Paper IV

IMPREGNATED RESINS CONTAINING DI-(2-ETHYLHEXYL) THIOPHOSPHORIC ACID FOR THE EXTRACTION OF PALLADIUM(II). I. PREPARATION AND STUDY OF THE RETENTION AND DISTRIBUTION OF THE EXTRACTANT ON THE RESIN

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ABSTRACT

Solvent impregnated resins containing di-(2-ethylhexyl) thiophosphoric acid(DEHTPA) were prepared by direct adsorption of the extractant onto Amberlite XAD2 using a dry impregnation method. The impregnated resins were characterized by means of potentiometric titrations and specific surface area measurements, and a new method to determine DEHTPA content in the resin based on surface area measurements, is proposed. The distribution of DEHTPA between the aqueous phase and the resin phase was studied, and the data obtained have been treated by the program LETAGROP-DISTR in order to determine the distribution constant K_D, the dimerization constant K_2 and the acidity constant K_a.

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INTRODUCTION

The introduction of impregnated resins into extraction and recovery processes dates back to the work done in the 1970s by Warshawsky (1), Grinstead (2) and Kroebel and Meyer (3).

In recent years, impregnated resins have acquired great importance as a technique with interesting features for the selective separation of metal ions from dilute solutions; their characteristics and applications were thoroughly reviewed recently by Cortina and Warshawsky (4). Impregnated resins are selective adsorption resins based on the incorporation of complexing organic reagents onto macroporous polymeric supports, and establish a link between solvent extraction and ion-exchange technologies by combining the properties of the organic phase in solvent extraction with the operation advantages of ion-exchange processes.

The concept of impregnated resins is well developed nowadays and has a firmly established place in the extraction, separation and preconcentration of metals, in both: analytical separation and preconcentration procedures as stationary phases in extraction chromatography (5, 6, 7, 8) and technological applications in the processing of spent nuclear fuel focused on actinide separation from various types of irradiated nuclear fuels and/or waste solutions (9, 10). Similarly, bis(2-ethylhexyl) sulphoxide supported on chromosorb provided a simple and effective method for the separation of actinides such as U and Pu in view of environmental concern from PUREX process effluents (11). Decontamination processes based on extraction chromatography using novel solid sorbents may prove feasible in polishing raffinates from solvent extraction systems before low level radioactive waste disposal (12, 13). Impregnated resins also have attractive properties as selective adsorption systems in hydrometallurgical schemes in the mineral processing industry and in the recovery of precious metals from solid and liquid wastes. Because precious metals usually occur as minor components of common metal ores, new materials with high concentration efficiency and high selectivity

against non desirable metals are required.

Precious metals, particularly those included in the platinum group of metals, are obtained by leaching with hydrochloric acid solutions and are usually accompained by base metals such as Cu, Fe, Pb and Zn. Various resins containing tertiary amines (14-17) and triisobutylphosphine (18) have been described in the literature for Pd(II) and Au(III) recovery, although their selectivity is less than could be desired. In addition, impregnated resins have been combined with fluidized bed technology for the extraction of precious metals (19, 20).

Pd(II) has unique physical and chemical properties and is widely used in electronics and catalysis. Because of its scarcity and high cost, the development of recovery and separation methods for Pd(II) is essential. Soft metal ions such as Pd(II), Pt(II) and Hg(II) are selectively extracted by dialkylthiophosphoric acids due to the softness that sulphur atoms give to the molecules (21-23), and preliminary solvent extraction results with di-(2-ethylhexyl) thiophosphoric acid (DEHTPA) (24) have shown a good extraction efficiency with high selectivity factors over other base metals.

In this study, a new selective adsorbent is presented for the extraction and separation of Pd(II) from other metals based on the immobilization of DEHTPA onto Amberlite XAD2 using a dry impregnation method (4).

Surface area measurements combined with extraction studies were introduced by Warshawsky, Jerabek and Strikovsky (25, 26) as a powerful tool in the characterization of impregnated resins. The physicochemical characterization of the impregnated macroporous support must be known in order to investigate the factors relating to the impregnation process that influence the activity of the extractant on the solid support and specify the best experimental conditions under which metal recovery should be performed. Thus, this paper presents the results obtained in the characterization studies of impregnated resins with DEHTPA and in the evaluation of ligand losses by solubility when the resin is brought into

contact with an aqueous phase, using the program LETAGROP-DISTR (27) for the treatment of data.

EXPERIMENTAL

Reagents and Solutions

Di-(2-ethylhexyl) thiophosphoric acid (DEHTPA or HL) was kindly supplied by Bayer. The following procedure was used to purify the extractant: 25g of the reagent was dissolved in n-hexane (100ml) and converted into the potassium salt by addition of an ethanol-water (2:1) solution (100ml) with excess of KOH. The obtained potassium salt of DEHTPA in the ethanol-water solution was washed with n-hexane (100ml) and H_2SO_4 2 M (100ml). The organic phase was separated and washed three times with H_2SO_4 0.25 M (200ml) and three more times with deionized water (200ml). Purified extractant was obtained by rotaevaporating the solvent. The purities of the purified and non-purified products were determined by potentiometric titration with NaOH of the extractants dissolved in ethanol-water (3:1) using an automatic titrator MicroTT 2050, Crison, connected to a pH electrode, Crison.

