A STUDY ON THE COMPLEXATION OF PICOLINIC ACID DERIVATIVES WITH Cd^{2+}, Ni^{2+} AND Zn^{2+}

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Dedicated to the Memory of Prof. Dr. Juan de Dios Guevara, great peruvian chemist, in occasion of his 100 birthday on 1 march 2010

ABSTRACT

In the present study we report the complexation of picolinic acid and two of its derivatives, 4-(3-heptyl)pyridine-2-carboxylic acid (43HP2CA) and 6-(3-pentyl)pyridine-2-carboxylic acid (63PP2CA) with Ni^{2+}, Zn^{2+} and Cd^{2+}. The acid dissociation of the three ligands and complex formation constants with these metal ions were determined by potentiometry in dioxane/water 75% (v/v) as solvent at $25^{\circ}C$. The complexation of either ligands with the metal ions studied follows the order $Ni^{2+} > Zn^{2+} > Cd^{2+}$.

The acid dissociation constants of 43HP2CA measured potentiometrically in various dioxane/water mixtures with a composition in the range of 85-15% (v/v), show that the pK_a value increases with the increase of the concentration of dioxane in the medium. The stability constants of 4-(3-heptyl)pyridine-2-carboxylic acid with Zn^{2+} and Cd^{2+} were estimated in water solutions at different temperatures and it was found that the processes were exothermic in both cases.

Key words: extraction of cadmium, nickel and zinc; picolinic acids; acid dissociation - and stability constants

RESUMEN

Presentamos, en esta contribución, un informe sobre la formación de complejos del ácido picolínico y dos de sus derivados, 4-(3-heptil)piridina-2-ácido carboxílico (43HP2CA) y 6-(3-pentil)piridina-2-ácido carboxílico (63PP2CA) con Ni^{2+}, Zn^{2+} y Cd^{2+}. Las constantes de acidez de los tres ligandos y las constantes de formación de complejos con los metales mencionados han sido determinados por potenciometría en mezcla dioxano/agua 75% (v/v) como solvente a temperatura $25^{\circ}C$. La formación de complejos de cada uno de los ligandos con los metales sigue la serie $Ni^{2+} > Zn^{2+} > Cd^{2+}$.

La constante de acidez de 43HP2CA ha sido medida por potenciometría en varias mezclas de dioxano/agua en un rango de 85-15% (v/v). Estas medidas confirman que los valores pK_a se aumentan con el aumento de la concentración del dioxano en el sistema. Las constantes de la estabilidad del ácido 4-(3-heptil)piridina 2-carboxílico con Zn^{2+} and Cd^{2+} han sido valoradas en solución acuosa a temperaturas diferentes. Hemos encontrado que los procesos son exotérmicos en los dos casos.

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Palabras clave: extracción de cadmio, níquel y zinc ; ácidos picolínicos ; constantes de acidez y estabilidad de complejos

INTRODUCTION

Development of chelating agents for liquid-liquid extraction of metal ions has received great interest, in particular for their application in the recovery and the recycling of base metals in solution with low pH.

Picolinic acid, pyridine-2-carboxylic acid, forms stable complexes with base metal Ni^{2+}, Zn^{2+}, and Cd^{2+} [1,2]. This compound is water-soluble and it cannot be used as an extraction reagent. The introduction of a lipophilic group renders the reagent to be water insoluble, hence becomes suitable for liquid-liquid extraction. Several lipophilic groups, nucleophile, and electrophile [3-5] can be introduced at different positions, affecting, but not drastically altering, the interaction of the functional group and the metal iones. Howewer, the position of the substituted liophilic group on the pyridine nucleus is important for the ability of the reagent to react with metal ions as it may limit the formation of the chelating ring. The electronic nature of the substituent may also be important due to the electron withdrawing which reduces the electron donor capacity of nitrogen atom.

The study of the complexation of these ligands with different metal ions enables us to predict the extraction characteristics. The use of dioxane-water mixtures makes possible to study the water-insoluble derivatives of picolinic acid equilibria in one phase. The advantage of using dioxane is that it is miscible with water through the entire composition range and there are thermodynamic data available (e. g. dielectric constants, ionization products) [6-8] for mixtures with different composition. The formation constants of the complexes between transition metals and similar reagents to these studied here; 4-chloro and 4-amino picolinic acid N-oxide have been studied in aquo organic media; it has been observed that the stability of these complexes increases compared to aqueous system for all the mixed aqueous system studied, dioxane-water, acetone-water, isopropanol-water, and ethanol-water[6]. The stability of complexes containing either O-H or O-M bonds increases with increasing organic content of the solvent [7] due to the decrease in the dielectric constant of the bulk solvent. In studies of the protonation and complexation of ligands with metal ions as acetyl acetone [8], N-benzoyl N-phenyl hydroxylamine [9] , and other ligands containing O and N as donors [10, 11] it has been also observed an increase on the complex stability with the increase of the organic concentration in the organic-aqueous mixtures. As the dielectric constant decreases, the ion-ion interaction involving protons or metal-ion and the anionic oxygen donor of the ligand increases to a greater extent than the ion-dipole interaction between the cations and the solvent molecules. Howewer, there is apparently no simple relationship between the stability of complexes containing N-M bonds and solvent composition. The effect of solvent composition on the stability of chelates containing O-M-N bonds might be an indication of the relative importance of these bonds.

