1510 *J. Chem. Eng. Data* **2002,** *47,* 1510−1513

Solubility of Alkali and Alkali Earth Salts of Dihydrogen Ethylenediaminetetraacetate in Aqueous Solutions

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The solid metal−EDTA compounds $K_2H_2Y{\cdot}2H_2O$, $MgH_2Y{\cdot}6H_2O$, $CaH_2Y{\cdot}2H_2O$, $SrH_2Y{\cdot}2H_2O$, and $BaH_2Y{\cdot}3H_2O$ (H_2Y^{2-} is dihydrogen ethylenediaminetetraacetate anion) prepared from aqueous media were characterized by elemental analysis, IR spectrometry, and thermogravimetry (TG). The solubilities of these EDTA salts and reagent grade disodium salt ($Na_2H_2Y{\cdot}2H_2O$) in water at 25.0 °C were determined by potentiometric titrations with NaOH using a combined glass electrode. The infrared spectra showed that metal ions do not form chelates with EDTA in the studied salts.

Introduction

The metal-ion complexes of ethylenediaminetetraacetic acid (EDTA, H_4Y) present widespread applications in analysis, industry, foodstuffs, pharmacy, and medicine.[1−4] A number of these applications are described in reviews and reports.[5−7] The structure and bonding character of solid compounds of EDTA have been extensively studied, and these data are well summarized in reviews.[8,9] However, there are few measurements on the solubility of EDTA compounds.[10−13]

Astakhov *et al.*[10] prepared disodium salts of inner complexes of EDTA with Ca^{2+}, Sr^{2+}, and Ba^{2+} and determined their solubility. Vorob'ev *et al.*[11] determined the solubility for dicalcium, dibarium, distrontium, and disodium complex salts of EDTA in addition to those determined by Astakhov. The solubilities of $Mg(H_2Y){\cdot}6H_2O$[12] and Ag_4Y (Y^{4-} is ethylenediaminetetraacetate anion) in water have also been determined.[13]

There is a large use of strong chelating agents such as EDTA in industry.[14,15] Because of the slow biodegradation process of these substances,[16] the solubility data of metal−EDTA salts can be used for optimization of EDTA recovery from industrial process wastewater.[17]

In the present work salts of generic formula $M_{z/2}H_2Y{\cdot}xH_2O$ ($M^{z+} = Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}$, or Ba^{2+} and $x = 2, 3, 4$, or 6) have been prepared. After characterization by elemental analysis, infrared analysis (IR), and thermogravimetry (TG), their solubilities in water at 25.0 °C were determined by potentiometric titrations with standard NaOH.

Experimental Section

The solutions were prepared with distilled and deionized water. The reagents were of analytical grade (PA) and used as received. EDTA in acidic form from Synth (Brazil), NaOH, KOH, $MgCl_2$, $BaCO_3$, $CaCl_2$ from Mallinckrodt (USA), and $SrCO_3$ from Riedel-De Haen (Germany) were used in the preparation of the salts.

Preparation of the Salts. $MgH_2Y{\cdot}6H_2O$ and $CaH_2Y{\cdot}2H_2O$. Stoichiometric aqueous solution volumes of metal chloride and H_2Y^{2-} from $Na_2H_2Y{\cdot}2H_2O$ at 0.1 mol L^{-1} were mixed and stirred for 1 h for complete precipitation. The $MgH_2Y{\cdot}6H_2O$ coarse crystals formed were separated immediately by filtration in a syntherized glass funnel under vacuum and washed with small amounts of cold water. Since $CaH_2Y{\cdot}2H_2O$ is much more soluble and precipitation is a slower process, the $CaH_2Y{\cdot}2H_2O$ crystals were filtered off after a week.

$BaH_2Y{\cdot}3H_2O$ and $SrH_2Y{\cdot}4H_2O$. In a 250 mL beaker, 15.0 mmol of metal carbonate, 15.0 mmol of EDTA acid (H_4Y), and approximately 100 mL of water were mixed. After evaporation of the solvent, the solid was completely dried in a vacuum oven. This methodology was used instead of the precipitation of $BaH_2Y{\cdot}3H_2O$ from a mixture of $BaCl_2$ and $Na_2H_2Y{\cdot}2H_2O$ aqueous solutions, because a gel is formed which was difficult to separate from solution by filtration in a syntherized glass funnel under vacuum. In the case of the strontium salt, the solubility is so high that solvent evaporation was found to be the best method of salt isolation.