Amberlite XAD2 with particle diameter between 0.3 and 0.9 mm, supplied by Rohm and Hass, was used as a macroporous polymer adsorbent. To remove impurities, the resin was kept in contact with a 50% methanol-water solution containing HCl 4 M for 12 hours, then the polymer was washed with water until chloride ion was not detected, and finally dried at 50°C.

All the chemicals used were of reagent grade and, unless otherwise stated, purified DEHTPA was used in the experiments.

Impregnation Procedure

Impregnated resins were prepared by using a dry impregnation method, mixing an appropiate amount of DEHTPA dissolved in acetone with 25g of dry

XAD2 until total evaporation of the diluent was reached. Then the polymeric beads were washed several times with deionized water and dried at 50°C. The content of DEHTPA adsorbed on the resin was determined after contacting three times 0.2g of impregnated resin with 20ml of ethanol, which completely elutes the ligand, and subsequent potentiometric titration of the sample with NaOH. Some efforts were also made to determine the ligand concentration in ethanol after its elution from the resin by using UV spectrophotometry. The maxima of the absorption spectra of DEHTPA in ethanol was at 210nm, but DEHTPA quantification was not always reproducible, probably due to significant absorption at this wavelength caused by the presence of some monomeric or inorganic material stem from the macroporous support.

^{31}P-NMR Spectra

^{31}P-NMR were recorded under quantitative conditions with a 300 MHz Unity PLUS, Varian, using $(CH_3)_3P$ as a reference and $CDCl_3$ as solvent.

Determination of the Specific Surface Area of the Impregnated Resins

The free specific surface areas of the resins were measured using a Flowsorb II 2300, Micrometrics, and applying the Brunauer, Emmet and Teller (BET) equation (28), which describes the adsorption of gas upon a solid surface. A 30%-70% N_2-He gas mixture, at the temperature of liquid nitrogen and atmospheric pressure, was employed to obtain a monolayer of adsorbed nitrogen on the internal surface of the resins. Liquid nitrogen was used for the apparatus calibration. The samples were dried at 60°C for 24 hours prior to the measurement in order to eliminate the water content. Since impregnated resins cannot be heated to high temperatures, the samples were suitably degassed by adsorbing and desorbing nitrogen repeatedly untitl no variation in the determined surface area was found.

Distribution of DEHTPA between the Aqueous Phase and XAD2

The distribution experiments were carried out by means of batch experiments at room temperature. Samples of 0.2g of dry impregnated resins were shaken with 20 ml of aqueous phase for 24 hours to ensure that equilibrium was attained. Aqueous solutions with the following general composition were prepared: 0.05 M (Na^+, H^+) Cl^-, and pH was varied. After phase separation the equilibrium pH was measured. The total DEHTPA concentration in the aqueous phase was determined by analyzing the total phosphorus concentration by ICP at the 213.6nm first-order atomic emission line of phosphorus with ultrasonic nebulizer and incident plasma power of 1200W. A Spectroflame apparatus, Spectro Analytical Instruments, was used for the analysis. H_3PO_4 was used for the preparation of phosphorus standard solutions. The ligand concentrations on the sorbent after the distribution tests were calculated from a mass balance taking into account the phosphorus concentration in the aqueous phase.

RESULTS AND DISCUSSION

Characterization of DEHTPA

As can be seen in Figure 1, two end points were observed in the potentiometric titration of non-purified extractant, indicating the presence of two acidic compounds in the sample. In the case of purified DEHTPA, the second end point was still present but roughly defined. From these results it may be concluded that the second end point was due to the existence of an acidic impurity that is almost completely eliminated in the purification procedure as illustrated in Table 1. Further studies of the detected impurity were carried out by UV and IR analysis as well as ^{31}P-NMR. No additional information was obtained from UV and IR since no differences were observed between the spectra of purified and non-purified DEHTPA. ^{31}P-NMR showed a main singlet, assigned to the organothiophosphoric

TABLE 1
Purity of the extractant

	% DEHTPA	% Acidic impurity
Non-purified extractant	81.63±1.18	17.21±1.22
Purified extractant	96.92±0.53	1.43±0.23

extractant, at 60.633ppm and 59.734ppm for the non-purified and purified products respectively, and some other singlets, but in a very small proportion, attributable to other impurities. Thus, it can be concluded that the principal impurity present in the non-purified DEHTPA was acidic and did not contain phophorus.