The objective of the present work is to study the equilibria between picolinic acid and two of its derivatives (figure 1) with three divalent metal ions, Ni^{2+}, Zn^{2+}, and Cd^{2+} in water-dioxane mixtures at 25°C. Firstly, we determined the dissociation constant of the picolinic acid and their derivatives as well as their complexation with the metal ions in these media. Secondly, we characterized one of the ligands in different dioxane-water mixtures and propose a model to extrapolate thermodynamic data from organic-water mixtures into pure water solutions or pure organic solutions. This information is useful for making use of the reagents in liquid-liquid distribution studies, which is important for the extraction of metals from different aqueous solutions.
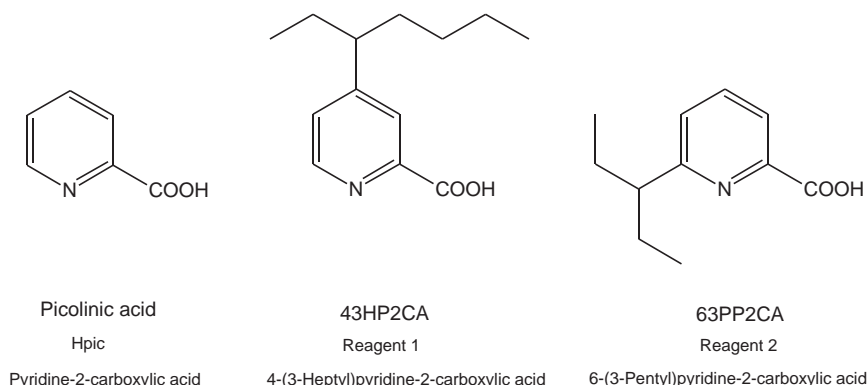
Figure 1. Chemical structure of picolinic acid derivatives.
Reagent 1: 4-3-heptyl)pyridine-2-carboxylic acid (43HP2CA)
Reagent 2: 6-(3-pentyl)pyridine-2-carboxylic acid (63PP2CA).

EXPERIMENTAL

Materials and reagents

Picolinic acid (figure 1) supplied by SIGMA chemicals was purified by recrystallization and used for the preparation of solutions for the potentiometric studies. Two derivatives of picolinic acid were synthesized according to the method and scheme reported in references [12], (also see References) and briefly described below.

Reagent 1, 4-(3-heptyl)pyridine-2-carboxylic acid, 43HP2CA, and reagent 2, 6-(3-pentyl)pyridine-2-carboxylic acid, 63PP2CA.

Reagent 1, c/o in figure 1, were prepared by dissolving $2.88 \cdot 10^{-2}$ mol of $(NH_4)_2S_2O_8$ (p.a. MERCK) in 40 ml of water and adding this solution to a mixture of $1.92 \cdot 10^{-2}$ mol of 2-cyanopyridine (SIGMA chemicals), $9.65 \cdot 10^{-2}$ mol of 2-ethylhexanoic acid (p.a. MERCK), $1.92 \cdot 10^{-3}$ mol of $AgNO_3$ (LABASCO, Sweden), and 58 ml of H_2SO_4 1 M (p.a. MERCK) at $70°C$. The yield of this first step was 3.56 g of crude product, which was chromatographed by silica gel column with CH_2Cl_2 (p.a. MERCK) as the mobile phase. Two different products were obtained; 2-cyano-6-(3-heptyl)pyridine, and 2-cyano-4-(3-heptyl)pyridine. An aliquot of $9.32 \cdot 10^{-3}$ mol of 2-cyano-4(3-heptyl)pyridine was reacted with $9.32 \cdot 10^{-2}$ mol of KOH (MERCK) in ethylene glycol at $130°C$.

Reagent 2, figure 1, was obtained in the way described above but by using 2-ethylbutyric acid instead of 2-ethylhexanoic acid. The second part of the reaction was initiated with 2-cyano-6(3-pentyl)pyridine. The products obtained were characterized by elemental analysis, NMR spectroscopy (GEMINI-200BB "G-2000") ad IR-FT (Perkin Elmer 200).

$[(CH_3)_4N]NO_3$, (p.a. FLUKA) was recrystallized before use. HNO_3 (65% p.a. MERCK) was used as supplied to prepare 0.1 M solutions, standardized with $KHCO_3$ (p.A. MERCK) which was recrystallized before use. KOH (p.a. MERCK) 0.02 M solutions were used as titrating solution in the potentiometric studies.

Metal salts $Ni(NO_3)_2$, $Zn(NO_3)_2$ and $Cd(NO_3)_2$ (p.a. MERCK), wre purified by recrystallization and used to prepare stock solutions of the metal ions to be studied.

1,4-dioxane (p.a. MERCK) was used without purification and mixed with distilled water to prepare the different mixtures. The composition of the dioxane-water mixtures used were in the range of 15-85% v/v.

