*n*-heptane). Moreover, the volumetric fraction of alcohol controls the number of extractant molecules participating in the interfacial product formation. This effect was more important for the extraction in low-polar solvent and was concretized in the reduction of number of Amberlite LA-2 molecules included in the interfacial compound from 3, in the absence of alcohol, to 1, for $\varphi = 20$ % alcohol. Indifferent to alcohol fraction in organic phase, for the reactive extraction with D2EHPA in *n*-heptane, the number of extractant molecules decreased from 2, in the absence of 1-octanol, to 1 in the presence of 1-octanol. The limitation of solute solvation by extractant due to the increase of solvent polarity led to the reduction of the extraction constant and to the amplification of the differences between the extraction constants obtained for the same extractant and the two solvents.

Key words:
p-Aminobenzoic acid, Amberlite LA-2, D2EHPA, 1-octanol, reactive extraction

Introduction

For many technologies, liquid-liquid extraction constitutes a viable solution, due to its technical accessibility and high efficiency. However, its application is limited for the ionizable compounds, especially carboxylic acids, due to their low solubility in usual organic solvents. In these cases, the performances of the extraction process can be enhanced by reactive extraction with an extractant added into the organic phase. Thus, the reactive extraction using extractants of organophosphoric or height molecular amine types have been successfully applied to the separation of some carboxylic acids, namely as: acetic acid, lactic acid, citric acid, succinic acid, malic acid, ascorbic acid or beta-lactamic antibiotics.[1–12]

In many processes of acids reactive extraction, the formation of a "third phase" has been observed. This phase consists of a stable emulsion with a high amount of acids or acid-extractant adducts, being insoluble both in the organic and aqueous phases.[3,13–15] This phenomenon is more important for extraction systems containing extractants of amine type and solvents with low polarity and leads to the increase of separation duration simultaneously with the diminution of its efficiency. The formation of the third phase can be avoided by addition of a "phase modifier" in the organic solvent. Generally, this compound is an alcohol with an aliphatic chain of at least 8 carbon atoms and modifies the polarity of the solvent, promoting the breakage of the stable emulsion and solubilization of its content.[3,15–17]

p-Aminobenzoic acid (PABA), also called vitamin B_{10} or factor R, was found to be part of the folic acids, its chemical structure being given in Fig. 1. Being a component of pteroylglutamate, it is considered to act as a provitamin for some bacteria and growth factor for some superior animals, in the human body possessing the capacity to synthesize folates.[18]

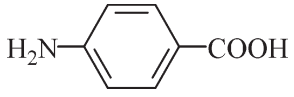


Fig. 1 – *Chemical structure of p-aminobenzoic acid*

*the corresponding author: email: dancasca@ch.tuiasi.ro, fax: + 40 232 271 311

PABA is used in the cosmetics industry as an additive in sunscreen lotions. The medical applications are for skin protection against vitiligo, sclerodermy and male infertility treatment. It is also used in diagnostic tests for the state of the gastrointestinal tract in medicine. It was established that PABA is an inducer of endogenous interferon and immunomodulator, displays a virucidal, synergistic antiviral effect when combined with chemical drugs and possesses the properties of a direct anticoagulant.[18] Although this compound is not considered an essential nutrient, it is included in vitamin B or multivitamin supplements.[18]

The most recent methods for PABA production are chemical synthesis using methyl-4-formylbenzoate as a starting material[20] or biosynthesis by mutant strains of *Escherichia* coli.[21] In both cases, the separation stages are complex and require significant energy and material consumption.

Due to the insolubility of PABA in organic solvents immiscible with water, its separation by physical extraction is impossible. Previous studies have indicated that its extraction is possible by adding an extractant into the solvent that could react with this acid, leading to the formation of a hydrophobic compound. Because the chemical structure of PABA contains an acidic group, –COOH, and a basic one, $–NH_2$, the reactive extraction has been performed by using extractants of aminic and organophosphoric acid types, namely Amberlite LA-2 (lauryl-trialkyl-methylamine) and di-(2-ethylhexyl) phosphoric acid (D2EHPA), respectively.[22] Because the formation of the third phase has been observed during the reactive extraction of PABA, these studies are continued and developed by investigating the mechanisms and, consequently, the factors that control the mechanisms of acid extraction with the two extractants in the presence of 1-octanol as phase modifier. Because the solvent polarity represents an important factor controlling the extraction efficiency, the extraction mechanisms and influencing factors have been analyzed in direct correlation with the polarity of the two used solvents (*n*-heptane and dichloromethane).

Materials and method

The experiments have been carried out using an extraction column with vibratory mixing, which offers high interfacial area and the possibility of reaching the equilibrium state rapidly. The laboratory equipment has been described in detail in previous papers.[11] The phase mixing was made by means of a perforated disk with 45 mm diameter and 20 % free section. The vibrations had a frequency of 50 s^{-1} and 5 mm amplitude. The perforated disk position was maintained at the initial contact interface between the aqueous and organic phases. The extraction time was 1 minute at a constant temperature of 25 °C. The resulting emulsion was broken in a centrifugal separator at 8000 rpm.

The initial concentration of PABA in aqueous solution was 5 g L^{-1} ($3.65 \cdot 10^{-2}$ mol L^{-1}). The reactive extraction was made with Amberlite LA-2 and D2EHPA, respectively, both solved in two solvents with different dielectric constants. The two solvents were *n*-heptane (dielectric constant of 1.90 at 25 °C[23]) and dichloromethane (dielectric constant of 9.08 at 25 °C[23]).