Evaluation of the Impregnation Procedure

The reproducibility of the impregnation process was studied, together with the effect exerted on it by different volumes of diluent. The concentration of adsorbed extractant was not dependent on the initial volume of acetone used for dissolving DEHTPA since in the dry impregnation method total evaporation of the diluent occurs. The good agreement between the values obtained for the different impregnations guarantees the reproducibility of the impregnation method used.

Two different series of impregnated resins were prepared with purified and non-purified DEHTPA. The results are shown in Figure 2. A significant increase in the impregnation was achieved when purified extractant was used, in concordance with its higher content in active compound in comparison with impure extractant. However, with purified reagent the efficiency of the impregnation was in general only a little higher than 50% and diminished by increasing the amount of DEHTPA used; thus a significant amount of extractant was not retained on the resin and consequently lost in the washing step described above in the experimental section. The potentiometric titrations to establish the amount of ligand sorbed on the resins

exhibited only one end point in all cases, and from this fact it can be concluded that the acidic impurity was not adsorbed onto the macroporous support.

In Figure 3, free and occupied specific surface areas of the impregnated resins are plotted against the ligand concentration on the polymeric support. At low DEHTPA concentrations, a small increase in the extractant content in the resin is associated with a considerable loss of free specific area, whereas with highly loaded resins the opposite effect is noticed: a major increase in the amount of extractant adsorbed on the resin is related to a small reduction in free specific surface area. This phenomenon is explained by the fact that, in the adsorption process of the extractant, DEHTPA molecules fill the pore space gradually from the smallest pores up to pores with a larger diameter (25).The pore volume distribution of Amberlite XAD2 shows that most of the pores present in the material have a diameter of between 1.5nm and 30nm. The approximate diameter of DEHTPA, d, was calculated from its molecular weight, M=338.5g/mol, density ρ=0.984g/cm^3, and the Avogadro number, N_A, and assuming spherical molecules as the most simple model (25):

$$d = \left(\frac{6M}{\pi \rho N_A} \right)^{1/3} \tag{1}$$

and was found to be 1.03nm. The similarity of this value to the diameter of the smallest pores in the resin implies that no efficient filling of these pores by DEHTPA molecules could be expected due to the steric exclusion effect. Moreover, it is well known that, owing to geometrical considerations, pores with a small volume have a relatively large area. With these assumptions, since in the adsorption mechanism DEHTPA began filling pores with a small diameter as mentioned above, it seems reasonable that at low ligand concentrations, small amounts of extractant will be responsible for a major decrease in specific surface area. The opposite behaviour is expected and observed for concentrated resins. The same phenomenon has been reported with a very similar molecule and Amberlite XAD2, but using the wet impregnation method (25).

The experimental data for free surface area presented in Figure 3 were successfully fitted by linear regression analysis to obtain the following equation:

$$\ln [HL]_{tr} = 0.28(\pm 0.03) - 0.0212(\pm 0.0004)S_f \qquad (2)$$

where $[HL]_{tr}$ is the concentration of DEHTPA in the resin phase in mol/kg and S_f is the free specific surface area in m^2/g, being both parameters referring to dry XAD2 resin. The goodness of the adjustment, shown in Figure 4, with a correlation factor $\rho_c=0.9995$, suggests that the measurement of free surface areas can be used as an analytical method for the determination of ligand content on the resin, following calibration of the method with impregnated resins of known concentration. The small error detected in the determination of free surface areas may ensure the validity and reliability of this procedure, but it should be noticed that in the case of resins with very high ligand content because of the negligible surface area available on the support, the proposed method will not give accurate results. Specifically, in the case of resins with a dry XAD2 resin concentration of over 1.30 mol/kg, the measurement of the free surface area was not possible due to its almost nil value.

Study of the Distribution of the Extractant

The distribution of the extractant from the polymeric phase into the aqueous phase was studied at different pH for the aqueous solution and for different ligand loadings on the resin.

The distribution coefficient of the extractant between the resin phase and the aqueous phase was defined as:

$$D = \frac{[HL]_r}{[HL]} \qquad (3)$$

where $[HL]_r$ is the equilibrium concentration of DEHTPA expressed in mol/kg dry impregnated resin and $[HL]$ is the concentration of the ligand in the aqueous phase in mol/l.

Taking into account the mass balance assumptions, Equation 3 can be

expressed as:

$$D = \frac{[HL]_{tr} - [HL](V / m_r)}{[HL]} \qquad (4)$$

where $[HL]_{tr}$, as defined previously, is the initial total concentration of extractant on the resin, now expressed in dry impregnated resin basis, V (expressed in liters) denotes the volume of the aqueous phase and m_r (in kg) is the mass of the dry impregnated resin.
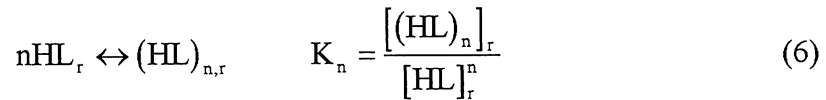
The dependence of DEHTPA distribution on pH for two different ligand concentrations is shown in Figure 5, where it can be seen that the distribution of the ligand in the aqueous phase is independent of pH at low pH values, approximately up to pH=3, decreasing as pH increases. In addition, the distribution ratio is also dependent on the amount of extractant adsorbed on the resin, and consequently the presence of DEHTPA aggregates on the polymeric support can be presumed.