Methodology

The potentiometric titration technique was used in one phase. The $[H^+]$ in the solution was measured using a glass electrode (METROHM 6.0101.000) and a reference electrode Ag/AgCl (METROHM 6.0726.100). The reference electrode contained two different solutions. The inner solution was a Ag/AgCl saturated solution with NaCl 10 mmol and ionic strength equal to 0.1 M. The outer solution of the reference electrode was $[(CH_3)_4N]NO_3$ 0.1 M. In both cases, a mixture of dioxane-water (15-85%) was used as a solvent. The potential, E, of the cell were measured with a precision 0.02 mV through a computer controlled system connected to a swich/control unit (HEWLETT PACKARD 3488 A) and a digital voltmeter (HEWLETT PACKARD 3456 A) The solution was added by an automatic burette (METROHM 715 Dosimat) controlled with the computer system. After the addition of the reagent, E_h became constant within 20-30 min and remained constant within 0.05 mV for a least 12 h. The emf measurements were carried out in an air thermostatic box kept at $25.00 \pm 0.05°C$. The ionic strength in the solvent was kept constant at 0.1 M using tetramethylammonium nitrate as an inert electrolyte. In this way, the activity coefficients of the different reacting species are kept constant [13].

The dissociation reaction of an acid HL in solutions is given by equation (1)

$$HL \; \rightleftharpoons \; L^- \; + \; H^+ \qquad (1)$$

And the dissociation constant is given by K_a. The study was carried out by varying the total concentration of H_{tot} by the addition of HNO_3 in tetramethylammoniumnitrate. The concentration of free hydrogen ions, h or $[H^+]$, was measured potentiometrically. The values of the total concentration of the reagent that was kept constant, L_{tot}, and the total amount of proton, H_{tot}, were analytically determined. The mass balance expressions are given by equation (2)

$$L_{tot} = [L^-] + [HL] \qquad (2)$$

$$H_{tot} + [OH^-] = [H^+] + [HL] \qquad (3)$$

The formation function, Z, i.g. the fraction of reagent bound to the proton, and is expressed by equation (4)

$$Z = \frac{[HL]}{L_{tot}} = \qquad (4a)$$

$$= \frac{H_{tot} - [OH^-] - [H^+]}{L_{tot}} = \qquad (4b)$$

$$= \frac{K_a^{-1} [H^+]}{K_a^{-1} [H^+] + 1} \qquad (4c)$$

This relationship indicates that Z is a function only of the concentration of the free hydrogen ions. The complex formation reactions of the reagents with the metal ions in solution can be expressed by the following general equation (5)

$$p \, Me^{2+} + q \, L^- \rightleftharpoons [Me_pL_q]^{2p-q} \qquad (5)$$

As the study was carried out at low metal concentration range (the low concentration should be given in figures), it is reasonable to assume that p = 1 i.g. the complexes formed are mononuclear with respect to the metal, while q = (1,2,…n). And the overall constants are thus given by equation (6)

$$\beta_q = \frac{[MeL_q^{2-q}]}{[Me^{2+}] [L^-]^q} \qquad (6)$$

Where the activity coefficient terms, , are included in the $_q$, being conditional equilibrium constants. The amount of ligand bounded to metal ion in solution, Z, is expressed by equation (7)

$$Z = \frac{L_T - [HL] - [L^-]}{MT} \qquad (7a)$$

$$Z = \frac{H_2 \sum_{q=1}^{n} q\beta_q[L^-]^q}{H_2 \sum_{q=0}^{n} \beta_q[L^-]^q} \qquad (7b)$$

In this case, Z depends on the concentration of free ligand, which is measured experimentally. Back-titrations were performed to test the reversibility of the reactions. The agreement of the data within the limit of the experimental error on both titrations indicated the reversibility of the reactions and that the equilibrium was reached.

RESULTS AND DISCUSSION

Determination of the acid dissociation constant, pK$_a$
The pK$_a$ values of picolinic acid and the two reagents, 43HP2CA, and 63PP2CA were determined in a dioxane/water mixture 75% (v/v). The ionization constant for water reported by Uhlig et al [14] is pK$_w$ = 16.74.
Emf titrations were performed by varying H$_{tot}$ and L$_{tot}$ for each reagent, the concentration range was 1.5 – 3.3 mM. A generous set of H$_{tot}$, L$_{tot}$ and [H⁺] or h data, were generated and processed. The data were treated using graphical and numerical methods.

