

## SORPTION OF Ga (III) ON FLEXIBLE OPEN CELL POLYURETHANE FOAM OF POLYETHER TYPE IMPREGNATED WITH TRI-N-BUTHYL PHOSPATE

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**Abstract.** The obtained results concerning the Ga (III) ion retention on flexible open cell polyurethane foam of polyether type pretreated with tri-n-butyl phosphate are presented. The influence of solution acidity, phases contact time, Ga (III) concentration and solution temperature have been investigated. The parameters of Ga (III) batch sorption have been optimized. On the basis of Langmuir isotherms, the sorption constants and the thermodynamic parameters,  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  have been calculated.

**Keywords:** sorption, polyurethane foam, tri-n-butyl phosphate, gallium.

### INTRODUCTION

The increasing demand for gallium in electronics industry has stimulated research on new materials and methods for the removal, recovery and determination of trace gallium in various natural and industrial samples. In this context, an alternative to the different ion - exchange resins can be represented by polyurethane foams [1]. Polyurethane foams have a wide range of applications in batch or dynamic separation and preconcentration of inorganic and organic species, gas and liquid chromatography and cells immunosorption [2,3].

Table 1

**The main physical and chemical features of polyurethane foams**

Character	Hydrophobic
Porosity	Large
Reversible swelling in	Water, HCl until 8M, H <sub>2</sub> SO <sub>4</sub> until 4M , HNO <sub>3</sub> until 2M, glacial CH <sub>3</sub> COOH, NH <sub>4</sub> OH 2M, NaOH 2M, organic solvents (benzene, carbon tetrachloride, chloroform, acetone, alcohols)
Dissolution in	Concentrated H <sub>2</sub> SO <sub>4</sub> ; concentrated HNO <sub>3</sub>
Degradation by	Heating to 180 – 220°C UV exposure
Anionic exchange capacity	Low
Surface area	High
Sorption rate of chemical species	Relative fast

The polyurethane foams can be efficiently used both in unloaded form [4-8] and after a physical or chemical treatment [9-15]. The remarkable properties (Tab. 1) make flexible open-cell polyurethane foam of polyether type an ideal support for immobilizing by physical adsorption of various selective organic reagents and extractants [16]. Thus, the excellent properties of the flexible open-cell polyether of polyurethane foam type impregnated with the organic extractant tri-n-butyl phosphate (TBP) allowed quantitative separation of silver, gold, bismuth, cadmium, cobalt, chrome, copper, mercury, nickel, lead, palladium, tin, tantalum, thorium [9], and the concentration of iron from chloride media [17] and phenols from waters [18].

This paper deals with the experimental results of the retention of gallium ions on polyurethane foam of polyether type pretreated with TBP under specific conditions, giving the sorption isotherms and the values of thermodynamic amounts.

## EXPERIMENTAL

### Reagents and Chemicals

The stock solution of Ga(III) (1.584 mg/mL) was prepared by dissolving  $\text{GaCl}_3$  and was gravimetrically standardized (by precipitation with ammonia). Working solutions were freshly prepared by appropriate dilutions of the stock solution.

The "SPUMATIM" flexible open-cell polyurethane foam of polyether type was purified according to the procedure described in Fig. 1.

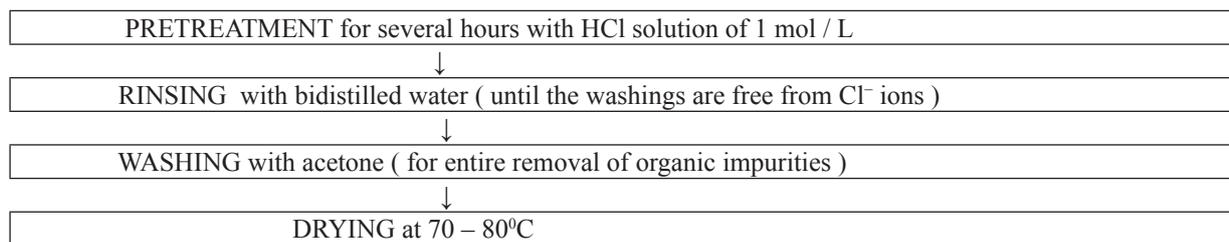


Fig.1. Scheme of polyurethane foam purification.

For foam impregnation, tri -n- butyl phosphate (Fluka, Buch, Switzerland) was used. An aqueous solution (0.5%) of rhodamine B was used for the spectrophotometric determination of gallium (III). All reagents were of analytical grade. Absorbance measurements were made on a S104D-WPA Linton Cambridge spectrophotometer.

