J. Chem. Eng. Data **2005,** *50,* 1833−1836

Solubility of Ca, Cu, Ni, Pb, and Zn Azelates in Pure Water at 20 °C

François Zimmermann,[†,‡] Eric Meux,*,[†] Nicolas Oget,[‡] Jean-Marie Lecuire,[†] and Jean-Luc Mieloszynski[‡]

Laboratoire d'Electrochimie des Matériaux, CNRS UMR 7555, and Laboratoire de Chimie et Applications, EA 3471, Université de Metz, 1 Boulevard Arago, CP 87811, 57078 Metz Cedex 3 France

---

This paper reports the solubility and solubility products at 20 °C of five metallic azelates (calcium, copper, nickel, lead, and zinc) that were synthesized and their stoichiometry controlled. The values of pK_{SP} obtained for $Ca(CH_2)_7(COO)_2$, $Cu(CH_2)_7(COO)_2$, $Ni(CH_2)_7(COO)_2$, $Pb(CH_2)_7(COO)_2$, and $Zn(CH_2)_7(COO)_2$, are respectively 5.59, 8.05, 3.97, 9.60, and 5.82. Using MINEQL+ software, conditional solubility curve of each azelate was represented. By comparing the curves of azelates, it is possible to predict the selective precipitation of metallic cations in solution. From a theoretical point of view, sodium azelate is able to precipitate selectively Pb^{2+} from $Pb^{2+} + Ca^{2+}$ or $Pb^{2+} + Ni^{2+}$ mixtures and Cu^{2+} from $Cu^{2+} + Ni^{2+}$ mixtures.

Introduction

Metallic carboxylates have considerable commercial importance. They find applications in areas such as detergents, driers in paints or inks, components of lubricating greases, stabilizers for plastics, fungicides, catalysts, waterproofing agents, fuel additive,[1,2] and recently as corrosion inhibitor.[3−6] Carboxylates are also used as collectors in extraction processes by flotation[7−9] and have shown the possibility to remove lead from aqueous solutions with sodium caprate.[10] Some carboxylic acids and sodium carboxylates find applications in separation processes by solvent extraction (Ni + Ca mixtures)[11] and recovery processes by precipitation.[12]

We have shown in a previous work[13] the possibility of using carboxylates for performing selective precipitation of metallic cations contained in a given mixture. In this paper, we focus our attention on the interaction between azelaic acid (or nonanedioic acid) and divalent metallic cations. This dicarboxylic acid, mainly produced by oxidation scission of fatty acid contained in vegetable oils,[14−18] has various industrial uses: plasticizers, lubricants, cosmetics, painting materials.[19,20]

There are few thermodynamic data concerning metallic azelates in the literature. Before studying selective precipitation of metallic cations, it was necessary to determine the solubility of these compounds in order to predict the feasibility of separation.

The aim of this work was to measure the solubility of five metallic azelates (calcium, copper, nickel, lead, and zinc). First, metallic azelates were prepared and their stoichiometry controlled using pH titration and chemical analysis. From these experimental data, the solubility product and the conditional solubility of each compound were calculated. Finally, the theoretical feasibility of selective precipitation for each binary mixture of cations was discussed.

Experimental Section

Reagent and Solutions. All reagents and solutions were prepared from Fisher Labosi or Acros Organics analytical grade chemicals with a stated purity of at least 99 %. The conductivity of double-ionized water used never exceeded 0.1 $\mu S \cdot cm^{-1}$.

Synthesis of Metallic Azelates. The precipitation reagent, a 0.1 $mol \cdot L^{-1}$ sodium azelate solution (noted Na_2Az), was prepared by neutralization of azelaic acid $(CH_2)_7(COOH)_2$ with sodium hydroxide. Metallic cation solutions, close to 0.1 $mol \cdot L^{-1}$, were prepared from sulfate, nitrate, or chloride salts. The metallic azelates were prepared by adding sodium azelate to metallic cation solutions. Throughout the experiments, the pulp was mixed for 1 h with a magnetic stirrer at 500 rpm. The precipitates were separated by filtration, washed thoroughly with pure water, and dried at 105 °C.