Graphical treatment of the data
The experimental data expressed as Z$_{exp}$ is easily using equation (4b), which has been transformed to equation (8) to calculate, graphically, the dissociation constant

$$\frac{Z_{exp}}{1 - Z_{exp}} \quad = \quad K_a^{-1} [H^+] \tag{8}$$

Equation (8) gives a linear relationship between $Z/1-Z$ as a function of $[H^+]$ with a slope equal to K_a^{-1}. The experimental data were fitted using linear regression, figure 2, showing the straight line that is the fit of the equation to the experimental points and pK_a values of 6.27 for picolinic acid, 6.62 for 43HP2CA, and 6.40 for 63PP2CA, were obtained.
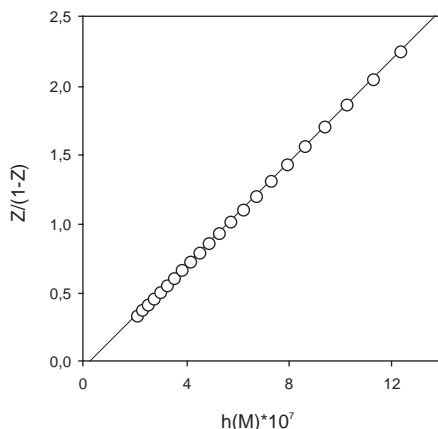

Figure 2. A plot for the experimental data given as $Z/(1-Z)$ versus the concentration of H^+ in solution. The straight line is obtained by fit measured linear regression.

Numercical analysis of the data
The general minimizing LETAGROP program [15, 16] was used for determining the "best" values of the equilibrium constants for complex formation from potentiometric titrations data. LETAGROP solves the set of mass balance equations for each component, as given by the equations (9) and (10)

$$A_{tot} = H_{tot} = h + \Sigma \ p \ \beta_{pq} \ h^p \ b^q \tag{9}$$

$$B_{tot} = B = b + \Sigma q \ \beta_{pq} \ h^p \ b^q \tag{10}$$

Where A and B are the analytical (total) concentrations of proton and ligand, respectively. The program determines the values of h and b, by solving the mass balance equations at a given set of conditions. The prorgram the varies the values of $_{pq}$ in order to minimize the error squaresum function U, defined by equation (11)

$$U = \sum_{i=1}^{N} (Z_{calc} - Z_{exp})^2 \tag{11}$$

where Z_{calc} is obtained using $_{pq}$ in equation (4c).
And Y, is defined by equation (12)

$$\sigma Y \;=\; (U/N)^{1/2} \qquad\qquad (12)$$

The best fit of the experimental data is that which gives the lowest values of U and Y. We first determined the mono-protonation of the three reagents, picolinic acid, 43HP2CA, and 63PP2CA. The pK_a values obtained are given in table 1. These values are in excellent agreement with the pK_a calculated with the graphical method (1).

Table 1

PK_a values of picolinic acid and ist derivatives in dioxane/water 75 % at 25°C calculated by graphical method and numerical analysis. The error is given as 3 (= standard deviation)

Ligand	pK$_a$	
	Graphical Method	**Numerical Method**
Picolinic acid	6.27 ± 0.06	6.30 ± 0.04
43HP2CA*	6.62 ± 0.06	6.62 ± 0.02
63PP2CA**	6.40 ± 0.02	6.37 ± 0.02

* 4-(3-heptyl)pyridine-2-carboxylic acid   ** 6-(3-pentyl)pyridine-2-carboxylic acid

Figure 3 shows the goodness of the fit of Z (pH) the curves using the pK_a determined obtained from the LETAGROP program. The symbols represent the experimental Z values, and the curve represents the Z values calculated by equation (4c) where the dissociation constant value pK_a = 6.27 for picolinic acid was used. Similar procedures were applied for the other two reagents. The fact that the Z curves for different concentrations of free reagent fall on the same line indicates that only mononuclear species with respect to the reagent are formed, which validate the earlier assumption made.
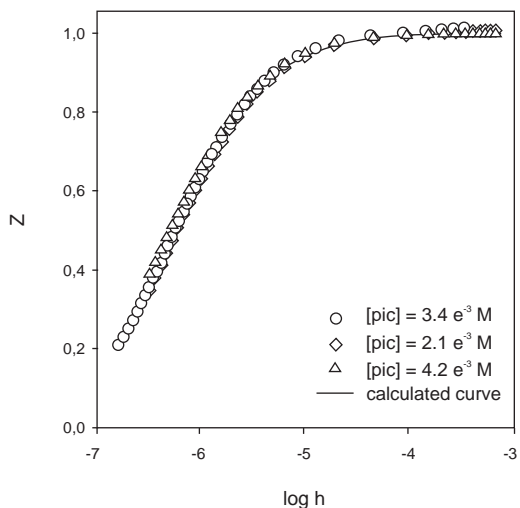
Figure 3. The formation function Z is plotted against the logarithm of the free hydrogen
concentration. The symbols î , , and represent the experimental data for different
concentration of picolinic acid, while the line shows
the calculated Z values using equation (8).

From the results, it is found that the acidity of the ligands decreases with the length of the
hydrocarbon chain, with the picolinic acid being the most acidic followed by reagent 2, with 5-
C in the alkyl chain and the most basic is reagent 1, with 7-C in the alkyl chain. It seems that the
position of the alkyl chain does not affect the protonation of the ligands as can be expected for
bigger ions.

Complexation of picolinic acid derivatives with Ni^{2+}, Zn^{2+}, and Cd^{2+}

We have also studied the complex formation of picolinic acid, 43HP2CA, and 63PP2CA with
Ni^{2+}, Zn^{2+}, and Cd^{2+}. The studies were carried out in dioxane/water mixtures 75% (v/v) as a
solvent. The eperiments were carried out using different ligand to metal molar ratio L_T/M_T in
the range 2.5 to 15. Under these conditions, the formation of polynuclear species with respect
to metal could be neglected. The stability constants for the different species have been
determined by graphical and numerical methods.