1-octanol (dielectric constant of 10.3 at 25 °C[23]) was dissolved into the two solvents, its volumetric fraction varying between 0.05 and 0.20 (φ = 5–20 %). The extractants concentration in organic phase (solvent and 1-octanol) was between 5 and 80 g L^{-1} ($1.3 \cdot 10^{-2}$ – 0.21 mol L^{-1} for Amberlite LA-2, $1.5 \cdot 10^{-2}$ – 0.24 mol L^{-1} for D2EHPA). The volumetric ratio of aqueous and organic phase was φ = 1 : 1 (20 mL of each phase).

The pH-value of the initial aqueous solution varied between 1 and 8. The pH was adjusted with a solution of w = 3 % sulfuric acid or w = 3 % sodium hydroxide, function on the prescribed pH-value. The pH-values were determined using a digital pH-meter of Consort C836 type and were recorded throughout each experiment. Any pH change was recorded during the extraction experiments.

The extraction process was analyzed by means of the extraction degree, distribution coefficient and extraction constant. The extraction degree was defined as the ratio between the extracted concentration of PABA and its initial concentration in the aqueous phase. For calculating these parameters, the acid concentrations in the initial solution were measured by the spectrophotometric technique, using a spectrophotometer of CAMSPEC M550 type. Therefore, the absorption of the aqueous solutions was determined at λ = 267 nm.[24] The mass balance was used to calculate the acid concentration in the organic phase.

Each experiment was carried out three or four times, for identical conditions, the average value of the considered parameters being used. The maximum experimental error was ± 4.62 %.

Results and discussion

Regardless of the extractant type, the reactive extraction of PABA occurs by the formation of a strong hydrophobic compound at the interface between the aqueous and organic phases. The chemi-

cal structure of this compound and the extraction parameters depend on the extractant type.

According to the previous studies, the carboxylic group of the PABA is involved in the reactive extraction process with Amberlite LA-2 (Q). The interfacial interactions between the acid and the extractant could be of hydrogen bonding type with the undissociated carboxylic groups, or of ionic type, if the acid dissociates in the aqueous solution:[22]

$$H_2N–C_6H_4–COOH_{(aq)} + n\ Q_{(o)} \rightleftharpoons \rightleftharpoons H_2N–C_6H_4–COOH \cdot Q_{n(o)}$$

Furthermore, in function of the structures of system components and solvent polarity, the acidic or aminic adducts could be formed at the interface.[3,5,11] However, as it was observed for the reactive extraction with Amberlite LA-2 of other compounds having voluminous molecules and due to the initial concentration of PABA, which is lower than that of Amberlite LA-2, it could be assumed that the formation of acidic adducts is steric hindered. Therefore, the interfacial compounds could be of ammonium salt type, formed by neutralization of the carboxylic group with one extractant molecule, or of aminic adducts type, where $n \geq 2$.[1,3,22]

In this context, in the absence of 1-octanol, the reactive extraction of PABA with Amberlite LA-2 occurs by means of the following interfacial mechanisms:[22]

– *extraction in n-heptane*

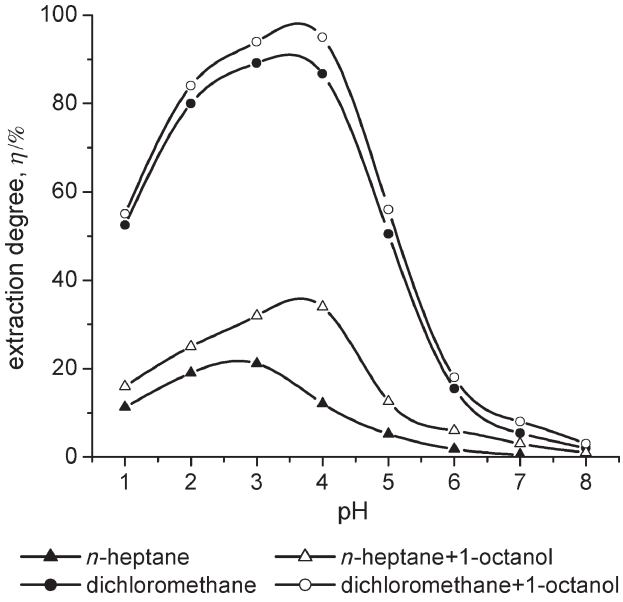
$$H_2N–C_6H_4–COOH_{(aq)} + 3\ Q_{(o)} \rightleftharpoons \rightleftharpoons H_2N–C_6H_4–COOH \cdot Q_{3(o)}$$

– *extraction in dichloromethane*

$$H_2N–C_6H_4–COOH_{(aq)} + Q_{(o)} \rightleftharpoons \rightleftharpoons H_2N–C_6H_4–COOH \cdot Q_{(o)}$$

which indicate the modification of the interfacial product as a function of the solvent polarity. Thus, the reactive extraction with Amberlite LA-2 in low-polar solvent (*n*-heptane) occurs by means of the interfacial formation of an aminic adduct with 3 extractant molecules. If the solvent with higher polarity is used (dichloromethane), each reactant participates with one molecule to the interfacial reaction.