### Foam impregnation

In order to impregnation with TBP, the purified foam (cut into cubes of about 5mm edge) was equilibrated with the extractant agent. To ensure complete saturation, the cubes of foam were remained overnight in contact with TBP. Then, to remove the excess of TBP, the impregnated foam was washed several times with 4 mol/L HCl saturated with TBP. Finally, the TBP- polyurethane foam sorbent was dried and kept in a dessicator. The amount of TBP retained by the foam was of 5.1714 TBP/ g foam. This amount corresponds to an 83.8% content of TBP in the loaded foam.

### General Sorption Procedure for Gallium

In the sorption systems under study batch conditions have been carried out. The weighed samples of about 0.1g of TBP- impregnated foam were equilibrated with volumes of 25 mL solution containing known and variable amounts of Ga (III) and HCl. After a determined time of contact, at constant temperature, the phases were separated. The Ga (III) content in supernatant was determined spectrophotometrically, with rhodamine B [19].

## RESULTS AND DISCUSSION

Because of their various functional groups or heteroatoms, unloaded polyurethane foam sorbents which are not chemically inert, take part in the processes of sorption by virtue of their own structure. Thus, the retention of Ga (III) as  $\text{HGaCl}_4$  on untreated polyether-type polyurethane foams was explained by a polyether extraction mechanism [20,21]. On the other hand, in the mechanism of the sorption by reagent- loaded polyurethane sorbents description, the nature of the physically or chemically immobilized reagent in the foam structure plays a leading role [2,9].

The selection of TBP as modifier agent for the cellular material has been determined by its double function: plasticizer which significantly increases the foam permeability and extractant with high solvation power in ionic association systems.

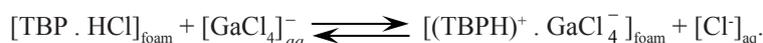
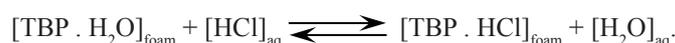
In order to establish the optimum conditions for Ga(III) sorption on flexible open cell polyurethane foam of polyether type loaded with tri-n-butyl-phosphate, the effect of solution acidity, phase contact time, Ga(III) concentration and solution temperature have been studied.

The effect of solution acidity on polyurethane foam-TBP-Ga (III) sorption systems is described by the means of Ga (III) distribution coefficients. The distribution coefficients ( $K_d$ ) were calculated as ratio between moles of Ga(III) taken up per gram of TBP- loaded foam and moles of Ga(III) left in 1 mL solution at equilibrium. Because the polyurethane foam is partially chemically destroyed in solutions with concentrations of HCl over 8 mol/L, the correlation is possible only in the range of HCl concentration 0- 8 mol/L [17].

It may be considered that in solutions with concentrations of 1-2 mol/L in HCl, the following equation describes rightly the Ga (III) retention equilibrium on TBP-loaded foam:



The solution acidity increase (4-6 mol/L in HCl) causes a mechanism of oxonium type for Ga (III) sorption (as  $[\text{GaCl}_4]^-$  chlorocomplex):



The dependence of Ga (III) distribution coefficients on hydrochloric acid concentrations until 8 mol/L is shown in Fig. 2.