A set of data was generated by varying M_{tot}, H_{tot}, and L_{tot} for each constant reagent
concentration. The working range of reagent and metal concentration was 1.5 – 3.3 mM and
0.2 – 0.6 mM respectively. An abundant set of data were collected and processed to determine
the value of the stability constants.

Graphical treatment of the data

The experimental data expressed as Z_{exp} are obtained using equation (7a). The data was used to graphically calculate the complex formation constant using the equation (13), which is obtained from equation (7b) assuming the formation of two species

$$\frac{Z_{exp}}{(1 - Z_{exp})\,[L^-]} \;=\; \beta_1 \;+\; \beta_2 \;\frac{(2 - Z_{exp})}{(1 - Z_{exp})}\;[L^-] \qquad (13)$$

Equation (13) shows a linear relationship of $Z/(1-Z)[L^-]$ as function of $[L^-]$ with the slope equal to β_2 and the intercept equal to β_1. Figure 4 shows that a straight line that is fitted to the experimental points for the system Cd-picolinic acid at 25°C. Similar calculations were applied for the other systems studied.
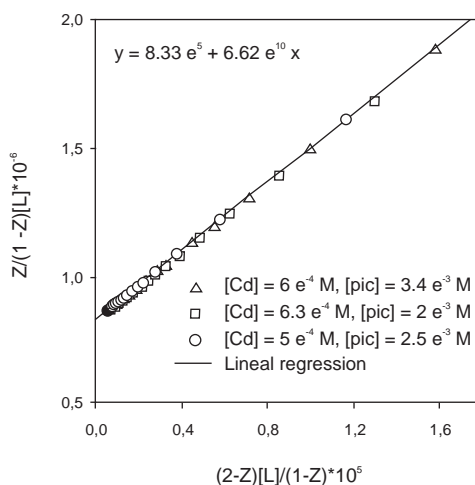

Figure 4. A plot for the experimental data given as $Z/(1-Z)[L]$ versus $(2-Z)[L]/(1-Z)$. The straight line is obtained by fit measured linear regression.

Numerical analysis

Using the LETAGROP program we determined the complexation of 43HP2CA, 63PP2CA, and picolinic acid with the metal ions. TABLE 2 gives a summary of the stability constants of the three ligands determined. These values are in good agreement with those obtained graphically. The system Ni-picolinic, and Ni-43HP2CA were also studied but even at low pH (pH 1) the metal was complexed with these reagents and as the method is interpreted from the difference between the analytical and measured hydrogen concentrations the method becomes increasingly insensitive at low pH values.

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Table 2. The determined complex formation constants of picolinic acid
and its derivatives in dioxane/water 75 % v/v at 25°C

System	Graphical Method		Numerical Method	
	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$
Ni-63PP2CA	5.98± 0.06	12.13 ± 0.05	6.04 ± 0.03	12.16 ± 0.02
Zn-pic[a]	7.20 ± 0.06	12.50 ± 0.04	7.24 ± 0.03	11.46 ± 0.02
Zn-43HP2CA[b]	7.72 ± 0.05	12.66 ± 0.05	7.69 ± 0.04	12.64 ± 0.02
Zn-63PP2CA[b]	5.48 ± 0.06	11.32 ± 0.06	5.53 ± 0.06	11.35 ± 0.02
Cd-pic[a]	5.94 ± 0.05	10.87 ± 0.05	5.92 ± 0.02	10.82 ± 0.03
Cd-43HP2CA[b]	7.20 ± 0.04	12.53 ± 0.04	7.16 ± 0.04	12.54 ± 0.04
Cd-63PP2CA[c]	5.33 ± 0.06	11.35 ± 0.05	5.29 ± 0.05	11.31 ± 0.02

[a] Picolinic acid, [b] 4-(3-heptyl)pyridine-2-carboxylic acid, [c] 6-(3-pentyl)pyridine-2-carboxylic acid

Figure 5 shows the goodness of the fit for the curve Z(log[pic]) using the stability constants obtained by LETAGROP program. All the experimental data falls on the same line, which indicates that there is formation of only mononuclear species with respect to the metal ions Ni^{2+}, Zn^{2+} and Cd^{2+}.
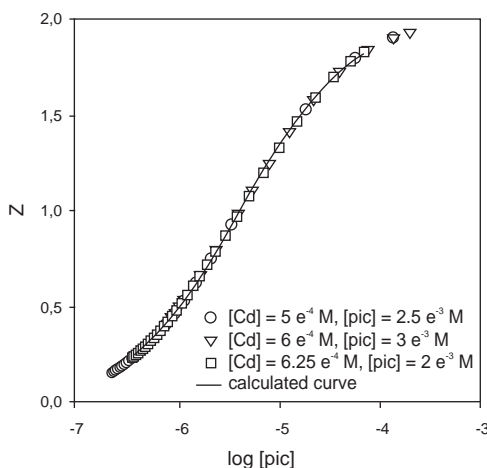

Figure 5. The formation function, Z, is plotted versus the logarithm of the concentration of the free picolinate in solution for the system Cd-picolinic acid.

