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Article

Studies on Indium Sorption from Iodide Medium by Polyurethane Foam

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A sorção de iodeto de índio em espuma de poliuretano do tipo poliéter (EPU) foi investigada. O sistema apresentou rápida cinética e máxima sorção numa faixa significativa de meio ácido ou básico e razões de distribuição acima de 10^4 L kg^{-1} ([KI] ∅0.6 mol kg^{-1}). A análise do equilíbrio de sorção indicou o tetraiodo-indato ($MInI_4$) como a principal espécie sorvida na matriz da espuma. A isoterma de Langmuir foi ajustada com êxito e valores de (1.55±0.02) x 10^{-1} mol kg^{-1} e (7.0±1.3) x 10^4 L g^{-1} foram obtidos para a capacidade de saturação K_s e coeficiente de adsorção b, respectivamente. O efeito da temperatura foi avaliado e os parâmetros termodinâmicos calculados. Os valores da constante de equilíbrio K_c diminuíram com o aumento da temperatura. Os valores negativos de ΔG, ΔH e ΔS indicaram um processo espontâneo e exotérmico caracterizado por sorção química.

The sorption behavior of indium iodide onto polyether-based polyurethane (PUF) foam was investigated. The system shows rapid kinetics and maximum sorption from a meaningful range of either acidic or basic media and achieves distribution ratios above 10^4 L kg^{-1} ([KI] ∅0.6 mol kg^{-1}). Sorption equilibrium analysis indicates tetraiodo-indate ($MInI_4$) as the main species sorbed on the foam matrix. A Langmuir isotherm was successfully fitted and values of (1.55±0.02) x 10^{-1} mol kg^{-1} and (7.0±1.3) x 10^4 L g^{-1} were obtained for the saturation capacity K_s and adsorption coefficient b, respectively. The temperature effect was evaluated and the thermodynamic parameters calculated. The values of the equilibrium constant, K_c, decreased with increasing temperature. The negative values of ΔG, ΔH and ΔS indicate a spontaneous and exothermic chemisorption process favored at low temperatures.

Keywords: polyurethane foam, indium, solid-phase extraction

Introduction

Indium and its compounds have numerous industrial applications and it is currently used in the manufacture of semiconductors, liquid crystal displays, low-temperature solders, infrared photodetectors besides many others. Indium is however widely distributed in the earth's crust at very low concentrations. It can be found associated at trace amounts to a few ores such as sphalerite (ZnS) and is mainly obtained as a by-product from zinc mining.

Accounting for its abundance, technological utilizations and the requirement to recover or determine indium at trace level amounts, techniques such as solvent extraction, co-precipitation or solid-phase extraction have been proposed for indium separation and/or pre-concentration from several materials. Extractions of anionic indium halogenates or organic acid complexes with high molar-mass amine liquid anionic exchangers[1-3] have been reported. Among other useful extractants are also included tributyl phosphate,[4] di-(2-ethylhexyl) orthophosphoric acid[5] and triphenylphosphine oxide.[6] Co-precipitation using ferric hydroxide[7] as collector has been used to pre-concentrate indium from flue dust and zinc ore; indium co-precipitation by gallium phosphate[8] from water and sea water has also been related.

Solid phase extraction as a concentration and separation technique has become increasingly popular compared to the more traditional liquid-liquid extraction methods regarding its easier manipulation of samples and the requirement of much smaller, or even no organic

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solvent, with higher concentration factors. Furthermore, the characteristics of modern solid sorbents such as faster kinetic sorption and elution ease have allowed the use of sorbents in cartridges, minicolumns or more recently as disk membranes for preconcentration analytical procedures in continuous flow systemns.[9] Several sorbents have been reported for indium separation or preconcentration including reagent loaded sorbents such as silica gel coated with trioctyl phosphine oxide[10] or high molar mass carboxylic acid,[11] anionic[12] and cationic exchangers resins,[13] chelating fibers like polyacrylonitrile with a dithiocarbamate group,[14] macroporous polystyrene resins functionalized with complexane-type ligands,[15] *etc.*