Stoichiometry. The stoichiometry of copper, zinc, calcium, and nickel azelates was verified by pH measurement during the dissolution of each compound. A known mass of solid was introduced in a beaker containing pure water. The resulting pulp was titrated with $5.25 \cdot 10^{-2}$ $mol \cdot L^{-1}$ aqueous H_2SO_4. For calcium azelate, $1.20 \cdot 10^{-1}$ $mol \cdot L^{-1}$ hydrochloric acid HCl was used to avoid precipitation of calcium sulfate. The experiments were carried out with a combined pH electrode (Radiometer Analytical XC100) using a pH meter (Meterlab PHM 210). Two ISO standard buffers at pH 4 and pH 10 were used for calibration. The sodium azelate was added with a buret Tacussel EBX 3. Buret and pH meter were monitored by a personal computer (PC).

The reaction between metallic azelates and protons can be written as follows:

$$(CH_2)_7(COO)_2M(s) + 2H^+ \leftrightarrow M^{2+} + (CH_2)_7(COOH)_2(s) \quad (1)$$

The equivalence point allows the determination of the mole number of azelate contained in the precipitate. At the end of the titration, the solution was recovered in a volumetric flask, and concentrations of dissolved metallic cations were measured by atomic absorption spectrometry (AAS) using a spectrometer Unicam 969 SOLAAR. The molar ratio $n_{M^{2+}}/n_{Az^{2-}}$ leads to the stoichiometry of the compound.

Titration of lead azelate was not possible because of the low solubility of this compound. Consequently, the stoichiometry of this compound was determined by pH measurement during lead precipitation.

---

* To whom correspondence should be addressed. Tel.: +33-3-87-31-54-38. Fax: +33-3-87-31-54-60. E-mail: meux@sciences.univ-metz.fr.

[†] Laboratoire d'Electrochimie des Matériaux.

[‡] Laboratoire de Chimie et Applications.

10.1021/je050008u CCC: $30.25

Solubility Study. The solubility measurements were performed with freshly precipitated metallic azelates. To obtain a saturated solution, a sufficient quantity of azelate was added to 50 cm^3 of pure water. The solution was covered with a double layer of Parafilm to prevent absorption of CO_2 from the atmosphere. The pulp was maintained at 20 (± 1) °C in a thermostated chamber and mixed with a magnetic stirrer at 500 rpm throughout the experiments.

For each compound, the time required to reach the equilibrium was determined by following the conductance using a Radiometer Analytical XE100 cell and a Radiometer Analytical CDM 210 conductivity meter. At the end of the experiment, the pH was measured, and the solution was filtered through a Millipore filter (0.22 μm, White GSWP, 47 mm) for AAS analysis. To determine uncertainty of measurement,[21,22] each experiment was replicated five times.

Theoretical Metal Speciation

The reaction corresponding to the solubility equilibrium of divalent metallic azelates in water is

$$(CH_2)_7(COO)_2M(s) \leftrightarrow (CH_2)_7(COO)_2{}^{2-} + M^{2+} \qquad (2)$$

The solubility product constant, noted K_{sp}, is given by

$$K_{sp} = \alpha(M^{2+})\cdot\alpha((CH_2)_7(COO)_2{}^{2-}) \qquad (3)$$

In pure water, in the case of slightly soluble compounds, we assume that activities and concentrations are equivalent. The solubility product constant is then

$$K_{sp} = [M^{2+}]\cdot[(CH_2)_7(COO)_2{}^{2-}] \qquad (4)$$

For a given pH value, the metallic cation can exist in different forms such as MOH^+, $M(OH)_2$, or $M(OH)_x{}^{(x-2)-}$, and the azelate anion reacts with H^+ leading to $(CH_2)_7(COOH)(COO^-)$ or $(CH_2)_7(COOH)_2$. In these conditions, K_{sp} is replaced by the conditional solubility product noted K_{sp}^{cond}. In our case, K_{sp}^{cond} will be written as follows:

$$K_{sp}^{cond} = [M]\cdot[Az] \qquad (5)$$

where [M] represents the total concentration of different species of the metal and [Az] represents the sum of the concentrations of the different acido-basic forms of azelaic acid.