$K_2H_2Y{\cdot}2H_2O$. In a 250 mL beaker, 50.0 mL of 0.462 mol L^{-1} KOH standard solution (23.1 mmol of KOH) and 3.144 g of EDTA acid (11.55 mol of H_4Y) were mixed. The solvent was then evaporated and a solid compound was obtained.

All the compounds prepared were dried after synthesis in a vacuum oven at 50 °C for at least 24 h. Apparently all of them were amorphous.

Characterization of the Salts. The elemental (C, H, N) analyses were carried out in an EA-1108 CHNS-O Fisons Instrument.

The infrared spectra were obtained using KBr pellets (4000−200 cm^{-1}) in a MB-102 BOMEN Hartmann & Braun spectrometer equipped with an Arid-Zone detector. The TG curves were recorded using a TGA-2050 thermogravimetric module (TA Instruments), coupled to a TA-2000 thermal analyzer (TA Instruments). A sample of about 10 mg of each EDTA salt was heated in an open alumina crucible at a rate of 10 °C min^{-1} under nitrogen flow (90 mL min^{-1}) at atmospheric pressure.

To characterize the magnesium, calcium, and barium contents in their respective salts, a sample (approximately 0.10 g for $MgH_2Y{\cdot}6H_2O$, 0.40 g for $CaH_2Y{\cdot}2H_2O$, 0.46 g for $SrH_2Y{\cdot}2H_2O$, and 0.24 g for $BaH_2Y{\cdot}3H_2O$) was heated at 900 °C (or 600 °C for $MgH_2Y{\cdot}6H_2O$) for at least 1.5 h.

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10.1021/je025550m CCC: $22.00

Table 1. Elemental Analysis of the Metal−EDTA Compounds and TG Data for the Dehydration Process

	elemental analysis, found (calc)/%				TG data	
compound	C	H	N	M	mass loss (calc)/% xH_2O^a	Δt^b/°C
$Na_2H_2Y{\cdot}2H_2O$	32.3 (32.3)	5.05 (4.87)	7.70 (7.53)	*c*	9.50 (9.68)	89−238
$K_2H_2Y{\cdot}2H_2O$	29.9 (29.7)	4.48 (4.49)	7.30 (6.93)	*c*	8.96 (8.91)	30−214
$MgH_2Y{\cdot}6H_2O$	28.2 (28.4)	6.00 (6.20)	6.00 (6.60)	5.60 (5.70)	26.0 (25.6)	94−169
$CaH_2Y{\cdot}2H_2O$	32.7 (32.8)	5.33 (5.50)	8.34 (7.65)	10.5 (10.9)	10.2 (9.80)	25−188
$SrH_2Y{\cdot}2H_2O$	29.1 (29.0)	4.54 (4.38)	6.80 (6.77)	20.4 (21.2)	8.68 (8.71)	26−124
$BaH_2Y{\cdot}3H_2O$	25.0 (24.9)	4.27 (4.19)	5.64 (5.82)	29.0 (28.5)	11.0 (11.2)	35−203

[a] x = 2, 3, or 6. [b] Dehydration temperature interval related to the proposed mass loss. [c] Not determined.

Then the $MgH_2Y{\cdot}6H_2O$ residue was dissolved with HCl (50% v/v), transferred quantitatively to a beaker, and diluted with water. The pH of the resulting solution was adjusted to 5.0 with 0.1 mol L^{-1} NaOH and then buffered at pH 10 with NH_3/NH_4Cl buffer. The titration of the magnesium ions with the disodium salt of EDTA in the presence of Eriochrome Black T was performed at 60 °C according to the procedure proposed by Flaschka *et al.*[2]

The $CaH_2Y{\cdot}2H_2O$ and $BaH_2Y{\cdot}3H_2O$ residues were dissolved with HCl (50% v/v), and the resulting solutions were transferred quantitatively to a 100 mL volumetric flask and diluted to the mark with water. The pH of an aliquot of the resulting solutions was adjusted to 12 (1.0 mol L^{-1} NaOH). The titration of the metallic ions with the disodium salt of EDTA was carried out in the presence of a methylthymol blue and KNO_3 mixture for Ba^{2+} (ref 18) or calcein for Ca^{2+} (ref 19) indicator.