The addition of 1-octanol into the organic solvent does not change the general shape of the dependence between the extraction efficiency and pH of the aqueous phase. However, as it can be seen from Fig. 2, the pH corresponding to the maximum extraction degree is moved to higher value in the presence of 1-octanol.



F i g . 2 – *Influence of pH of aqueous phase on efficiency of PABA reactive extraction with Amberlite LA-2 (Amberlite LA-2, concentration, γ = 20 g L^{-1}; 1-octanol volume fraction, φ = 10 %)*

The existence of the maximum extraction degree is the result of PABA aminic group ionization at strong acidic pH-domain ($pK_{a1} = 2.50$[23]), this phenomena limiting the extraction efficiency. On the other hand, the increase in pH-value induces the dissociation of –COOH group ($pK_{a2} = 4.87$[23]) and, implicitly, the reduction of extraction yield. Thus, indifferent of the used solvent, as the result of the two contrary effects generated by the increase of pH, the optimum value of aqueous phase pH for the reactive extraction with Amberlite LA-2 without 1-octanol was 3.[22] Owing to the increase in organic phase polarity, the addition of phase modifier leads to the extension of the pH-domain that corresponds to a positive influence of this parameter, by also solubilizing partially the dissociated PABA molecules. In these circumstances, the maximum efficiency of acid reactive extraction with Amberlite LA-1 in the presence of 1-octanol is reached at pH 4.

Moreover, the alcohol induces the increase in extraction yield, an effect that is more pronounced for the solvent with lower dielectric constant. For φ = 10 % 1-octanol in solvent, the extraction degree in *n*-heptane increases by 2.5–21.8 %, respectively by 1–8.3 % in dichloromethane. The most important differences between the extraction efficiencies for the systems with and without 1-octanol have been recorded for pH-domain of 3–4, due to the supplementary contribution to the overall extraction yield of the solubilization of dissociated

PABA molecules by increasing organic phase polarity in the presence of 1-octanol.

Because PABA also contains N aminic, it can react with acidic extractants, such as D2EHPA (HP). In this case, according to the previous results, the reactive extraction occurs by means of an interfacial reaction of ion-exchanging type, which requires the acid to be in protonated form in the aqueous solution:[22]

$$HOOC–C_6H_4–N^+H_{3(aq)} + n\ HP_{(o)} \rightleftharpoons$$
$$\rightleftharpoons HOOC–C_6H_4–N^+H_3P^- \cdot (n–1)HP_{(o)} + H^+_{(aq)}$$

the number of extractant molecules, n, depending on solvent polarity:

– *extraction in n-heptan*

$$HOOC–C_6H_4–N^+H_{3(aq)} + 2\ HP_{(o)} \rightleftharpoons$$
$$\rightleftharpoons HOOC–C_6H_4–N^+H_3P^- \cdot HP_{(o)} + H^+_{(aq)}$$

– *extraction in dichloromethane*

$$HOOC–C_6H_4–N^+H_{3(aq)} + HP_{(o)} \rightleftharpoons$$
$$\rightleftharpoons HOOC–C_6H_4–N^+H_3P^-_{(o)} + H^+_{(aq)}$$

At strong acidic pH, the extractant is protonated and thus unable to react with PABA.[25,26] Therefore, in the absence of 1-octanol, the optimum pH-value for the extraction with D2EHPA was also 3.[22]

As in the case of reactive extraction with Amberlite LA-2, for the extraction systems containing D2EHPA and 1-octanol, the shape of the variation of extraction yield in function of pH-value of aqueous is similar to that plotted for systems without alcohol. For the same reason, the optimum pH has been recorded at higher value, namely at pH 4 (Fig. 3).

The influence of 1-octanol is more pronounced for the reactive extraction with D2EHPA, because the solvent polarity exhibits a more important effect on the solubilization of ionic compounds.[16] Thus, by adding $\varphi = 10$ % alcohol, the extraction yield in *n*-heptane was increased by 2–18.5 %, and in dichloromethane by 3.5–30 %.

By comparing the reactive extraction degrees for the two extractants and solvents, it can be concluded that Amberlite LA-2-dichloromethane is the most efficient combination. The maximum difference between the extraction degrees with Amberlite LA-2 and D2EHPA, respectively, has been recorded for pH 4 (for the extractant mass fraction of $w = 20$ %, this difference was 35.5 % for dichloromethane and 13 % for *n*-heptane). Owing to the favorable effect of 1-octanol, this difference was diminished compared with that corresponding to the similar extraction systems without alcohol.[22]

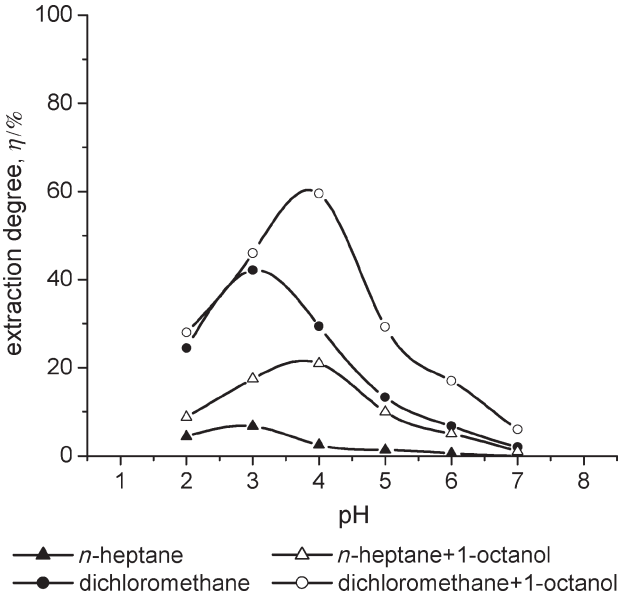


Fig. 3 – *Influence of pH of aqueous phase on efficiency of PABA reactive extraction with D2EHPA (D2EHPA concentration, $\gamma = 20$ g L^{-1}; 1-octanol volume fraction, $\varphi = 10$ %)*