The distribution data obtained were treated in order to determine the equilibrium HL distribution defined by the following equations and constants, also illustrated schematically in Figure 6:
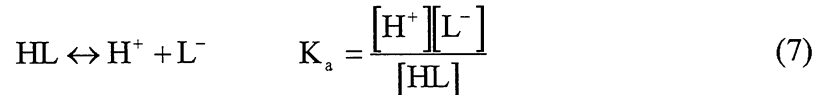
- Distribution of ligand between the resin and the aqueous phase:

$$HL \leftrightarrow HL_r \qquad K_D = \frac{[HL]_r}{[HL]} \qquad (5)$$
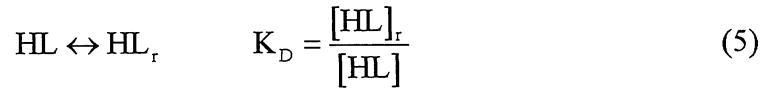
- Aggregattion of ligand on the resin:

$$nHL_r \leftrightarrow (HL)_{n,r} \qquad K_n = \frac{[(HL)_n]_r}{[HL]_r^n} \qquad (6)$$

- Dissociation of ligand in the aqueous phase:

$$HL \leftrightarrow H^+ + L^- \qquad K_a = \frac{[H^+][L^-]}{[HL]} \qquad (7)$$

where K_D, K_n and K_a are the distribution, dimerization and acidity constants respectively. The experimental distribution data were evaluated by the computer program LETAGROP-DISTR. In this program, for a given model, the computer

searches for the best set of equilibrium constants, which includes K_D, K_n and K_a, that would minimize the error squares summatory defined by:

$$U = \sum \left(\log D_{exp} - \log D_{calc} \right)^2 \tag{8}$$

where D_{exp} is the distribution ratio of the organothiophosphoric acid determined experimentally and D_{calc} is the value calculated by the program. The program also calculates the standard deviation σ defined as:

$$\sigma(\log D) = \left(\frac{U}{N_p} \right)^{1/2} \tag{9}$$

where N_p is the total number of experimental points. Several models with different aggregation numbers for the ligand HL were tried, in order to investigate the possibility of finding species which could improve the fit with the experimental data. The constants calculated are given in Table 2 and these values were used to calculate the solid lines in Figure 5, where good fitting of data is observed. The small difference between experimental and calculated values shown in Figure 7 gives us great confidence in the proposed model.

On the basis of the constants listed in Table 2 several points may be made. The value of the distribution coefficient indicates that the equilibrium distribution of DEHTPA between the resin and the liquid phase is displaced toward the solid phase. Furthermore, the aggregation constant found confirms that DEHTPA tends to form dimers in the resin phase, probably due to hydrogen bonding between the P=S and P-OH groups on adjacent molecules as represented in Figure 8. The distribution species diagram for DEHTPA presented in Figure 9 highlights the presence of dimerized ligand, which becomes more noticeable as the extractant content on the resin increases. The value of the dimerization constant for DEHTPA on XAD2 is lower than the value obtained for toluene (29). This fact, which is due to the aggregation constants of extractants adsorbed on resins being smaller than those of organic solvents, has been reported in the literature (30, 31) for other extractants and solvents. The pK$_a$ determined in this work is in agreement with the

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TABLE 2

Equilibrium constants of DEHTPA

log K_D	log K_2	pk_a	References
2.65	0.04±0.06	3.64±0.07	This work
-	1.76	-	(29)
-	-	3.62	(32)

value, pK_a=3.62, obtained by linearized pH-metric titration in water with 16.7% ethanol (32). In Figure 10, the distribution species diagram is presented with varying pH and a significant presence of dissociated DEHTPA (L⁻) is predominant over pH=4.

Numerical treatment concerning the distribution of the extractant di-(2-ethylhexyl) dithiophosphoric acid between the resin and the aqueous phase using the program LETAGROP-DISTR gave the following results (26): log K_D=4.91, K_n=0 and pK_a=3.17. In comparison with the data in this work, the distribution constant value found in the literature is considerably higher, indicating that the distribution of the extractant in the aqueous phase will be greater for the dialkylthiophosphoric reagent. Moreover, as can be easily predicted, the molecule containing two sulphur atoms does not aggregate due to the weakness of the hydrogen bonding between the P=S and P-SH groups, and presents a lower pK_a because of the lower electronegativity of the sulphur atom compared with that of the oxygen atom.

CONCLUSIONS

The extractant used in this study was successfully purified through a procedure consisting of the the formation of its potassium salt. By potentiometric titration analysis and ^{31}P-NMR, the main impurity in the initial product was found to be an acidic compound which did not contain phosphorus.