The $SrH_2Y{\cdot}2H_2O$ residue was dissolved with 5.0 mL of 10 mmol L^{-1} HCl and water. The strontium ion in the resulting solution was determined by a gravimetric procedure using sodium dihydrogenphosphate.[18]

Solubility Determinations. The solubility of the salts in water at (25.0 ± 0.1) °C was determined by treating a solid sample (approximately 5.2 g for $Na_2H_2Y{\cdot}2H_2O$, 8.0 g for $K_2H_2Y{\cdot}2H_2O$, 0.2 g for $MgH_2Y{\cdot}6H_2O$, 1.0 g for $CaH_2Y{\cdot}2H_2O$, 3.0 g for $SrH_2Y{\cdot}2H_2O$, and 7.0 g for $BaH_2Y{\cdot}3H_2O$) with a volume of water (50.0 mL for $Na_2H_2Y{\cdot}2H_2O$, 10.0 mL for $K_2H_2Y{\cdot}2H_2O$, 100 mL for $MgH_2Y{\cdot}6H_2O$, 50.0 mL for $CaH_2Y{\cdot}2H_2O$, 15.0 mL for $SrH_2Y{\cdot}2H_2O$, and 50.0 for $BaH_2Y{\cdot}3H_2O$) under efficient magnetic stirring for at least 2 h in a 100 mL capacity glass cell with a external jacket for controlling the temperature. The excess of solid was separated by filtration, and an aliquot of saturated solution of the salt (14.93 mL for $Na_2H_2Y{\cdot}2H_2O$, 0.500 mL for $K_2H_2Y{\cdot}2H_2O$, 50.02 mL for $MgH_2Y{\cdot}6H_2O$, 5.00 mL for $CaH_2Y{\cdot}2H_2O$, 0.750 mL for $SrH_2Y{\cdot}2H_2O$, and 1.00 mL for $BaH_2Y{\cdot}3H_2O$) was transferred with the help of a previously calibrated pipet and then titrated with NaOH standard solution using a previously calibrated combined glass electrode.

Potentiometric titrations were performed with a Corning 430 pH meter coupled to a Digimed DME-CV1 combined glass electrode. A hydrogenphthalate (pH = 4.00) and a phosphate buffer (pH = 7.00) were used to calibrate the glass electrode.

Results and Discussion

Complexes' Characterization. The analytical data for the metal−EDTA compounds are listed in Table 1. These results agree with the formulas proposed in the Table 1. According to the carbon content results (experimental/calculated × 100%) it is possible to estimate the purity of the compounds as follows: Na, 100; K, 101; Mg, 99.3; Ca, 99.7; Sr, 100; Ba, 100%. Carbon content was chosen, since it is the major component in the formulas and thus presents better results in elemental analysis.

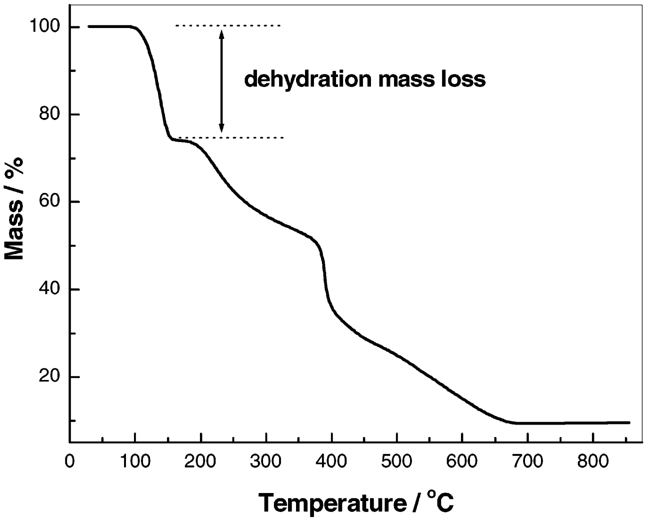

Figure 1. Thermogravimetric curve of $MgH_2Y{\cdot}6H_2O$. Sample mass 10 mg, in an open alumina sample holder; heating rate of 10 °C min^{-1} under nitrogen flow (90 mL min^{-1}) at atmospheric pressure.