The potential possibilities of polyurethane foam as a suitable sorbent was pointed out by Bowen in 1970.[16] Braun and Farag[17,18] verified that open-cell type resilient polyurethane foams have remarkable mass-transfer properties and rapid sorption owing to their quasi-spherical geometric membrane. These features allow their utilization in separation and preconcentration procedures with relatively high flow rates in batch and column systems. These pioneering studies have resulted in many others using untreated or reagent loaded polyurethane foam (polyether or polyester type) with wide applications in separation chemistry.[19,20] Recently, the use of a PUF minicolumn in a continuous flow system was reported by Jesus *et al.*[21] for zinc preconcentration and spectrophotometric determination in biological materials. A batch process was developed by Carvalho and co-workers for gallium recovery from aluminium industry residues, achieving a 92% efficiency.[22] The same authors have proposed analytical procedures to separate and determine gallium in bauxite,[23] uranium[24] and thorium[25] at μg L^{-1} levels in natural water samples using the XRF technique after preconcentration on ground PUF.

Braun and Abbas[26] have investigated the extraction of indium, zinc and mercury from a thiocyanate medium using unloaded polyether based polyurethane foam and have reported a high distribution coefficient of 1.75 x 10^4 L kg^{-1} for indium (KSCN 1.0 mol L^{-1}). This system however, is non selective and would not be appropriate for trace indium preconcentration and separation from some materials, in view of the concomitant extraction of zinc and many other metal thiocyanate complexes by PUF.[27]

The purpose of the present work was to investigate the sorption behaviour of indium from an iodide medium by polyether based polyurethane foam. The effect of medium acidity and alkalinity, equilibrium kinetics and iodide concentration were evaluated. Also studies using the Langmuir isotherm and the effect of temperature on sorption for determination of the thermodynamic functions ΔH, ΔS, ΔG and the equilibrium constant K_c are within the scope of this paper. The most probable indium iodide species sorbed and the mechanism of sorption are discussed.

Experimental

Apparatus

A GBC 918 spectrophotometer with matched 1.00 cm quartz cells was used for indium spectrophotometric determination. A Hanna pocket pH meter was used for pH values measurements. A Haake thermostatic water bath was used for temperature effect studies. A VKS-100 mechanical shaker (100 cpm) was used for shaking the system for the batch process. A Corning stirrer-heater was used to carry out the experiments relating to temperature variation.

Reagents

Doubly distilled water was used to prepare the solutions and all reagents were of analytical grade unless otherwise stated. Indium stock solution (1.0 g L^{-1} in 0.1 mol L^{-1} H_2SO_4 medium) was prepared from pure metallic indium (99.99%) by heating in a 4.5 mol L^{-1} sulfuric acid solution. After dissolution the volume was set to 0.5 L with doubly distilled water. A 2.0 mol L^{-1} potassium iodide solution was prepared by dissolution of the reagent (Carlo Erba) in doubly distilled water. A 0.1% 4-(2-pyridylazo)-resorcinol monosodium salt monohydrate solution (PAR) was prepared by dissolution of a suitable mass of the reagent (Merck) in doubly distilled water. A buffer solution of sodium tetraborate was prepared by dissolution of 30.92 g of boric acid and 17.56 g of NaOH in 800 mL of water followed by adjustment of pH to 9.75 with a 6 mol L^{-1} NaOH solution and dilution to 1000 mL. A 0.1 mol L^{-1} sodium thiosulfate solution was prepared from dissolution of the reagent (Reagen) in doubly distilled water. A 2.0 mol L^{-1} sulfuric acid solution was prepared from dilution of the concentrated acid (Merck) with doubly distilled water. An open cell polyether type commercial polyurethane foam (PUF), Scotch-Brite™ (3M), was ground in a blender with doubly distilled water, squeezed, dried in an oven at 80 °C and stored in a polypropylene flask.