According to Ringbom,[23] the conditional solubility product K_{sp}^{cond} can be calculated with the following equation:

$$K_{sp}^{cond} = K_{sp}\cdot\alpha_M\cdot\alpha_{Az} \qquad (6)$$

The side reaction coefficients α_M and α_{Az} are expressed in the form:

$$\alpha_M = \frac{[M]}{[M^{2+}]} = 1 + \frac{[MOH^+]}{[M^{2+}]} + \frac{[M(OH)_2]}{[M^{2+}]} + ... + \frac{[M(OH)_x{}^{(x-2)-}]}{[M^{2+}]} \qquad (7)$$

$$\alpha_{Az} = \frac{[Az]}{[(CH_2)_7(COO)_2{}^{2-}]} = 1 + \frac{[(CH_2)_7(COOH)(COO)^-]}{[(CH_2)_7(COO)_2{}^{2-}]} + \frac{[(CH_2)_7(COOH)_2]}{[(CH_2)_7(COO)_2{}^{2-}]} \qquad (8)$$

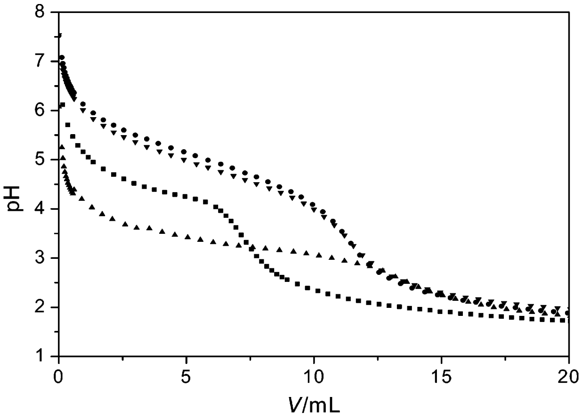

Figure 1. pH metric following of dissolution of zinc, nickel, copper, and calcium azelate by various volume of H_2SO_4. ▲, CuAz; ●, CaAz; ▼, NiAz; ■, ZnAz.

By substituting in both these expressions the acidity constants[24] of M^{2+} and $(CH_2)_7(COOH)_2$ according to the reactions below:

$$\begin{gathered} M^{2+} + H_2O \leftrightarrow MOH^+ + H^+ \quad K_{a1} \\ MOH^+ + H_2O \leftrightarrow M(OH)_2 + H^+ \quad K_{a2} \\ \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \\ MOH_{n-1}{}^{(n-3)-} + H_2O \leftrightarrow M(OH)_n{}^{(n-2)-} + H^+ \quad K_{an} \end{gathered} \qquad (9)$$

$$(CH_2)_7(COOH)_2 \leftrightarrow (CH_2)_7(COOH)(COO)^- + H^+ \qquad K_{a1} = 10^{-4.55}$$

$$(CH_2)_7(COOH)(COO)^- \leftrightarrow (CH_2)_7(COO)_2{}^{2-} + H^+ \qquad K_{a2} = 10^{-5.42} \qquad (10)$$

we obtain

$$\alpha_M = 1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}\cdot K_{a2}}{[H^+]^2} + ... + \frac{K_{a1}\cdot K_{a2} ... K_{an}}{[H^+]^n} \qquad (11)$$

and

$$\alpha_{Az} = 1 + \frac{[H^+]}{10^{-5.42}} + \frac{[H^+]^2}{10^{-9.42}} \qquad (12)$$

Results and Discussion

Stoichiometry. The pH measured during the dissolution of calcium, copper, nickel, and zinc azelates was presented in Figure 1. The equivalence point of each curve allows to determine the mole number contained in the precipitate. Metal concentration measured by AAS leads to the mole number of cation in the compound. These values were used to calculate the molar ratio $n_{M^{2+}}/n_{Az^{2+}}$ presented in Table 1.