The degrees of hydration for the compounds estimated by thermogravimetry are in agreement with the elemental analysis data. An example of a TG curve ($MgH_2Y{\cdot}6H_2O$) is presented in Figure 1, the mass losses attributed to water were related with the mole weight proposed.

The mass losses and temperature intervals for the dehydration events in these compounds are presented in Table 1. According to the TG curves, the dehydration process takes place in a single step for $Na_2H_2Y{\cdot}2H_2O$, $K_2H_2Y{\cdot}2H_2O$, and $MgH_2Y{\cdot}6H_2O$ while more complex processes are suggested in TG curves of $CaH_2Y{\cdot}2H_2O$, $SrH_2Y{\cdot}2H_2O$, and $BaH_2Y{\cdot}3H_2O$. The low temperature for the starting of the dehydration process suggests that the water molecules are weakly bounded in these compounds.

The infrared spectra bands for some characteristic groups of the metal−EDTA salts are listed in Table 2. The vibration frequencies of interest are the characteristic frequencies of the carboxyl group[20,21] and the C−N antisymmetrical and symmetrical stretching.[21] The frequency of the band due to COO group vibrations indicates the nature of its bond with the metal (covalent or ionic)[8,22,23] and/or its protonation.[22]

The interpretation of metallic ion−EDTA salts' infrared data has shown the presence of un-ionized and uncoordinated carboxyl groups in the whole series of the salts investigated. The peaks of the protonated carboxyl group at frequencies below 1700 cm^{-1} suggest that an internal hydrogen bonding is formed.[21,24]

The strongest and the most characteristic absorption band for the carboxyl group (COO^-) due to its antisymmetrical vibration is present in the spectra of all metal ion−EDTA salts here prepared. The occurrence of this band at a frequency near 1634 cm^{-1} for sodium, potassium, and

Table 2. Infrared Data (wavenumber/cm^{-1}) for the Salts $M_{2/z}H_2Y\cdot xH_2O$[a]

	CH_2COOH group						amminic group		carboxylate group	
compound	$\nu_{C=O}$ (s)	δ_{OH} (m)	ν_{C-O} (m)	b (w)	ν_{C-H} (s)	$\delta_{OH}{}^{c}$ (m)	$\nu_{s\ C-N}$ (m)	$\nu_{a\ C-N}$ (w)	$\nu_{a\ COO^-}$ (s)	$\nu_{s\ COO^-}$ (m)
$Na_2H_2Y\cdot 2H_2O$	1675	1476	1316	1224	3027	958	817	1055	1628	1395
$K_2H_2Y\cdot 2H_2O$	1673	1481	1334	1219	3009	962	810	1057	1631	1397
$MgH_2Y\cdot 6H_2O$	1682[d]	1444	1322	1222	3066	965	910	1055	1614	1413
$CaH_2Y\cdot 2H_2O$	1677[d]	1449	1318	1214	3017	960	861	1052	1638	1414
$SrH_2Y\cdot 2H_2O$	1644[d]	1440	1328	1214	3010	915	861	1090	1613	1405
$BaH_2Y\cdot 3H_2O$	1619	1443[d]	1322	1204	3012	958	871	1070	1571[d]	1413

[a] s, strong; m, medium; w, weak; ν, stretching; δ, deformation. Subscripts: s, symmetrical; a, antisymmetrical. [b] Absorption at 1250−1210 cm^{-1} attributed tentatively to the $-CH_2COOH$ group.[21,23,26] [c] Out of plane. [d] These bands appear as a shoulder.

calcium salts is related to the fact that the ionized COO^- is not coordinated to any metal ions.[24] The absorption near 1634 cm^{-1} has been assigned to the interaction between ionized and uncoordinated COO^- groups and un-ionized COO groups by internal hydrogen bonding.[24]

Since the carboxyl group (COO^-) antisymmetrical vibration in tetrasodium and tetrapotassium salts and the disodium salt of the calcium complex occurs at lower frequencies than those described in the literature[25] ($Na_4Y\cdot 0.5H_2O$, 1600 cm^{-1}; K_4Y, 1595 cm^{-1}; $Na_2CaY\cdot 3.5H_2O$, 1605 cm^{-1}), the assignment of this band in those salts to the interaction between the metal ion and the ionized COO^- group cannot be established, which also confirms the presence of internal hydrogen bonding.