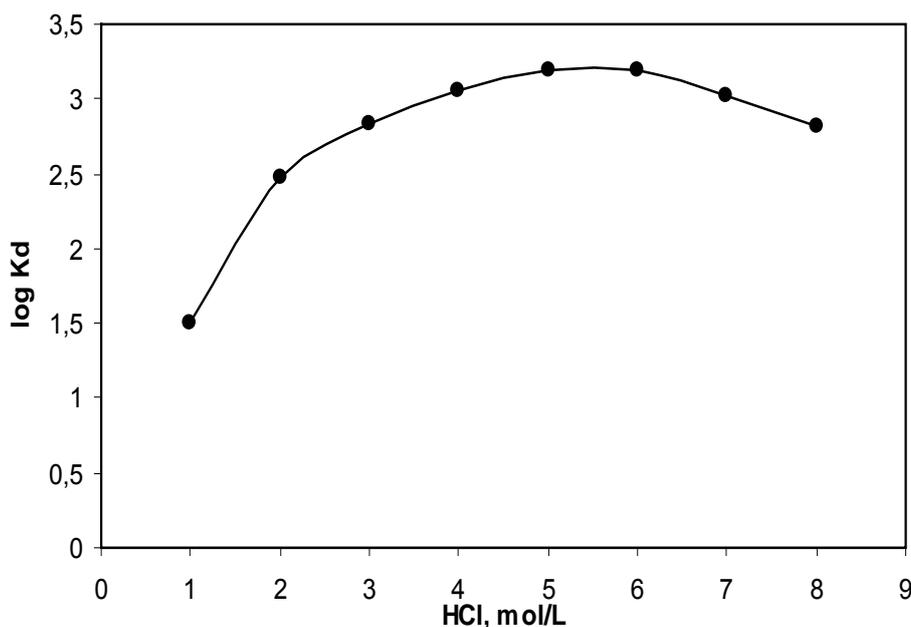


Fig. 2. The effect of HCl concentration (mol/L) on Ga (III) retention by polyurethane foam impregnated with TBP ( $C_0 = 0.1584$  mg Ga(III)/mL; shaking time = 1h).

The competitive effect of HCl extraction, predominantly to increase of medium acidity, determines a decrease in Ga (III) retention for HCl concentrations over 6 mol/L. This behavior is in good agreement with the proposed mechanism for extraction of Fe (III) from solutions 4 mol/L in HCl on polyurethane foam pretreated with TBP [17].

The experiments carried out in solutions 6 mol/L in HCl with an initial concentration of 0.1584 mg Ga (III)/mL revealed an increase of the Ga (III) retention degree with phase contact time increasing (Fig.3).

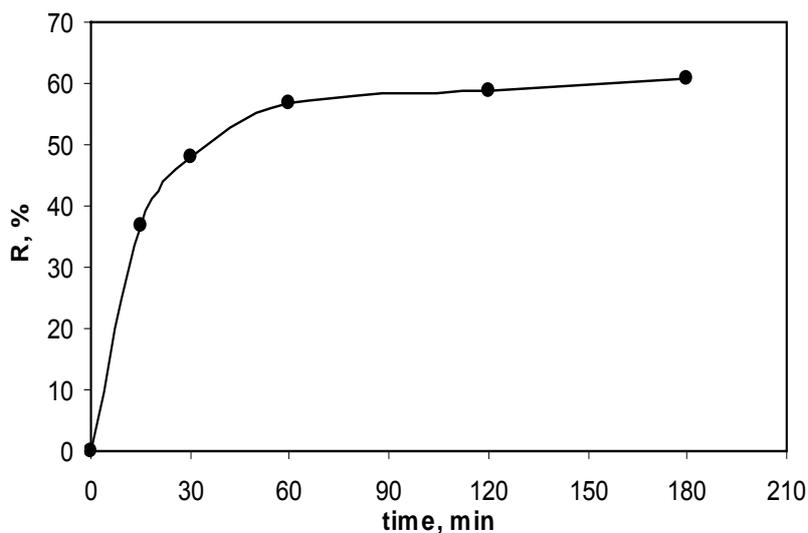


Fig. 3. The effect of phase contact time on Ga (III) retention by TBP-loaded polyurethane foam ( $C_0 = 0.1584$  mg Ga(III)/mL).

The equilibrium of Ga (III) sorption on polyurethane foam impregnated with TBP is reached after about 2h from phase contact.

The influence of the initial concentration ( $C_0$ ) on Ga (III) sorption by TBP – polyurethane foam is giving in Fig. 4.

The amount of Ga (III) sorbed from solutions 6 mol/L in HCl, at two different temperatures, increases with increasing initial concentrations. This trend can be explained by assuming that surface sorption sites play a leading role in the systems under study. Higher initial concentrations might be closely associated with high values of the ratio between the initial number of Ga (III) mmoles and the finite number of surface active sites, thus resulting in an enhancement of the metal uptake.