General procedure

The experiments were carried out by a batch process at ambient temperature (25 ± 2 °C) or as specified. An aliquot of the metal stock solution was transferred to a stoppered polypropylene flask. The proper iodide and sulfuric acid concentrations were adjusted by suitable aliquot additions of 2.0 mol L^{-1} solutions of KI and H_2SO_4, respectively. A 0.5 mL aliquot of 0.1 mol L^{-1} sodium thiosulfate was added to avoid iodine formation and the appropriate volume set with doubly distilled water. Afterwards a 0.055 g portion of ground PUF was added and the system was mechanically shaken until equilibrium was established. In the studies concerning temperature variation (from 25 to 85 °C) a glass stoppered cell containing a water jacket circuit coupled to a thermostatic bath was used instead of the polypropylene flask and the system was continuously stirred with a magnetic stirrer bar and plate. After filtration through an ashless rapid filter paper the PUF was separated and the aqueous phase reserved for indium determination by spectrophotometric measurement of the indium complex with 4-(2-pyridylazo)resorcinol (PAR); the indium sorbed was calculated by the difference between the concentration measured before (c_i) and after extraction (c_f). The distribution coefficient D (L kg^{-1}) was calculated from the degree of extraction (%E) according to the equations,

$$\%E = [(c_i - c_f) / c_i]\, 100 \qquad (1)$$

$$D = [(\%E) / (100 - \%E)]\, [(V / W)] \qquad (2)$$

where V is the volume of sample solution (mL) and W is the weight of PUF (g).

A linear regression computer program with one independent variable was used for statistical treatment of the data and to set the slope and intercept parameters of the linear plots obtained.

Spectrophotometric determination of indium using PAR reagent

Solution aliquots containing indium in the mass range from 1.0 to 6.0 μg were added to 10 mL volumetric flasks. Drops of 0.01 mol L^{-1} sodium thiosulfate were added to reduce iodine to iodide until the solution turned colorless. Then, in this order were added 1.0 mL 0.1% solution of PAR, 1.0 mL sodium tetraborate buffer and the volume was set with doubly distilled water. After 20 min the In-PAR complex absorbance was measured at 509.7 nm in a 1 cm cell against a blank prepared in the same way but without indium (6.4 x10^4 L mol^{-1} cm^{-1} molar absorptivity).

Results and Discussion

Effect of acidic and basic medium on indium sorption

The effect of acidic and basic medium were evaluated after extraction of 0.02 L solutions containing 2.18x10^{-4} mol L^{-1} In and 1.0 mol L^{-1} KI for 20 min. The acid medium was adjusted in the range from 2.5x10^{-3} to 1.0 mol L^{-1} by proper addittion of H_2SO_4. The system sorption was maximum and constant under these conditions although, as the acid concentration increases a greater amount of sodium thiosulphate is required to maintain the iodide solution concentration and to avoid a decrease of indium extraction due to the occupation of the sorption sites of the foam by iodine. The system sorption was investigated in NH_4OH medium by adjusting the pH of the solution to about 6 with NaOH followed by ammonia solution addition to give a final concentration from 10^{-4} to 0.1 mol L^{-1}. The results showed an efficient and maximum extraction of indium from 10^{-4} to 10^{-2} mol L^{-1} NH_4OH and a decrease of about 75% (E %= 24.5) at 0.1 mol L^{-1} NH_4OH. Although the sorption system permits a broad range of working conditions a sulfuric acid concentration of 0.1 mol L^{-1} was chosen to be used in all experiments, unless otherwise stated.

Effect of iodide concentration

In order to find the optimum iodide concentration to achieve the highest distribution coefficient for the system, 2.18x10^{-4} mol L^{-1} In in 0.02 L iodide solutions in the concentration range from 0.05 to 0.8 mol L^{-1} were extracted by PUF for 20 min. The effect of iodide concentration on indium sorption is shown in Figure 1. The distribution ratio (D) increased from 52.9±0.5 L kg^{-1} at 0.05 mol L^{-1} iodide concentration to (2.1±0.3)10^4 L kg^{-1} at 0.7 mol L^{-1} and then remained constant. The dependence on iodide concentration indicates that indium iodide complex species are involved in the sorption process.