The magnesium, strontium, and barium salts present metal ion−ionized carboxyl group interactions with primarily ionic character instead of interaction between un-ionized and ionized COO groups. This statement is established by experimental evidence. The peak due to the antisymmetrical stretching vibration of the COO^- group for $MgH_2Y\cdot 6H_2O$, $SrH_2Y\cdot 2H_2O$, and $BaH_2Y\cdot 3H_2O$ occurs at the characteristic range between 1615 and 1590 cm^{-1} (refs 8, 22, and 26) for metal−carboxyl bonding with predominant ionic character. Besides, the difference (Δ) in frequency between the peak for the symmetrical vibration ($\nu_{s\ COO^-}$) and the peak for the antisymmetrical vibration ($\nu_{ass\ COO^-}$) of the group COO^- also indicates the primarily ionic character of this bonding. According to Sawyer and McKinnie,[27] if Δ is lower than 225 cm^{-1}, the bonding is primarily ionic, as has been found for magnesium, strontium, and barium compounds ($\Delta = 201$, 208, and 159 cm^{-1}, respectively).

The C−H stretching vibration for all salts in the 3065−3009 cm^{-1} range indicates the absence of chelate ring formation. The formation of a chelate ring is accompanied by absorption of a C−H vibration[8,25,27,28] at (3000 to 2900) cm^{-1}.

Solubility Determinations. The experimental solubility has been determined from measurement of the concentration of dihydrogen ethylenediaminetetraacetate anion, H_2Y^{2-}, present in the saturated solution.

The titration of H_2Y^{2-} species involves a one-proton neutralization reaction (for sodium and potassium salts) or a two-proton neutralization reaction with simultaneous formation of a metal ion−EDTA complex for the other salts. These processes are represented by the following equations, respectively:

$$H_2Y^{2-} + OH^- \rightarrow HY^{3-} + H_2O \qquad (1)$$

$$M^{2+} + H_2Y^{2-} + 2OH^- \rightarrow [MY]^{2-} + 2H_2O \qquad (2)$$

in which M^{2+} is an alkali earth metal ion.

Table 3. Solubility and pH of Saturated Solutions of Investigated EDTA Salts at 25.0 °C

	solubility[a]				r_M
salt	mmol L^{-1}	pH_{satur}	pH_{calc}	log K_{ML}	Å
$Na_2H_2Y\cdot 2H_2O$	264.2 ± 5.5	4.38	4.70	1.72	1.02[b]
$K_2H_2Y\cdot 2H_2O$	2026 ± 6	4.73	4.74	2.76	1.38[b]
$MgH_2Y\cdot 6H_2O$	0.8049 ± 0.010	4.46	4.81	9.13	0.72[b]
$CaH_2Y\cdot 2H_2O$	7.027 ± 0.008	3.63	3.90	10.97	1.00[b,c]
$SrH_2Y\cdot 2H_2O$	156.1 ± 0.1	3.95	4.13	8.74	1.25[b]
$BaH_2Y\cdot 3H_2O$	168.1 ± 6.2	4.23	4.36	7.86	1.35[c]

[a] Mean of two determinations ± standard deviation. [b] According to ref 33. [c] Reference 31.

The experimental solubility results and the pH values of saturated solutions of the EDTA salts at (25.0 ± 0.1) °C are presented in Table 3, as the mean of two determinations with the respective standard deviations. The calculated pH values, using thermodynamic formation constants without any correction due to ionic strength of the medium, are quite close to the experimental ones.

Careful determination of solubility was previously described only for $MgH_2Y\cdot 6H_2O$,[12] and the authors found 1.14 mmol L^{-1} (at room temperature). Sodium and potassium salts are usually described as “soluble” in the literature, but no solubility data are presented.