The pH titration of the precipitation of lead is shown in Figure 2. The precipitation was performed by adding $9.7\cdot10^{-2}$ mol·L^{-1} sodium azelate to 6 mL of $1.46\cdot10^{-1}$ mol·L^{-1} $Pb(NO_3)_2$ slightly acidified with HNO_3. The difference between the second equivalence point (corresponding to the formation of lead azelate) and the first one (relative to the neutralization of free acidity of the solution) was equal to 9.05 mL. In these conditions, the value of the $n_{Pb^{2+}}/n_{Az^{2+}}$ ratio is 1.00. To confirm this value, 175.6 mg of lead azelate was digested with concentrated HNO_3, and

Table 1. Experimental Ratios between M^{2+} and Az^{2-} in Calcium, Copper, Nickel, and Zinc Azelates

	Zn^{2+}	Ni^{2+}	Cu^{2+}	Ca^{2+}
mass of metallic azelate/mg	102.6	167.4	171.8	171.8
equivalent point/mL	7.25	11.53	13.20	11.45
moles of azelate	$3.81 \cdot 10^{-4}$	$6.05 \cdot 10^{-4}$	$6.93 \cdot 10^{-4}$	$6.84 \cdot 10^{-4}$
moles of cation	$4.09 \cdot 10^{-4}$	$6.17 \cdot 10^{-4}$	$7.06 \cdot 10^{-4}$	$7.06 \cdot 10^{-4}$
ratio $n_{M^{2+}}/n_{Az^{2+}}$	1.07	1.02	1.02	1.03

Table 2. Metallic Azelate Solubilities

compound	total M^{2+}/ mol·L^{-1}	confidence interval/ mol·L^{-1}	pH
PbAz	$1.89 \cdot 10^{-5}$	$0.39 \cdot 10^{-5}$	6.1
CuAz	$1.24 \cdot 10^{-4}$	$0.24 \cdot 10^{-4}$	6.0
ZnAz	$1.89 \cdot 10^{-3}$	$0.13 \cdot 10^{-3}$	6.7
CaAz	$1.17 \cdot 10^{-2}$	$0.10 \cdot 10^{-2}$	6.9
NiAz	$3.72 \cdot 10^{-2}$	$0.02 \cdot 10^{-2}$	6.9

Table 3. Solubility Products of Metallic Azelates

	CaAz	CuAz	NiAz	PbAz	ZnAz
K_{sp}	$1.32 \cdot 10^{-4}$	$1.10 \cdot 10^{-8}$	$1.35 \cdot 10^{-3}$	$2.69 \cdot 10^{-10}$	$3.35 \cdot 10^{-6}$
$pK_{sp} = -\log K_{sp}$	3.88	7.96	2.87	9.57	5.48
ionic strength/ ol·L^{-1}	$4.70 \cdot 10^{-2}$	$4.96 \cdot 10^{-4}$	$1.49 \cdot 10^{-1}$	$7.50 \cdot 10^{-5}$	$7.56 \cdot 10^{-3}$
$\gamma_M = \gamma_{Az}$	0.44	0.90	0.28	0.96	0.67
K_{sp}^{corr}	$2.55 \cdot 10^{-6}$	$8.91 \cdot 10^{-9}$	$1.06 \cdot 10^{-4}$	$2.48 \cdot 10^{-10}$	$1.50 \cdot 10^{-6}$
pK_{sp}^{corr}	5.59	8.05	3.97	9.60	5.82

lead was measured using AAS. The calculation of the mass percentage of lead in the compound gives 53.3 % for a theoretical value of 52.7 %. The ratios obtained for all cations confirm the exclusive precipitation of $M(CH_2)_7(COO)_2$ type compounds.

Solubility. The variation of conductance, presented in Figure 3, gives the time required to reach the equilibrium. This time was obtained when the conductance reaches a plateau. The curves indicate that a time of 8 h is sufficient to reach the equilibrium. Table 2 presents the metal concentrations and the pH measured for each compound.