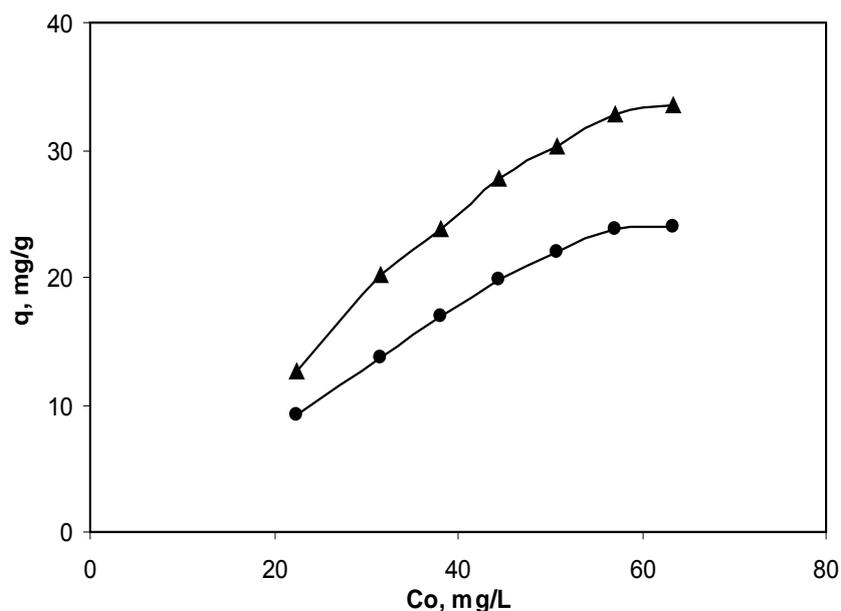


Fig. 4. The influence of initial concentration on Ga (III) - TBP – polyurethane foam sorption systems, at different temperatures (●)- 278 K; (▲)- 313 K.

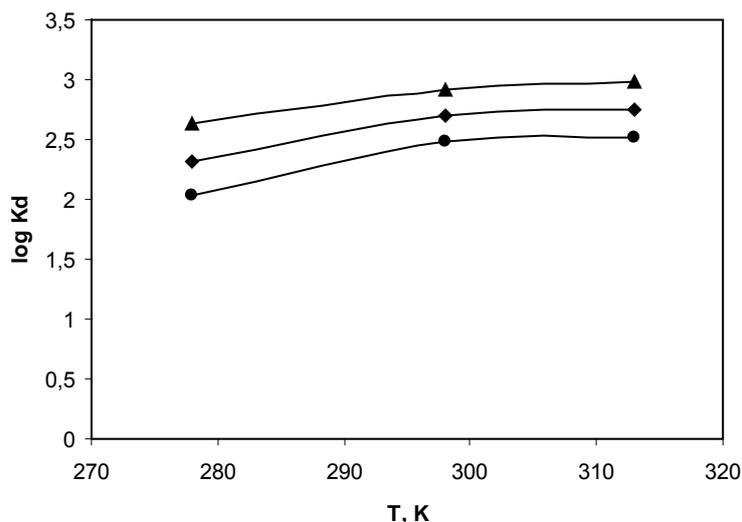


Fig.5. The effect of the temperature on Ga (III) retention by TBP – impregnated polyurethane foam, (●)- $C_0 = 19$  mg/L; (◆)-  $C_0 = 31.7$  mg/L; (▲)-  $C_0 = 44.3$  mg/L.

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Fig. 5 presents the influence of temperature on Ga (III) retention by TBP – loaded polyurethane foam from solutions of different initial concentrations.

The  $\lg K_d = f(T)$  curves in Fig. 5 have the same shape in all solutions. The high values of distribution coefficients ( $K_d$ ) indicate a good affinity of the TBP–polyurethane foam toward Ga (III); with increasing temperature the retention of Ga (III) is higher, suggesting an endothermic chemical process.

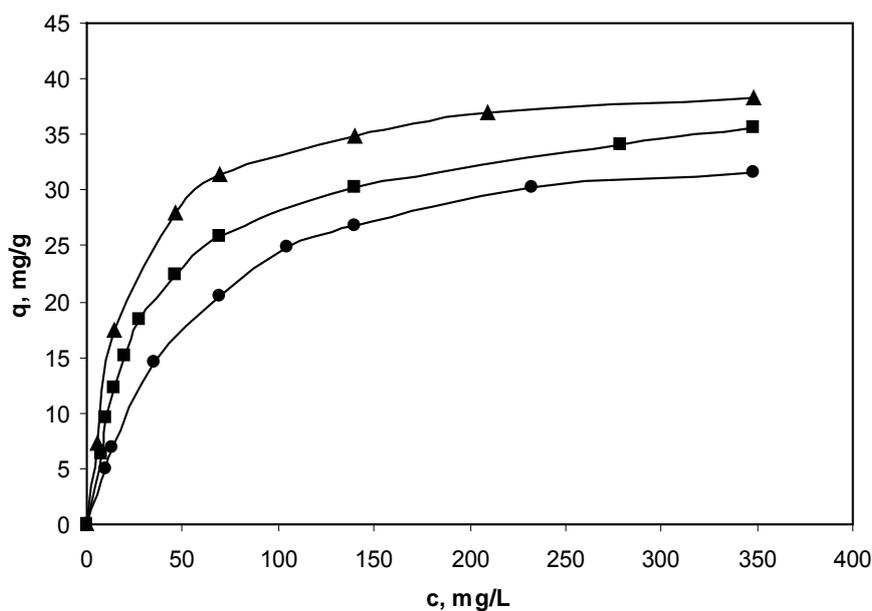


Fig. 6. Ga (III) isotherms of sorption on TBP loaded polyurethane foam, at different temperatures (●)–278 K; (■)–295 K; (▲)–313 K.