DEHTPA was used to prepare impregnated resins by adsorption of this

extractant on Amberlite XAD2 by means of a dry impregnation method.

The measurements of free specific surface area provides an alternative method for the determination of the extractant content on the resin. Furthermore, the mechanism proposed in the literature for the adsorption process of an organodithiophosphoric extractant when the wet impregnation method is used was also found for the extractant in this work and using a dry impregnation method. Therefore, the adsorption of DEHTPA filling the pore space gradually from the smallest pores up to larger pores is independent of the impregnation method used.

The immobilized extractant on the resin is involved in the following reactions: distribution between the resin phase and the aqueous phase, dimerization in the resin phase and dissociation of the extractant in the aqueous phase, which becomes important at pH>4. From the last of these observations it is concluded that the use of DEHTPA in highly acidic media will minimize the extractant loss. Taking into account that processes involved in the recovery of precious metals contain major concentrations of mineral acid, DEHTPA may constitute a suitable extractant for Pd(II) extraction.

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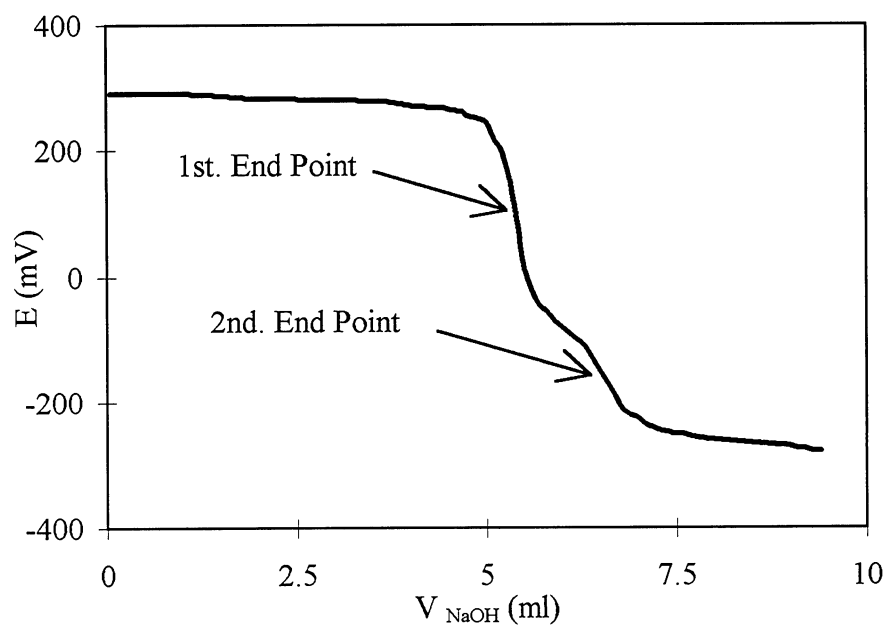
FIGURE 1. Potentiometric titration of non-purified DEHTPA with NaOH in ethanol.
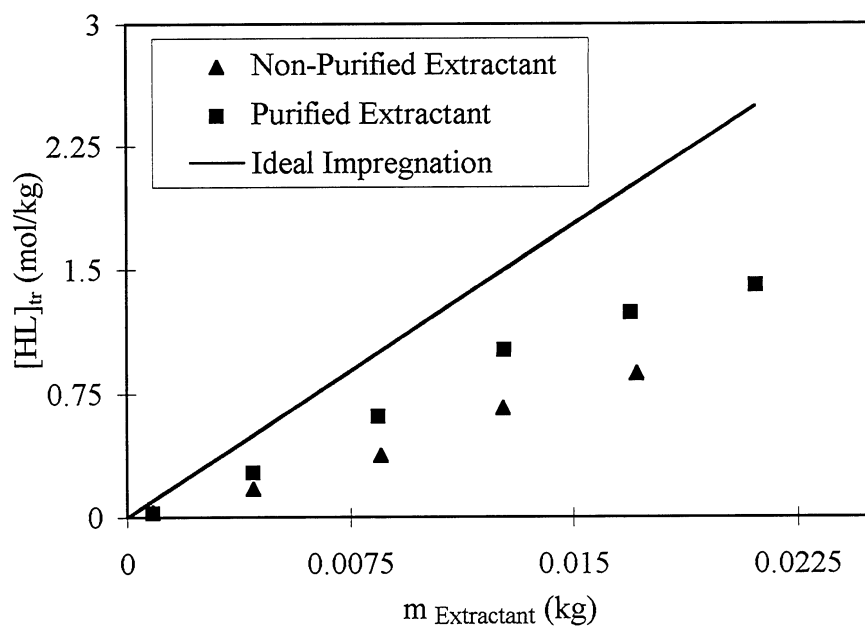
FIGURE 2. Concentration of extractant on dry XAD2 resin as a function of extractant mass used in the impregnation of 0.025 kg