The increase of 1-octanol volume fraction amplifies the alcohol positive effect on the efficiency of PABA reactive extraction (Fig. 4). As mentioned above, the lowest influence of alcohol addition is recorded for the reactive extraction with Amberlite LA-2 in dichloromethane. For the other studied extraction systems, the volumetric fraction of

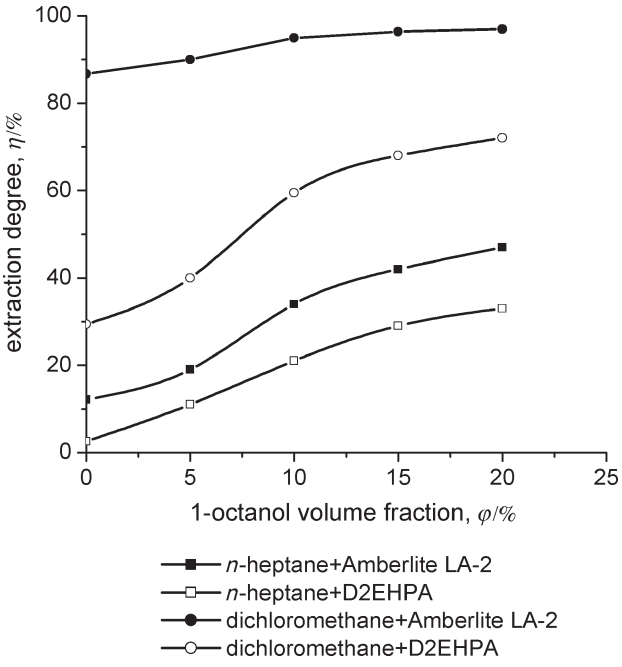


Fig. 4 – *Influence of 1-octanol volume fraction on efficiency of PABA reactive extraction (extractants concentrations $\gamma = 20$ g L^{-1}; pH 4)*

1-octanol in organic phase exhibits a significant influence on reactive extraction degree. Therefore, comparatively with an increase of only 1.1 times for extraction with Amberlite LA-2 in dichloromethane, by increasing the alcohol volume fraction from 0 to $\varphi = 20$ %, the PABA extraction yield was increased as follows: 3.8 times for extraction with Amberlite LA-2 in *n*-heptane, 13.2 times for extraction with D2EHPA in *n*-heptane, respectively 2.4 times for extraction with D2EHPA in dichloromethane.

For analyzing the extraction mechanism of PABA with the two extractants in the presence of 1-octanol, for both extractants and solvents it was assumed that n extractant (E) molecules and one acid (HAc) molecule participate in the formation of the interfacial compound. Thus, the mechanisms of the reactive extraction with the two extractants will be separately analyzed.

Reactive extraction with Amberlite LA-2

The reactive extraction of PABA with Amberlite LA-2 can be described by the following interfacial equilibrium:

$$HAc_{(aq)} + n\ E_{(o)} \rightleftharpoons HAcE_{n(o)}$$

Therefore, the distribution coefficient, D, is calculated with the relationship:

$$D = \frac{\lfloor HAcE_{n(o)} \rfloor}{[HAc_{(aq)}]} \tag{1}$$

where $[HAc_{(aq)}]$ and $[HAcE_{n(o)}]$ symbolize the undissociated concentration of PABA and the overall concentration of extracted compound at the equilibrium state.

According to the interfacial equilibrium, the extraction constant, K_E, can be calculated with the following expression:

$$K_E = \frac{[HAcE_{n(o)}]}{[\overline{HAc_{(aq)}}] \cdot [E_{(o)}]^n} \tag{2}$$

$$\Rightarrow [HAcE_{n(o)}] = K_E \cdot [\overline{HAc_{(aq)}}] \cdot [E_{(o)}]^n \tag{3}$$

The study on the mechanism of reactive extraction was carried out at the optimum pH-value of 4, therefore the concentration of undissociated acid from aqueous phase, $\lfloor HAc_{(aq)} \rfloor$, is calculated by means of its overall concentration in aqueous phase, $\lfloor \overline{HAc_{(aq)}} \rfloor$, and the dissociated acid concentration, $\lfloor Ac^-_{(aq)} \rfloor$. The dissociation constant, K_{a2}, corresponds to the following dissociation equilibrium:

$$HAc \rightleftharpoons Ac^- + H^+$$

Thus, the concentration of undissociated PABA is:

$$[HAc_{(aq)}] = \frac{\lfloor \overline{HAc_{(aq)}} \rfloor}{1 + \frac{K_{a2}}{[H^+]}} \tag{4}$$