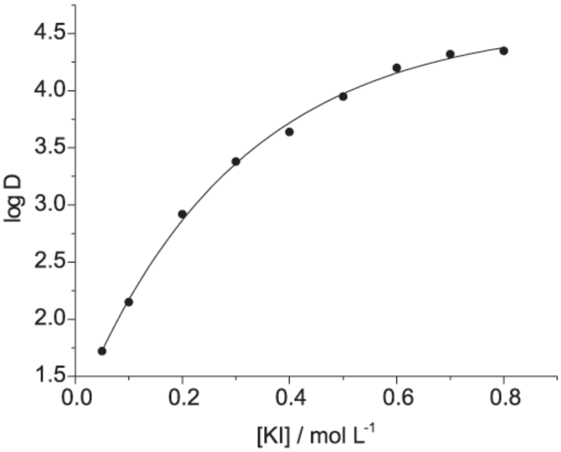

Figure 1. Effect of KI concentration on In(III)-PUF sorption (2.18x10^{-4} mol L^{-1} In(III), 0.055 g PUF, 0.1 mol L^{-1} H_2SO_4, 20 min, and 0.020 L).

Effect of shaking time

The time dependence of indium sorption was studied by varying the time of contact from 1 to 30 min. The results shown in Figure 2 indicate that the extraction equilibrium was attained within 5 min shaking for 2.18×10^{-4} mol L^{-1} indium in 0.7 mol L^{-1} potassium iodide. A time of 10 min shaking was found appropriate to guarantee maximal extraction.

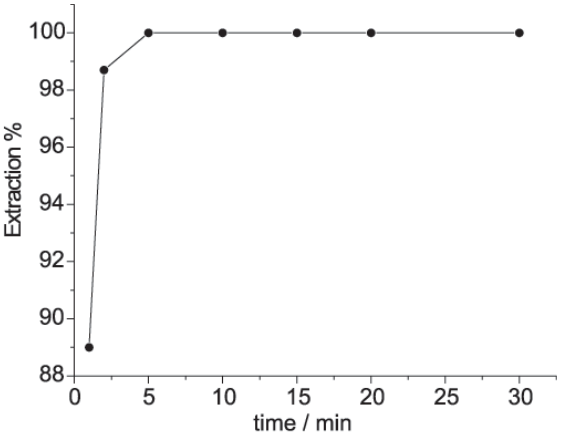

Figure 2. Effect of shaking time on the system sorption (2.18×10^{-4} mol L^{-1} In(III), 0.055 g PUF, 0.1 mol L^{-1} H_2SO_4, 0.7 mol L^{-1} KI, and 0.020 L).

Evaluation of the $(InI_n)^{n-3}$ species sorbed by the In/KI/PUF system

The soption equilibrium of indium iodide complexes on PUF can be expressed by the association equilibrium of the complex in the aqueous phase (aq), with an association constant, K_a, and its equilibrium sorption from the aqueous phase to the polymer phase with, a sorption constant, K_d, where K_a and K_d are respectively defined in the equations below as:

$$[In]_{aq} + (n\text{-}3)\,[M]_{aq} + n\,[I]_{aq} \Leftarrow ([M]_{n-3}[In][I]_n)_{aq}$$
$$K_a = ([M]_{n-3}[In][I]_n)_{aq} \,/\, [In]_{aq}\,[M]^{(n-3)}_{aq}\,[I]^n_{aq} \qquad (3)$$

$$([M]_{n-3}[In][I]_n)_{aq} \Leftarrow ([M]_{n-3}[In][I]_n)_{PUF}$$
$$K_d = ([M]_{n-3}[In][I]_n)_{PUF} / ([M]_{n-3}[In][I]_n)_{aq} \qquad (4)$$

(where M could be H_3O^+ or K^+)

Proper substitutions in equations (3) and (4) leads to indium iodide concentration in the polymer phase expressed in equation (5) as:

$$([M]_{n-3}[In][I]_n)_{PUF} = K_a K_d\,[In]_{aq}\,[M]^{(n-3)}_{aq}\,[I]^n_{aq} \qquad (5)$$