of dry XAD2. The line "Ideal Impregnation" was plotted assuming 100% purity for DEHTPA and its complete adsorption on the resin.
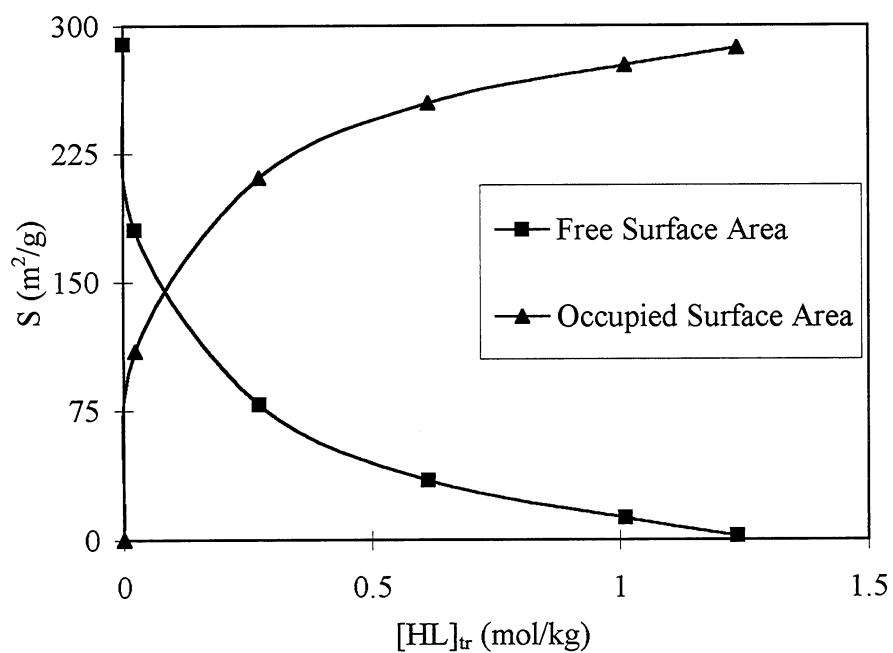
FIGURE 3. Free and occupied specific surface area as a function of extractant concentration on dry XAD2 resin.
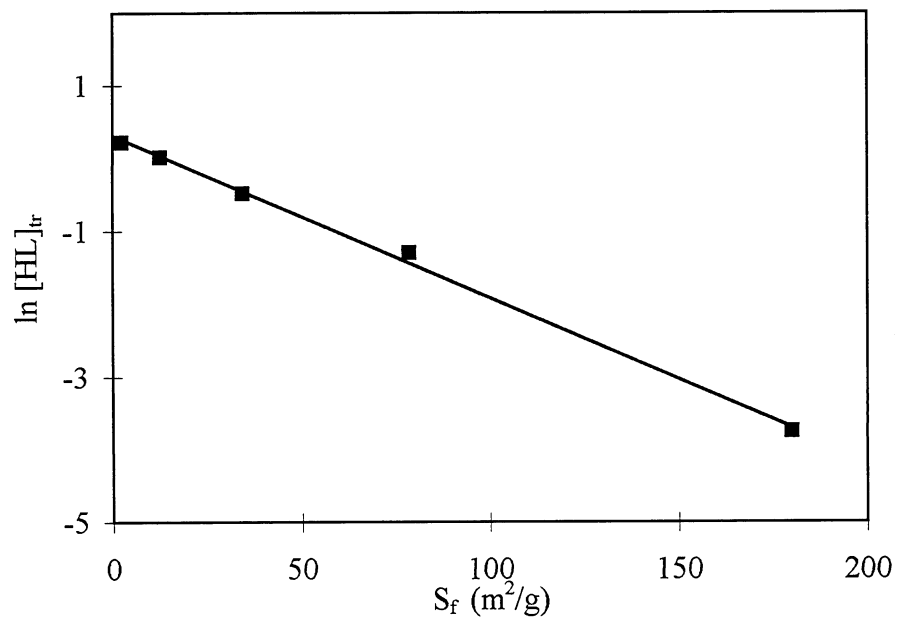
FIGURE 4. Linear fit for determination of DEHTPA content on the resin from surface area measurements.
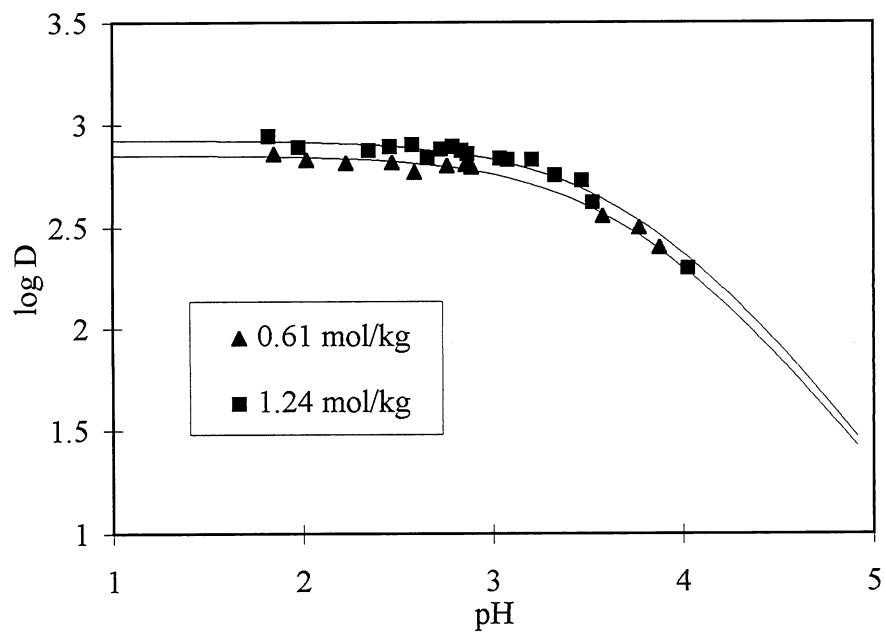
FIGURE 5. log D plotted as a function of pH for different DEHTPA dry XAD2 resin concentrations in XAD2 in 0.05 M (Na^+, H^+) Cl^-. Full drawn lines calculated by the program LETAPL using the constants given in Table 2.
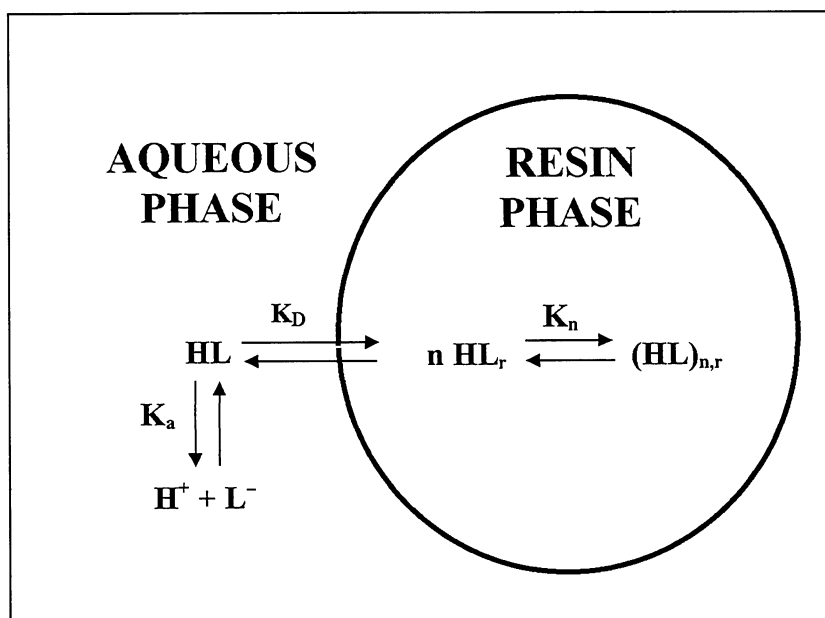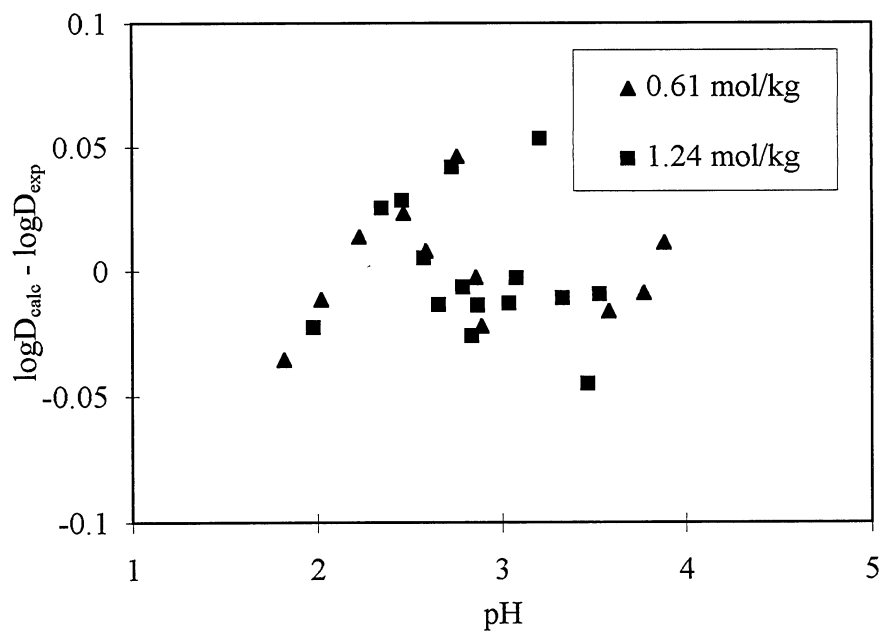
FIGURE 6. DEHTPA equilibrium reactions.