Therefore, by combining eqs. (1), (3) and (4), the following expression for the distribution coefficient, D, is obtained:

$$D = K_E \cdot [E_{(o)}]^n \cdot \left(1 + \frac{K_{a2}}{[H^+]}\right) \tag{5}$$

The correlation (5) represents in logarithmic form the equation of a straight line:

$$\ln D - \ln\left(1 + \frac{K_{a2}}{[H^+]}\right) = \ln K_E + n \cdot \ln [E_{(o)}] \tag{6}$$

Because the initial concentration of extractant is higher than the initial concentration of PABA, $[E_{(o)}]$ could be assumed to be the initial concentration of Amberlite LA-2 in organic phase. Consequently, from the slope of the straight line given by eq. (6) it is possible to determine the number of extractant molecules, n, which participate in the formation of the interfacial compound, and from its intercept the value of extraction constant, K_E.

Reactive extraction with D2EHPA

The study on the mechanism of reactive extraction with D2EHPA was carried out also at pH 4. In this case, the N of the aminic group is the active center of the solute, the extraction efficiency being controlled by its ionization capacity. The interfacial reaction could be described by the following equilibrium:

$$H_2Ac^+_{(aq)} + n\ E_{(o)} \rightleftharpoons HAcE_{n(o)} + H^+_{(aq)}$$

According to this interfacial equilibrium, the distribution coefficient, D, is:

$$D = \frac{\lfloor HAcE_{n(o)} \rfloor}{[H_2Ac^+_{(aq)}]} \tag{7}$$

where $[H_2Ac^+_{(aq)}]$ and $[HAcE_{n(o)}]$ represent the overall concentrations of the considered components at the equilibrium state.

The extraction constant, K_E, can be calculated with the following relationship:

$$[HAcE_{n(o)}]^2 = K_E \cdot \lfloor H_2Ac^+_{(aq)} \rfloor \cdot [E_{(o)}]^n \tag{8}$$

The ionization constant of N aminic is K_{a1} is related to the following equilibrium:

$$H_2Ac^+_{(aq)} \rightleftharpoons HAc_{(aq)} + H^+$$

The concentration of protonated PABA from aqueous phase, $[H_2Ac^+_{(aq)}]$, is calculated by means of its overall concentration in aqueous phase, $[\overline{HAc_{(aq)}}]$, and its non-ionized molecules concentration, $\lfloor HAc_{(aq)} \rfloor$:

$$[H_2Ac^+_{(aq)}] = [\overline{HAc_{(aq)}}] - [HAc_{(aq)}] \quad (9)$$

$$[HAc_{(aq)}] = K_{a1}\frac{[H_2Ac^+_{(aq)}]}{[H^+]} \quad (10)$$

$$\Rightarrow [H_2Ac^+_{(aq)}] = \frac{\lfloor [\overline{HAc_{(aq)}}] \rfloor}{1+\frac{K_{a1}}{[H^+]}} \quad (11)$$

Thus, the expression for distribution coefficient becomes:

$$D^2 = \frac{[HAcE_{n(o)}]^2}{[H_2Ac^+_{(aq)}]^2} = \frac{K_E \cdot [E_{(o)}]^n}{[H_2Ac^+_{(aq)}]} = \frac{K_E \cdot [E_{(o)}]^n \cdot \left(1+\frac{K_{a1}}{[H^+]}\right)}{[\overline{HAc_{(aq)}}]} \quad (12)$$

The logarithmic form of eq. (12) gives a straight line equation:

$$2\ln D - \ln\frac{1+\frac{K_{a1}}{[H^+]}}{[\overline{HAc_{(aq)}}]} = \ln K_E + n \cdot \ln[E_{(o)}] \quad (13)$$

which is used for n and K_E graphic determination, similar to the calculations for reactive extraction with Amberlite LA-2 ($[E_{(o)}]$ could also be assumed equal with the initial concentration of D2EHPA in the organic solvent).

For determining the number of extractant molecules that reacts with PABA, as well as for quantifying the influence of 1-octanol on the extraction mechanism, the influence of extractant concentration on extraction efficiency has been plotted and analyzed for each considered extractant-solvent combination (Fig. 5).

The experimental results indicated that the extraction efficiency increases significantly with solvent polarity for both used extractants. Therefore, for the 1-octanol volume fraction of $\varphi = 10$ % and extractant concentration of $\gamma = 20$ g L^{-1}, the reactive extraction yield of PABA in dichloromethane was higher than that in *n*-heptane by about 2.5 times when Amberlite LA-2 was used, respectively by about 3 times when D2EHPA was the extractant.

By means of the experimental data from Fig. 5 and by plotting the eqs. (6) and (13), the straight lines from Fig. 6 were obtained for the two extractants and two solvents studied.