Due to the complexity of the equilibrium involving EDTA species in sodium and potassium salt solutions, we can consider the solubilities determined as estimated values, with good approximation, since they were determined at the first equivalence point at which the reaction can be not totally quantitative. Theoretical calculations point to 90% completeness at such conditions. Better results could be obtained at the second equivalence point, which should appear at pH > 11; however, at such pH the alkaline error of the glass electrode could lead us to higher errors. Therefore, we decided to present the values at the first equivalence point, considering them as estimated values.

To establish relationships between the solubility and the properties of metal ions, the Mitchell approach,[29] which correlates trends of properties investigated with ones that vary periodically, was used. To visualize the relationships, log *S*’s (solubility), log *K*’s (stability constant for EDTA species Y^{4-} and HY^{3-}),[30] and $1/r$ reciprocals of the Pauling ionic radii[31] and the Glueckauf hydrated ionic radii[32] were plotted against atomic number for alkali earth cations (Figure 2).

For this group, log *S* increases with increasing atomic number of metallic ion, correlating well with the increase of the reciprocal of the Glueckauf hydrated ionic radii.

The correlation of log *S* with log *K* for the EDTA species HY^{3-} is less satisfactory, especially considering the magnesium complex behavior.

A linear relationship was found for solubility and ionic radii in aqueous solutions[33] (Table 3) for alkali earth ions according to

$$(\log S)^3 = 12.2_6 - 21.7_5(1/r_M{}^2) \qquad (3)$$

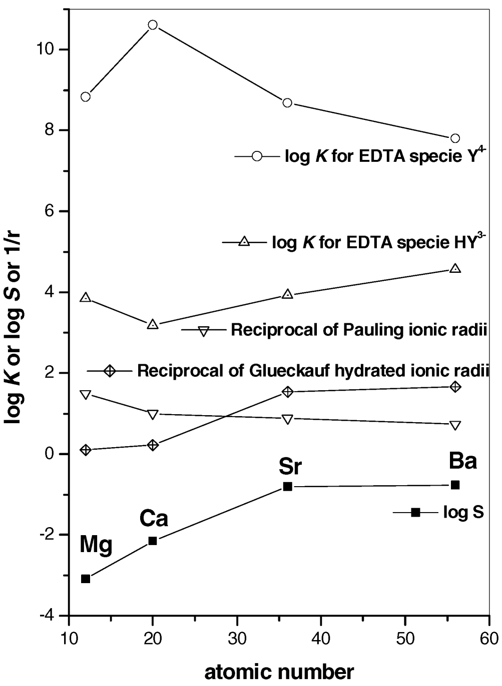

Figure 2. Plots of log S (solubility) for EDTA salts, log K (stability complex constant) for EDTA complexes, reciprocals of the Pauling ionic radii, and reciprocals of the Glueckauf hydrated ionic radii ($1/r$) vs atomic number for alkali earth metals.

with the correlation coefficient and the standard deviation obtained of -0.998_2 and 1.01_9, respectively ($n = 4$: Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}).

The relationship found by correlating the solubility (S), complex formation constants[30] (K_{ML}) for EDTA metal complexes, and pH is expressed by the following equation:

$$\log S + 3.6\mathrm{pH}_{\mathrm{satur}} = 23.3_4 - 1.13_4 \log K_{ML} \qquad (4)$$

in which S values are expressed in mol L^{-1}. The correlation coefficient and the standard deviation obtained for the linear fit were -0.999_7 and 0.043_5.The saturation pH depends only on the chemical equilibria of the aqueous phase, in the region where H_2Y^{2-} is the predominant EDTA species.

Conclusions

The solubility values of $Na_2H_2Y{\cdot}2H_2O$, $K_2H_2Y{\cdot}2H_2O$, $MgH_2Y{\cdot}6H_2O$, $CaH_2Y{\cdot}2H_2O$, $SrH_2Y{\cdot}2H_2O$, and $BaH_2Y{\cdot}3H_2O$ (H_2Y^{2-} is dihydrogen ethylenediaminetetraacetate anion) determined for investigated salts of EDTA in its dineutralized form (H_2Y^{2-}) indicate that the solubility decreases with the mole weight of the metal ion in the alkali and alkali earth families.

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Received for review May 20, 2002. Accepted August 15, 2002. The authors are greatly indebted to Brazilian agencies Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for the financial support and scholarships to A.R.F. and L.R.P., respectively.

JE025550M