Determination of the dissociation constants of 43HP2CA in dioxane/water mixtures
The acid dissociation constants of 4-(3-heptyl)pyridine-2-carboxylic acid (43HP2CA) have been measured pH-potentiometrically in dioxane/water mixtures ranging from 85% to 15% (v/v), the ligand is not soluble in mixtures containing dioxane in a concentration below 15% (v/v). The measurements were carried out following similar procedures and the conditions were identical to the ones explained in previous sections (A and B).
The data was treated graphically and numerically with LETAGROP program. The constants obtianed are reported in table 3 as well as the values of the pK_w of the different dioxane/water mixtures from reference [14].

Table 3. pK_w at different dioxane/water mixtures and pK_a of 43HP2CA at different ratio of dioxane/water. The error is hiven as 3 (=standard deviation)

% Dioxane	pK_W *	pK_a **
0	13.74	
15	14.12	5.71 ± 0.05
25	14.44	5.72 ± 0.04
40	15.00	5.92 ± 0.02
50	15.40	6.13 ± 0.02
60	15.86	6.25 ± 0.02
75	16.74	6.62 ± 0.02
85	18.00	7.13 ± 0.05

* from reference [14]   ** determined experimentally at 25°C

The results reveal that the increase of the dioxane concentration in the reaction medium gives lower values of the acid dissociation constant. The dissociation constant in dioxane-water mixtures solvent is influenced by the different solvent characteritics as, the dielectric constant of the medium, and the structure of water and change in hydrogen bonding in water by dioxane [9,8].
From the linear relation between pK_a of 43HP2CA and pK_w it is possible to obtain the value of the dissociation constant of 43HP2CA in 100% water and ionic strength equal to 0.1 M [(CH₃)₄N]NO₃. From figure 6, the calculated pK_a of 43HP2CA in 100% water is 5.440.05, which is comparable with the picolinic acid dissociation constant found in literature for $I = 0.1$ M which is 5.21 [18,19].

In this case, the substituted picolinic acid has a higher basic character as was seen in the studies with dioxane/water 75% v/v mixture.
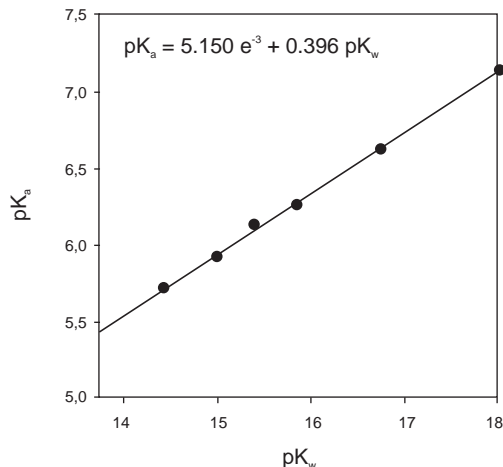

Figure 6. The pK_a of 43HP2CA is plotted versus pK_w of water in dioxane/water mixtures at $25^{\circ}C$.

Another way to determine the dissociation constant in water is from the relationship between the dissociation constant and the concentration of dioxane in water. The results were treated by regression analysis and the following relation is obtained (equation 14):

$$pK_a \ = \ 5.46 \ + \ 0.14 \ e^{0.029 \, (\% \, Dioxane)} \qquad (14)$$

where this pK_a value of 43HP2CA in water which is 5.46, in a good agreement with the value obtained in figure 6, that is 5.44.
For the pK_w of water, we obtained by equation (15)

$$pK_w \ = \ 13.71 \ + \ 0.41 \ e^{0.028(\% \, Dioxane)} \qquad (15)$$

where the ionization product of water determined is 13.71 under the conditions studied, which is in very good agreement with the value reported in literature of 13.74 by Uhlig et al [14].

Estimation of the stability constants of Zn^{2+}, and Cd^{2+} with 43HP2CA in water
Water and 1,4-dioxane are miscible in all proportions, and at $25^{\circ}C$, the dielectric constants, D, of pure water and pure dioxane are 78.2 and 2.2, respectively. The dielectric constant for different dioxane/water composition data over the entire composition range of dioxane/water mixtures has been reported by Jahagirdar et al [20] and Clemett et al [21]. The data could be fitted to the polynomial equation given by equation (16)

$$D \ = \ 78.41 \ - \ 93.36 \ w \ - \ 7.80 \ w^2 \ + \ 24.8 \ w^3 \qquad (16)$$

where D is the solution dielectric constant at 25°C, and w is the weight fraction of 1,4-dioxane in water. The electrostatic energy of an isolated pair of ions, of fixed charges and radii, separated from each other by a distance **a** in a medium of dielectric constants, D, is given by equation (17)[22]

$$ u = \frac{e_i^2}{2\,D\,r_i} + \frac{e_i^2}{2\,D\,r_j} + \frac{e_i\,e_j}{D\,a} \qquad (17) $$