The distribution ratio D expresses the indium equilibrium concentration ratio between the PUF and the aqueous phase as:

$$D = [In]_{PUF} \,/\, [In_t]_{aq} = K_a K_d\,[In]_{aq}\,[M]^{(n-3)}_{aq}\,[I]^n_{aq} \,/\, [In_t]_{aq} \qquad (6)$$

The total indium concentration, $[In_t]_{aq}$, in the aqueous phase is defined as the sum of all the indium species concentrations present in the bulk solution and could be expressed from their stepwise iodide complex formation constants[28] as follows:
(charges were omitted for simplicity)

$$[In_t]_{aq} = [In]_{aq}\,(1 + K_1 I + K_1 K_2 I^2 + ... + K_1 K_2 ... K_n I^n) = [In]_{aq}\beta \qquad (7)$$

where $\beta = (1 + K_1 I + K_1 K_2 I^2 + ... + K_1 K_2 ... K_n I^n)$

Appropriate substitution of $[In_t]_{aq}$ in equation (6) leads to:

$$\beta D = K_a K_d\,[M]^{(n-3)}_{aq}\,[I]^n_{aq} \qquad (8)$$
$$\log \beta D = \log(K_a K_d) + (n\text{-}3)\log[M]_{aq} + n\log[I]_{aq} \qquad (9)$$

Therefore, the log-log plot of βD *versus* $[I]_{aq}$, as expressed from equation (9), should fit a linear plot, with a slope corresponding to the co-ordination number n. The straight line in Figure 3 obtained by using the least square method gave a n value of 4.03 and indicates the species $MIn(I)_4$ as that most probably sorbed by the foam. The result also indicates an ion-association complex sorption on the polymer matrix similar to the solvent extraction mechanism of univalent complex anions such as $(FeCl_4)^-$ and $(AuCl_4)^-$ in diethylether or to the cation chelation mechanism proposed by Hamon *et al.*[29] This latter states that the polyethylene oxide portion of the foam can assume

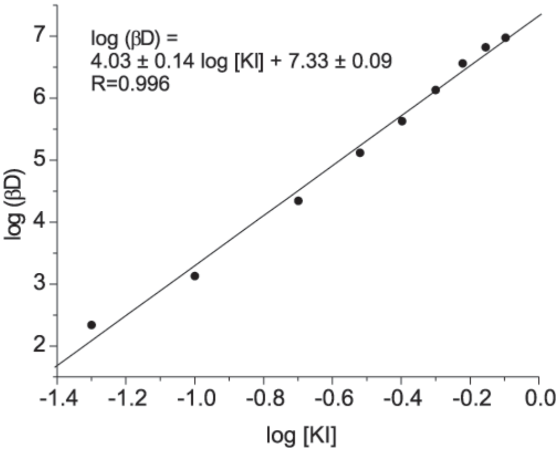

Figure 3. log-log plot of βD *vs.* KI concentration.

a helical structure with inwardly-directed oxygen atoms defining cavities where the complexation of simple cations M^{p+} (such as K^+, Na^+, Pb^{+2}, including H_3O^+) occurs. The complex anions as $(InI_4)^-$ are retained as counter ions to the cations captured in the cavities.

Effect of indium concentration from adsorption isotherms

The dependence of indium concentration on sorption into PUF was subjected to analysis in terms of Freundlich and Langmuir isotherms. Studies were carried out following the general procedure under the optimized conditions of acidity, shaking time and iodide concentration. Indium amounts in solution were varied from 1.8 x 10^{-4} to 1.8 x 10^{-3} mol L^{-1}.

At the indium concentration range studied the data did not fit for Freundlich equation but were successfully applied for the Langmuir isotherm.

The Langmuir model from 1918 has been used in studies of solute adsorption onto various sorbents from aqueous solution. It assumes that sorption occurs on defined sites of the sorbent with no interaction between the sorbed species and that each site can accomodate only one molecule (monolayer adsorption) with the same enthalpy sorption, independent of surface coverage.