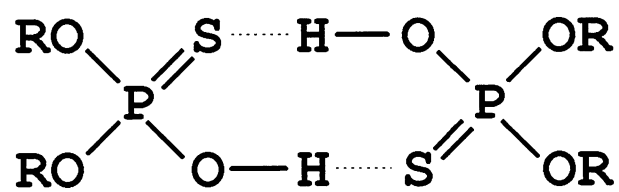FIGURE 7. Values of (log D_{exp}-log D_{cal}) calculated by the LETAGROP program as a function of pH.

FIGURE 8. Hydrogen bonding between molecules of DEHTPA where R represents the group 2-ethylhexyl.
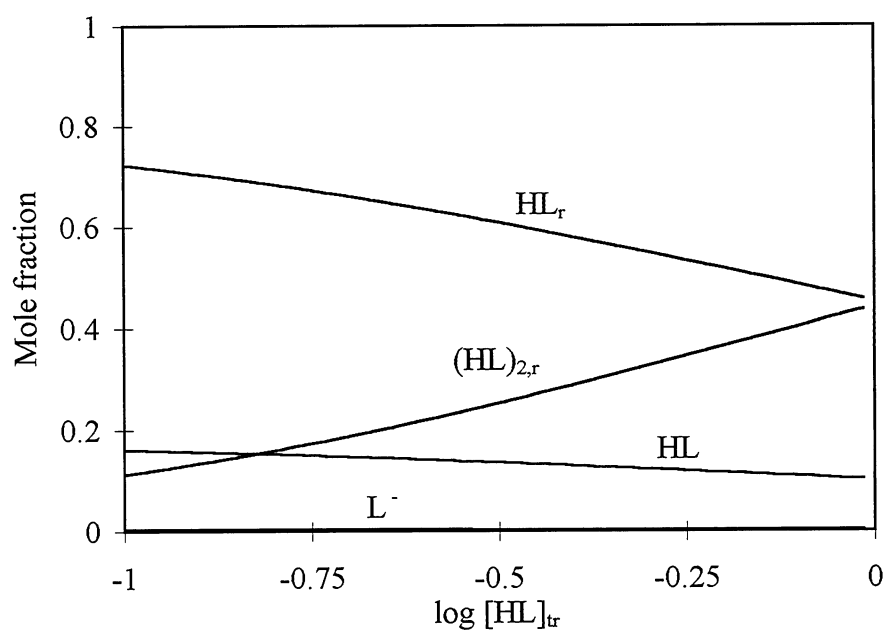
FIGURE 9. Fraction of the different species present in the system plotted as a function of the total DEHTPA concentration on dry impregnated resin at pH=2 and for a phase ratio $(m_r/V)=0.01$.
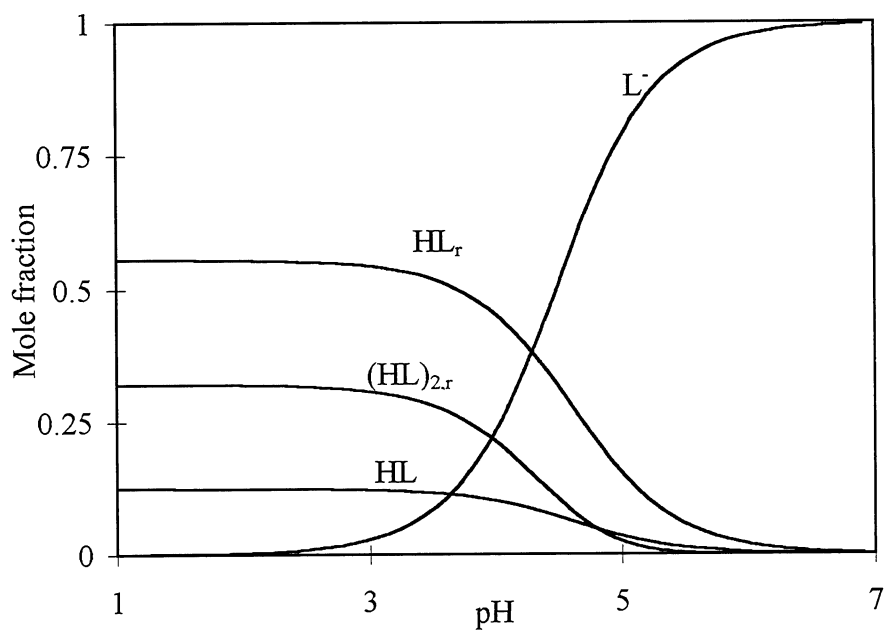
FIGURE 10. Fraction of the different species present in the system plotted as a function of pH at total DEHTPA concentration on dry XAD2 resin of 1.24 mol/kg for a phase ratio $(m_r/V)=0.01$.