There is a gain in energy, Äu, when the ions are removed to infinity from their closest distance. Äu is given by equation (18)

$$ \Delta u = u_{a=\infty} - u_{a=r_i + r_j} = - \frac{e_i\,e_j}{D\,(r_i + r_j)} \qquad (18) $$

By including an electrostatic component into the expression for the total energy required for ionizing a given molecule, the standard gain in chemical potential attending ionization may thus be written as equation (19)

$$ \Delta \mu^0 = \Delta \mu_n^0 - \frac{e_i\,e_j}{D\,(r_i + r_j)} \qquad (19) $$

where Äuₙ° represents all non-electrostatics contributions to the standard gain in chemical potential. Since Ä° = -kTlnK, it follows equation (20):

$$ \ln K = \ln K^0 + \frac{e_i\,e_j}{D\,(r_i + r_j)} \qquad (20) $$

Equation (20) can be rewritten as equation (21)[23]

$$ K = K^0 \exp\left\{ - \left[\frac{(z\,q)^2}{(2\,\langle b\rangle\,k\,T)} \right] \frac{1}{D} \right\} \qquad (21) $$

In this expression (21), K^0 is the equilibrium constant in pure solvent, q is the unit electrostatic charge, 4.802×10^{-10} e.s.u. , b is the mean ionic radius, $k = 1.3803 \times 10^{-16}$ erg/deg/K, and T is temperature.
The acid dissociation constant for the reagent, determined at different dioxane/water mixtures, is plotted against the reciprocal of the dielectric constant, as seen in figure 7;
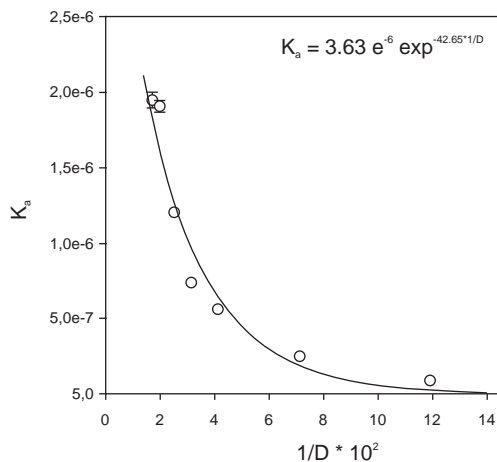
Figure 7. The dependence of pK_a of 43HP2CA on the dielectric constant in dioxane/water
mixtures. The curve is calculated using equation (22)

and is fitted by regression analysis to a 2-parameters exponential equation. Equation (22)
gives a good fit to the experimental data

$$y = A e^{-B\frac{1}{x}} \qquad (22)$$

$$K_a = 3.63 \cdot 10^{-6} \; e^{-42.65\frac{1}{D}} \qquad (22a)$$

The coefficient A gives the K_a of 43HP2CA in water. The second parameter B can be used for
the calculation of the ionic Stokes radii of the studied ligand in water, and a value of $r_{43HP2CA} =$
6.32 Å is obtained. The value seems to be reasonable as compared with to radii of picolinic
acid, $r_{pic} = 3.08$ Å [24], considering that the picolinic acid derivative studied has a lipophilic chain
of seven carbons attached to the picolinic acid ring.
This information makes it possible to calculate the stability constants for the complex
formation between Zn^{2+}, Cd^{2+}, and 43HP2CA in 100% water and ionic strenght 0.1 M
$[(CH_3)_4N]NO_3$. The Stokes radii for the metals are $r_{Zn2+} = r_{Cd2+} = 1.70$ Å [24], and values of the
complex formation are given in table 4 for comparing the value of the complex formation
constants of the two metal ions with picolinic acid in water [18,19] are also given.

Table 4. Estimates of the stability constants of Zn^{2+} and Cd^{2+} with 43HP2CA and picolinic
acid in water determined by extrapolation towards dioxane concentration

Metal	43HP2CA		Picolinic acid	
	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$
Zn^{2+}	5.53	10.23	5.23	9.56
Cd^{2+}	5.00	10.13	4.36	7.99

As seen, the reagent 43HP2CA forms stronger complexes with both Zn and Cd compared to the picolinic acid.

Determination of ΔH^0 for the formation of Zn^{2+}, Cd^{2+} and 43HP2CA complexes

Using equation (21) it is possible to establish a relation between the stability constants obtained potentiometrically and the constants determined by solvent extraction experiments at different temperatures obtained for the study of the extraction of metal ions from aqueous solutions [12].

The complex formation constants of Zn^{2+}, and Cd^{2+} with 43HP2CA in organic solution of Shellsol A (Trade Mark of Shell) were measured. This solvent has a dielectric constant, $D = 2.4$ [25]. Table 5 gives a list of the complex formation between the reagent 43HP2CA and the metal ions Cd and Zn at different temperatures determined from the distribution studies in Shellsol A and water calculated using equation (21).