Therefore, considering the surface coordination reaction below:

$$X + C_{aq} \Leftarrow XC \text{ (or } C_{ads}\text{)}$$

where X is an adsorptive site on the polyurethane foam, C_{aq} is the equilibrium concentration of indium in the aqueous phase (mol L^{-1}) and XC is the surface density that can also be represented as the equilibrium concentration of indium in the PUF phase, C_{ads} (mol g^{-1}). The mass law for this reaction is:

$$b = (XC) / (C_{aq}) (X) \qquad (10)$$

where the constant b or adsorption coefficient is related to the binding energy of the solute and adsorption enthalpy.

The mass balance for X can be expressed as:

$$K_S = X + XC \qquad (11)$$

Therefore, at high C_{aq}, K_S represents the saturation of the polyurethane foam ($C_{ads} = K_S$) with a monolayer coverage of indium iodide species.

Appropriate substitution and rearrangement of equation (10) and (11) leads to the Langmuir isotherm expression in equation (12) and to its linearized form in equation (13)

$$C_{ads} = b\, K_S\, C_{aq} / (1 + b\, C_{aq}) \qquad (12)$$

$$C_{aq} / C_{ads} = 1 / b\, K_S + C_{aq} / K_S \qquad (13)$$

The linear plot of C_{aq} / C_{ads} versus C_{aq} is shown in Figure 4. The saturation capacity K_S is calculated by the inverse of the slope and the adsorption coefficient b is determined from the slope and intercept. The values found at 25 °C were of (0.15 ± 0.02) mol kg^{-1} and (7.0 ± 1.3)x10^4 L g^{-1} respectively.

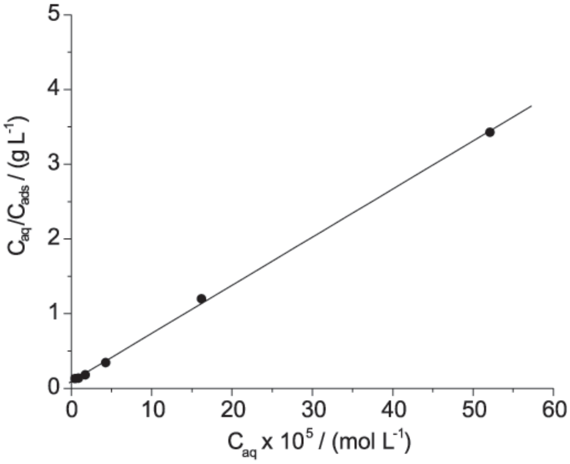

Figure 4. Langmuir plot for indium iodide sorption on PUF (1.8x10^{-3} – 1.8x10^{-4} mol L^{-1} In(III), 0.055 g PUF, 0.1 mol L^{-1} H_2SO_4, 0.7 mol L^{-1} KI, 10 min, and 0.020L). Caq/Cads= 6.44x10^{-2} ± 8.0x10^{-4} Caq + 9.2x10^{-2} ± 1.9x10^{-2} (R= 0.9997).

Thermodynamic studies

The effect of temperature on indium iodide sorption was evaluated under the optimized conditions in the range from 298 to 358 K using the Van't Hoff equation below for determination of enthalpy (ΔH) and entropy (ΔS) change values

$$\log K_c = - \Delta H / (2.303\, R\, T) + \Delta S / (2.303\, R) \qquad (14)$$

where R is the gas constant (8.3143 J mol^{-1} K^{-1}), T is the temperature (K) and K_c is the equilibrium constant depending upon the fractional attainment (F_e) of the sorption of indium iodide complex at equilibrium expressed as:

$$K_c = (F_e) / (1 - F_e) = (\%E) / (100 - \%E) \qquad (15)$$

The plot of log K_c with reciprocal temperature 1/T shown in Figure 5 gives the numerical values of ΔH and ΔS from the slope and intercept respectively.