The values of the straight lines slope depend on extractant type and solvent polarity, varying as follows:

– **reactive extraction with Amberlite LA-2**

n-heptane + $\varphi = 10$ % 1-octanol n = 1.93
n-heptane + $\varphi = 20$ % 1-octanol n = 1.02
dichloromethane + $\varphi = 10$ % 1-octanol n = 1.11

– **reactive extraction with D2EHPA**

n-heptane + $\varphi = 10$ % 1-octanol n = 1.17
dichloromethane + $\varphi = 10$ % 1-octanol n = 1.07

The obtained values for n indicate the modification of the chemical structure of the interfacial compound in function both of the used extractant-solvent combination and of the 1-octanol volume fraction, respectively of the polarity of organic phase. Therefore, the reactive extraction with Amberlite LA-2 in low-polar solvent (*n*-heptane) occurs by the interfacial formation either of an aminic adduct with 2 extractant molecules, for $\varphi = 10$ % alcohol, or of a compound including one molecule of each reactant, for $\varphi = 20$ % alcohol. If the solvent with higher polarity is used (dichloromethane), the addition of 1-octanol does not modify the interfacial mechanism, each reactant participating with one molecule to the interfacial reaction.

These results confirm the strong dependence between the chemical structures of the interfacial product and the organic phase polarity, because the solvent polarity represents an important parameter that controls the extraction of ionizable solutes. The dielectric constant is considered a characteristic of solvent-solute local interactions, inducing the limitation of solute solvation by solvent or extractant, owing to the presence of ionizable groups in the solute chemical structure.[27] Thus, compared with the previous results obtained for the reactive extraction of PABA in *n*-heptane using the same two extractants, but without 1-octanol addition,[21] by increasing the alcohol concentration from $\varphi = 0$ to 20 %, the number of Amberlite LA-2 molecules included in the structure of the interfacial product decreased from 3 to 1, and that of D2EHPA molecules from 2 to 1. Due to the higher polarity of dichloromethane, close to that of 1-octanol, the extraction

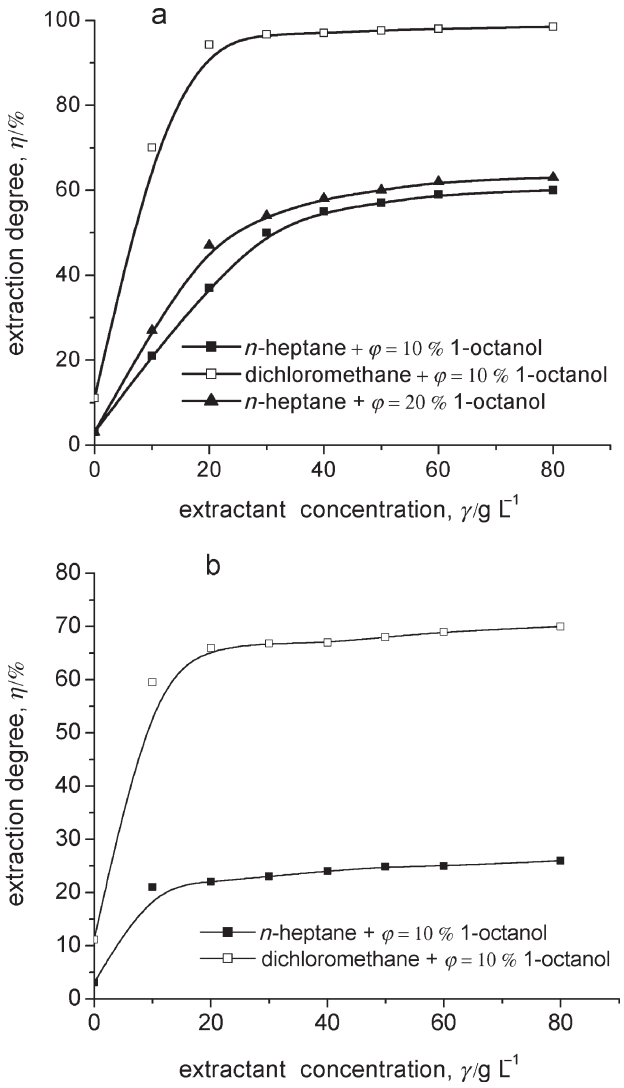
mechanism is affected by the presence of alcohol. In this case, the interfacial product is of salt type, being formed by reaction between one molecule of each reactant.

The above conclusions are also suggested by the variation of reactive extraction yield plotted in Fig. 5. From Fig. 5a, it can be observed that for Amberlite LA-2-*n*-heptane combination and $\varphi = 10$ % 1-octanol the PABA extraction degree strongly increases with the extractant concentration increase to 30 g L^{-1}, a limit that corresponds to a mole ratio between the solute and the extractant of about $r = 1 : 2$. For higher volumetric fraction of alcohol in the organic phase ($\varphi = 20$ % 1-octanol), the extractant concentration influences significantly the extraction efficiency only for a concentration domain up to $\gamma = 15$ g L^{-1}, this value corresponding to a mole ratio of $r = 1 : 1$ between PABA and Amberlite LA-2.

On the other hand, regardless of the alcohol presence, the yield of extraction with Amberlite LA-2 in dichloromethane increases with the increase of extractant concentration only for extractant concentration below 15 g L^{-1}, this limit indicating the formation of an interfacial compound by the reaction between one molecule of PABA and one of amine.

For the reactive extraction with D2EHPA in both solvents and for the entire considered domain of alcohol fraction, the influence of extractant concentration on the extraction yield becomes less important over 15 g L^{-1}, respectively after the mole ratio of $r = 1 : 1$ between PABA and extractant is reached (Fig. 5b).