Table 5. Stability constants of 43HP2CA with Zn^{2+}, and Cd^{2+} in water and in Shellsol A at different temperature

| | Aqueous solution | | | | SHELLSOL A (TM) | | | |
| | Zn²⁺ | | Cd²⁺ | | Zn²⁺ | | Cd²⁺ | |
T (°C)	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_1$	$\log \beta_1$	$\log \beta_1$
25 .	5.53	10.23	5.00	10.13	4.38	7.32	2.55	5.27
35	5.19	9.91	4.81	9.53	4.08	7.09	2.44	4.83
55	4.85	9.41	4.33	8.72	3.81	6.77	1.96	4.02
70	4.55	8.75	3.65	7.91	3.55	6.22	1.53	3.69
[a]ΔH^0_{calc}	-17	-31.3	-24.8	-40.67	-	-	-	-
[b]ΔH^0_{lit}	-16	-33	-	-	-	-	-	-

[a]ΔH^0_{calc} (kj/mol), calculated standard variation of enthalpy.
[b]ΔH^0_{lit} (kJ/mol), standard variation enthalpy published (I = 0.1M)
The two [b]ΔH^0_{lit} values of the zinc complex of 43HP2CA in aqueous solution have been taken from the zinc complex of picolinic acid at I = 1.0 M (NIST 46)

It is found that the formation constants for Zn^{2+} and Cd^{2+} with 43HP2CA decrease with the increase of the temperature, which indicates that the complex formation process of the studied ligand with both metal ions, Cd and Zn, is exothermic. The temperature-dependence of a stability constant is obtained from the thermodynamic second-law equation (23)

$$\Delta G_n^0 = \Delta H_n^0 - T \Delta S_n^0 = - R T \ln \beta_n \qquad (23)$$

where $\ddot{A}G^0_n$, $\ddot{A}H^0_n$ and $\ddot{A}S^0_n$ are the standard changes in free energy, enthalpy and entropy accompanying the complex formation equations (6,7) for which β_n is the equilibrium constant. It follows that equation (24),

$$\ln \frac{\beta_{n'}}{\beta_{n''}} = - \frac{\Delta H_n^0}{R} (1/T' - 1/T'') \qquad (24)$$

where $\beta_{n'}$ and $\beta_{n''}$ are the values of the formation constant of the complexes between the reagents and metal ions at temperatures T' and T'' in a range through which the standard variation of enthalpy is constant. As the logarithm of the constants vary linearly with the temperature in all the cases, as seen figure 8, it can be assumed that $\ddot{A}H^0\beta_n$ is constant in the range of temperature studied.
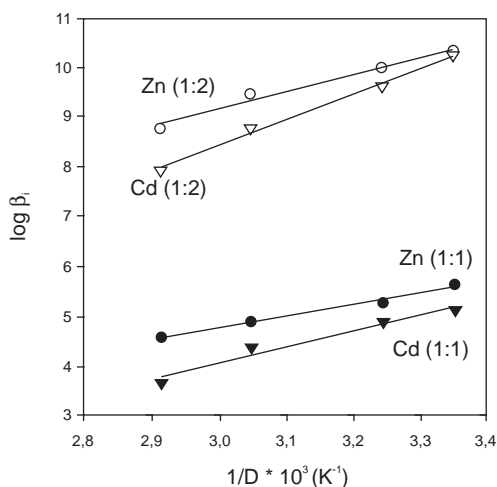

Figure 8. A gradient plot of the logarithm of the formation constant plotted against the reciprocal of the temperature (K^{-1}) . o Zn(43HP2CA)$_2$; ∇ Cd(43HP2CA)$_2$; • Zn(43HP2CA); ▼ Cd(43HP2CA)

The results are given in table 5, where the determined values are compared with the ones reported in the literature [18,19]. For the system Zn-43HP2CA, the values of the thermodynamic quantities calculated are very similar with the ones reported by Martell et al [18,19] for the Zn-picolinic acid. On the other hand, there are no published data for the Cd-picolinic acid and Cd-43HP2CA systems.

CONCLUSIONS

- We reported the preparation of two water-insoluble picolinic acid derivatives by introduction of a lipophilic chain of different lengths and in different positions.
- The acidic character of the ligands decreases with the lenghth of the substituted alkyl chain, and is in the order picolinic acid 63PP2CA 43HP2CA.
- Substitution of H by a lipophilic chain seems to affect the complexation of the ligands to metal ions, whereby the ligand 43HP2CA forms stronger complexes than picolinic acid. However the reagent 63PP2CA forms weaker complexes probably due to the position of the hydrocarbon chain causing steric hindrance in the interaction between the metal ion and the N of the pyridine ring. On the other hand, the complexation of either ligands with the metal ions follows the Irving-Williams order.
- The value of pK_a of 43HP2CA increases with the increase of the dioxane concentration, and follows the same trend of the pK_w in the dioxane-water mixture.
- The values of formation constants of different complexes between 43HP2CA with Zn^{2+}, and Cd^{2+} in water could be obtained by extrapolation of the experimental data of different dioxane/water mixtures systems. This allows us to estimate the formation constants at different temperatures from the established correlation of the potentiometric and solvent extraction data, obtaining in this way a thermodynamic set of data for the system studied.

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