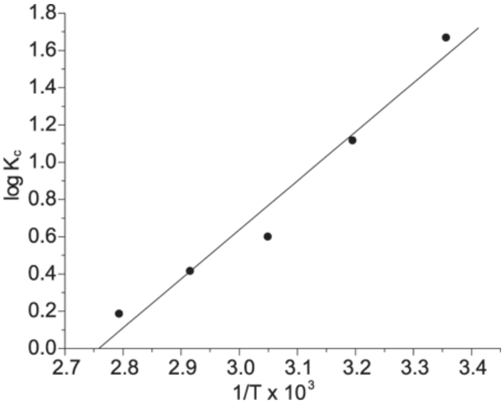

Figure 5. Van't Hoff plot of log K_c *vs.*1/T (2.18×10^{-4} mol L^{-1} In(III), 0.055 g PUF, 0.1 mol L^{-1} H_2SO_4, 0.7 mol L^{-1} KI, 20 min, and 0.050L). log K_c= 2.63 ± 0.28 1/T - 7.25 ± 0.86 (R= 0.983).

The Gibbs free energy ΔG was calculated from the relations expressed in equations (16) and (17):

$$\Delta G = \Delta H - T\Delta S \qquad (16)$$

$$\Delta G = - RT \ln K_c \qquad (17)$$

The numerical values of ΔG obtained from both equations are in good agreement with each other. The calculated thermodinamics data are given in Table 1.

The negative values found for ΔG and ΔH indicate the exotermic and spontaneous nature of indium iodide sorption on PUF. Also, the decreasing values of ΔG and K_c with increasing temperature indicates a more favorabled sorption process at low temperatures. The ΔH numerical value of 50 ± 5 kJ mol^{-1} supports a chemisorption type adsorption as the enthalpy change related to physical sorption[30] is usually smaller than 25 kJ mol^{-1}. This also ratifies the assumption that the bond formation between $(InI_4)^-$ and PUF is of the ion association type. The negative entropy change found for the system reflects a decrease in the degree of freedom of the tetraiodo indate sorbed on PUF by ion association, giving rise to a negative entropy contribution without a compensatory disordering in the inner sphere of the sorbed complex. The thermodynamic data as a whole indicate the high sorption affinity of the system.

Conclusions

The effectiveness of polyether based polyurethane foam for the extraction of indium from an iodide medium was proven by the high distribution ratio and rapid kinetic sorption achieved for the system from a meaningful range of either acid or basic media. These features, allied with its low cost and the possibility of column operations, makes PUF an interesting sorbent for indium preconcentration procedures by solid phase extraction. The sorption equilibrium analysis indicate the neutral species $MInI_4$ as the species most probably sorbed by the foam by ion association complex sorption. This type of sorption involves the charge neutralization of $(InI_4)^-$ species with active sites of the PUF. The possible mechanisms of sorption are based on both solvent extraction and cation chelation. In the first, charge neutralization occurs through the protonation of PUF sites such as oxygen atoms of the ether group and nitrogen atoms of the isocyanate group and requires an acid medium. The cation chelation mechanism supports the chelation of K^+ and H_3O^+ cationic species and can also explain the high distribution ratio shown for the system in basic medium by the formation of neutral $KInI_4$ species.

The sorption behavior of the system followed the Langmuir isotherm and values of $(1.55 \pm 0.02) \times 10^{-1}$ mol kg^{-1} and $(7.0 \pm 1.3) \times 10^4$ L g^{-1} were obtained for the saturation capacity K_s and adsorption coefficient b, respectively. The negative values of the thermodynamic parameters ΔG, ΔH and ΔS reflect a spontaneous and exothermic chemisorption process favored at low temperatures. Therefore, an increase of the system temperature can contribute to the desorption of the indium complex from PUF.

Table 1. Thermodynamic parameters of indium iodide sorption on polyurethane foam

Temperature K	Extraction (E) %	Distribution Coefficient (D)	Equilibrium Constant (K_c)	ΔG kJ mol^{-1}	ΔH kJ mol^{-1}	ΔS kJ mol^{-1} K^{-1}
298	97.9	4.2×10^4	46.6	-9.5	-50 ± 5	-0.140 ± 0.015
313	92.9	1.2×10^4	13.1	-6.7		
328	79.9	3.6×10^3	4.0	-3.8		
343	72.3	2.4×10^3	2.6	-2.7		
358	60.6	1.4×10^3	1.5	-1.3		

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