As presented above, the modification of dielectric constant has a smaller effect on the solubility



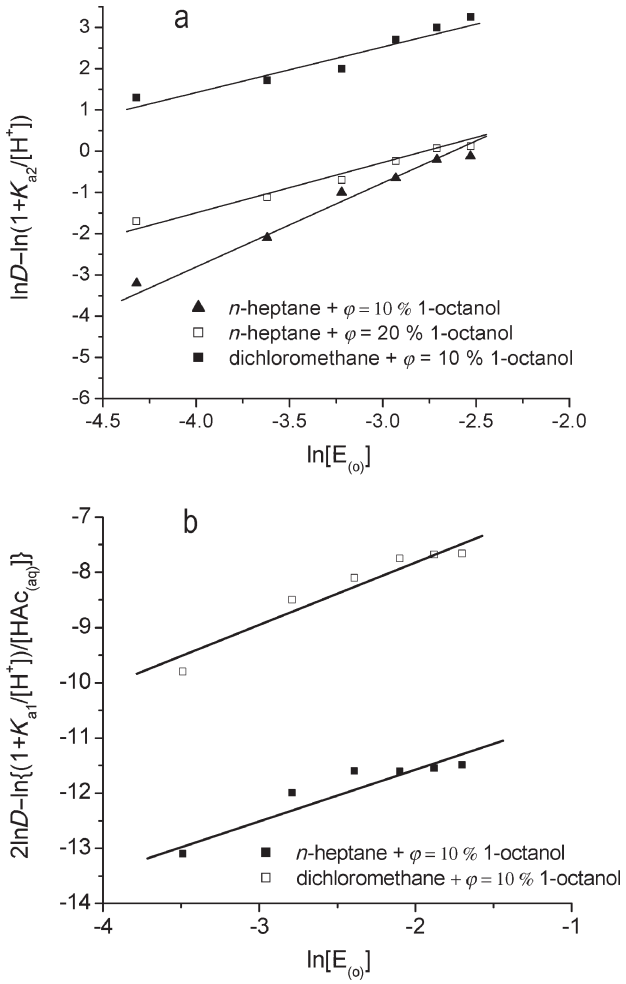
F i g . 5 – *Influence of concentration of Amberlite LA-2 (a) and D2EHPA (b) on efficiency of PABA reactive extraction (pH 4)*

T a b l e 1 – *Expressions and values of extraction constants for the studied systems*

Extractant	Solvent	Extraction constant	Value
Amberlite LA-2	*n*-heptane + $\varphi = 10$ % 1-octanol	$K_E = \frac{[HAcE_{2(o)}]}{[HAc_{(aq)}]\cdot[E_{(o)}]^2}$	$1.91 \cdot 10^2$ (L^2 mol^{-2})
	n-heptane + $\varphi = 20$ % 1-octanol	$K_E = \frac{[HAcE_{(o)}]}{[HAc_{(aq)}]\cdot[E_{(o)}]}$	14.88 (L mol^{-1})
	dichloromethane	$K_E = \frac{[HAcE_{(o)}]}{[HAc_{(aq)}]\cdot[E_{(o)}]}$	$2.55 \cdot 10^2$ (L mol^{-1})
D2EHPA	*n*-heptane	$K_E = \frac{[HAcE_{(o)}]^2}{[H_2Ac^+_{(aq)}]\cdot[E_{(o)}]}$	$7.19 \cdot 10^{-5}$ (–)
	dichloromethane	$K_E = \frac{[HAcE_{(o)}]^2}{[H_2Ac^+_{(aq)}]\cdot[E_{(o)}]}$	$3.12 \cdot 10^{-3}$ (–)

and extraction of nonelectrolytes or weak electrolytes, but it becomes an important factor for the extraction of dissociable solutes.[27] Therefore, the solvent polarity controls the extraction constant through its influence on separation efficiency and mechanism. For the reactive extraction of PABA, Table 1 gives the values of extraction constants graphically determined for the two extractants and two solvents containing 1-octanol.

The obtained values suggest that, for the same mechanism of interfacial reaction, the increase of the dielectric constant of organic phase from *n*-heptane-1-octanol combination to dichloromethane-1-octanol one leads to a strong increase in the extraction constant (for 17.2 times for reactive extraction with Amberlite LA-2, respectively for 43.4 times for reactive extraction with D2EHPA). However, for the reactive extraction of PABA with Amberlite LA-2 in *n*-heptane, by changing the extraction mechanism due to the increase of alcohol concentration, the extraction constant was diminished. This phenomenon, cumulated with the more pronounced increase of the differences between the extraction constants in *n*-heptane and dichloromethane containing 1-octanol than without the alcohol, indicate that the limitation of the solute solvation by the extractant at higher solvent polarity exhibits a negative effect on the interfacial equilibrium.



F i g . 6 – *Graphical representations of the straight lines given by eq. (6), for reactive extraction with Amberlite LA-2 (a), and (13), for reactive extraction with D2EHPA (b)*

Conclusions

The studies on reactive extraction of PABA with Amberlite LA-2 and D2EHPA in two solvents with different polarities (*n*-heptane, dichloromethane), at various phase modifier (1-octanol) volume fractions in the organic phase indicated that the mechanism of the interfacial reaction is controlled by the extractant type and solvent polarity.

In all studied extraction systems, the addition of 1-octanol induced the increase of the extraction efficiency, the most important influence being recorded for the solvent with lower dielectric constant, namely *n*-heptane. Moreover, in the presence of alcohol, the pH of the aqueous phase corresponding to the maximum extraction yield has been moved to higher value (from 3 to 4), owing to the partial solubilization of dissociated molecules of PABA too.