Plotting the variation of the retained amount of Ga (III) on solid phase (mg/g) versus the Ga(III) concentration left in solution at equilibrium (mg/L), at constant temperatures, the sorption isotherms represented in Fig. 6 are obtained.

The shape of isotherms in Fig.6 allowed a quantitative characterization of Ga (III) sorption. In this context, we used the equation of Langmuir type in linear form:

$$c/q = c/q_0 + 1/K_L \cdot q_0$$

where: q is the amount of sorbed Ga (III) on solid phase (mg/g foam); c is the Ga(III) concentration in solution at equilibrium (mg/L); q<sub>0</sub> is the saturation sorption capacity (mmol/ g foam); K<sub>L</sub> is a parameter related to the strength of the sorbed ion– sorbent binding (L/mol).

The sorption isotherm constants (q<sub>0</sub> and K<sub>L</sub>) calculated from intercepts and slopes of corresponding linear Langmuir plots for Ga (III) sorption by untreated polyurethane foam and TBP- polyurethane foam at different temperatures, together with their correlation coefficients (R<sup>2</sup>) are given in Table 2.

Table 2

<b>Langmuir constants</b>			
T, K	R <sup>2</sup>	q <sub>0</sub> , mmol/g	K <sub>L</sub> , L/mol
Polyurethane foam impregnated with TBP			
278	0.9994	0.5301	1262.87
295	0.9993	0.5535	2216.2
313	0.9999	0.5835	3424
Untreated polyurethane foam			
295	0.9952	0.4873	1526.7

Although Ga (III) is well retained on untreated foam, Tab. 2 points out that the analytical performances of the cellular material in sorption of Ga (III) traces were significantly improved by its impregnation with tri-n-butyl phosphate. Therefore the combination between the advantages of liquid extraction and chromatography techniques in TBP-loaded foam case result in sorption systems with high practical applicability.

As can be seen from Table II, on temperature increase, the saturation sorption capacity increases. This finding is in good agreement with viscosity water decrease on rising temperature, so that the penetrability of water and sorbed species in polyurethane sorbent pores is increased.

For a thermodynamic description in polyurethane foam-TBP-Ga (III)-HCl sorption systems the ΔG, ΔH and ΔS values were calculated (Tab. 3) by means of the following usual relations:

$$\begin{aligned}\Delta G &= -RT \ln K_L \\ \ln K_L &= \text{constant} - \Delta H / RT \\ \Delta S &= (\Delta H - \Delta G) / RT\end{aligned}$$

where R is gas constant and T is the absolute temperature .

Table 3

<b>The thermodynamic parameters characteristic to Ga (III) sorption on polyurethane foam</b>			
T, K	ΔG, kJ/mol	ΔH, kJ/mol	ΔS, J/mol.K
Polyurethane foam impregnated with TBP			
278	- 16.496		132.42
295	- 18.883	20.317	132.88
313	- 21.967		132.53
Untreated polyurethane foam			
295	- 17.96	-	-

The negative values of free energy changes (ΔG) for all temperatures show a reasonable affinity of polyurethane foam against Ga (III) ions (spontaneous process of sorption). The positive value of ΔH (variation of enthalpy accompanying the Ga(III) sorption indicates an endothermic process, facilitated by higher temperatures. The positive entropy changes

( $\Delta S$ ) characterize an increase in the disorder of the system on Ga(III) sorption by the polyurethane foam (probably due to the release of hydration water molecules surrounding the gallium ions).

We experimentally found that temperature rising contributes to a faster attainment of equilibrium, namely an increase of the sorption rate explained by an increase in Ga (III) diffusion rate from chlorhydric solutions to impregnated foam.

## CONCLUSIONS

The affinity of flexible open cell polyurethane foam of polyether type for Ga (III) is improved by its impregnation with the organic extractant tri-n-butyl phosphate. If for untreated foam, Ga (III) retention may be explained by a polyether extraction mechanism, in the case of impregnated foam, the advantages of liquid-liquid extraction and chromatography techniques are combined.

The Ga (III) retention from solutions 6 mol/L in HCl on polyurethane foam pretreated with TBP is favored by the increase of phase contact time, the concentration of gallium in external solutions and the temperature.

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