The addition of 1-octanol and its volumetric fraction influence the mechanism of the interfacial reaction between the solute and the extractant, by controlling the number of extractant molecules participating in the interfacial product formation. This effect has been recorded for the extraction in *n*-heptane and has been quantified in the reduction the Amberlite LA-2 molecules number included in the interfacial compound from 3, in the absence of alcohol, to 2 for φ = 10 % alcohol, and, finally, to 1 for φ = 20 % alcohol. Similarly, for reactive extraction with D2EHPA in *n*-heptane, the number of extractant molecules has been reduced from 2 in the absence of 1-octanol, to 1 in the presence of 1-octanol and regardless of its concentration in organic phase.

The limitation of solute solvation by extractant due to increased solvent polarity led to the reduction of extraction constant for a certain extraction system and to the amplification of the differences between the extraction constants obtained for the same extractant dissolved in the two solvents.

ACKNOWLEDGEMENTS

This work was supported by the Grant ID 317/2007 authorized by The National University Research Council (UEFISCSU)

List of symbols

D – distribution coefficient
K_a – ionization constant
K_E – extraction constant
r – mole ratio
w – mass fraction, %
γ – mass concentration, g L^{-1}
η – extraction degree, %
λ – wavelength, nm
φ – volume fraction, %

References

1. *Schuegerl, K., Hansel, R., Schlichting, R., Halwachs, W.,* I. Ch. E. **28** (1988) 393.
2. *Baird, M. T. H.,* Can. J. Chem. Eng. **69** (1991) 1287.
3. *Schuegerl, K.,* Solvent Extraction in Biotechnology, Springer-Verlag, Berlin, 1994, pp. 108.
4. *Choudhury, B., Basha, A., Swaminathan, T.,* J. Chem. Technol. Biotechnol. **72** (1998) 111.
5. *Caşcaval, D., Tudose, R., Oniscu, C.,* Hung. J. Ind. Chem. **26** (1998) 141.
6. *Matsumoto, M., Takagi, T., Nakaso, T., Kondo, K.,* Solv. Extr. Res. Dev. Jpn. **6** (1999) 144.
7. *Jung, M., Schierbaum, B., Vogel, H.,* Chem. Eng. Technol. **23** (2000) 70.
8. *Caşcaval, D., Oniscu, C., Caşcaval, C.,* Biochem. Eng. J. **5** (2000) 45.
9. *Morales, A. F., Albert, J., Kyuchoukov, G., Malmary, G., Molinier, J.,* J. Chem. Eng. Data **48** (2003) 876.
10. *Yankov, D., Molinier, J., Albert, J., Malmary, G., Kyuchoukov, G.,* Biochem. Eng. J. **21** (2004) 63.
11. *Caşcaval, D., Blaga, A. C., Camarut, M., Galaction, A. I.,* Sep. Sci. Technol. **42** (2007) 389.
12. *Uslu, H., Ismail Kirbaslar, S. I.,* J. Chem. Therm. **41** (2009) 1042.
13. *Jeong, M. W., Oh, S. G., Kim, Y. C.,* Colloids Surf. **181** (2001) 247.
14. *Song, X. Y., Sun, S. X., Yin, Z. L., Zhang, W. M., Yang, Y. Z.,* Colloids Surf. A **209** (2002) 57.
15. *Caşcaval, D., Galaction, A. I., Oniscu, C.,* Sep. Sci. Technol. **39** (2004) 1907.
16. *Liu, Y. S., Dai, Y. Y.,* Sep. Sci. Technol. **36** (2001) 3473.
17. *Wanga, K., Chang, Z., Maa, Y., Lei, C., Wang, J., Zhu, T., Liu, H., Zuo, Y., Li, X.,* Bioresource Technol. **100** (2009) 2878.
18. *Galaction, A. I., Caşcaval, D.,* Secondary Metabolites with Pharmaceutical, Cosmetic and Food Applications, Venus, Iasi, 2006, pp. 287–289.
19. *Akberova, S. I.,* Biol. Bull. **29** (2002) 390.
20. *Park, S. S., Park, J. H., Kim, S. H., Hwang, S. H.,* Patent WO 072534/2003.
21. *Amaratunga, M., Lobos, J. H., Johnson, B. F., Wiliams, E. D.,* Patent US 6030819/2000.**9**
22. *Galaction, A. I., Camarut, M., Caşcaval, D.,* Chem. Ind. Chem. Eng. Q. **14** (2008) 159.
23. *Weast, R. C.* (Ed.), Handbook of Chemistry and Physics, 54th Edition, CRC Press, Cleveland, 1974.
24. *Chisvert, A., Izquierdo, J. V., Salvador, A.,* Anal. Bioanal. Chem. **374** (2002) 963.
25. *Caşcaval, D., Oniscu, C., Galaction, A. I.,* Biochem. Eng. J. **7** (2001) 171.
26. *Blaga, A. C., Galaction, A. I., Caşcaval, D.,* Chem. Biochem. Eng. Q. **22** (2008) 439.
27. *Prezho, V. V., Jagello, M., Melnik, I. I., Prezho, M. V.,* Sep. Sci. Technol. **3** (2002) 2875.