According to the mathematical relation between solubility and solubility product, K_{sp} was determined by calculating the K_{sp}^{cond} from experimental solubility and by replacing the values of $[H^+] = 10^{-pH}$ in α_M and α_{Az} expressions. These calculated values are given in Table 3. The solubility products K_{sp} were calculated on the basis of concentrations, assuming activity coefficients equal to 1. Corrected values, noted K_{sp}^{corr}, were determined taking ionic strength into account, which was calculated for each filtrate. Activity coefficients were calculated with the Debye−Hückel equation:

$$\log \gamma_i = -\frac{0.5 z_i^{\,2} \sqrt{I}}{1 + \sqrt{I}} \tag{13}$$

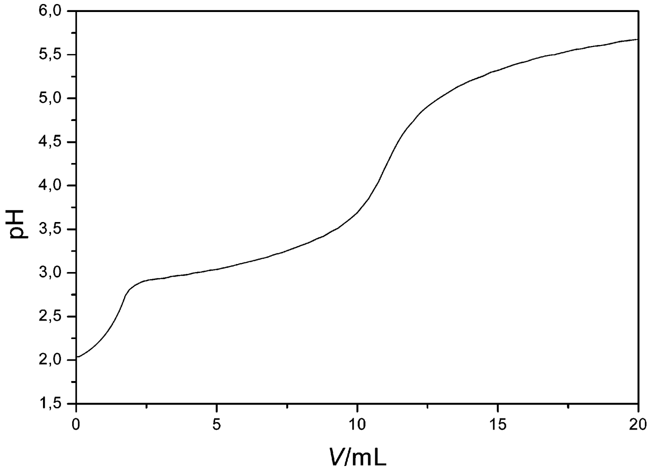

Figure 2. pH metric following of lead azelate formation by addition of volume (V) of sodium azelate.

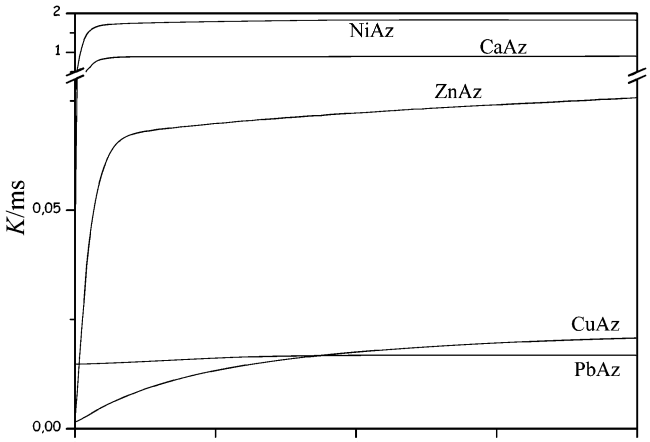

Figure 3. Conductometric following of metallic azelate solubilities determination as a function of time.

As expected, the values of K_{sp} and K_{sp}^{corr} are very close for slightly soluble compounds such as CuAz or PbAz. On the other hand, the results obtained for CaAz and NiAz clearly show that the equivalence between activities and concentrations is not valid.

Theoretical Calculation of Conditional Solubility

The values of pK_{sp}^{corr} presented in Table 3 were added to the database MINEQL+ software,[25] a widely used chemical equilibrium modeling interface. The solubility curves were plotted taking the possible formation of metallic hydroxides into account. Figure 4 presents the solubility of zinc azelate. Then, all curves are gathered in Figure 5.

Figure 5 allows us to predict the feasibility of a separation from a theoretical point of view. We consider a separation of binary mixture M_1−M_2 as possible when 99 % of the cation M_1 is precipitated without embedding more than 1 % of the cation M_2. The separation is effective when $\log([M_2]/[M_1]) > 2$. Table 4 presents all the M_1−M_2 mixtures. From both solubility curves the highest difference between log M_2 and log M_1 is determined. Log $([M_2]/[M_1])$

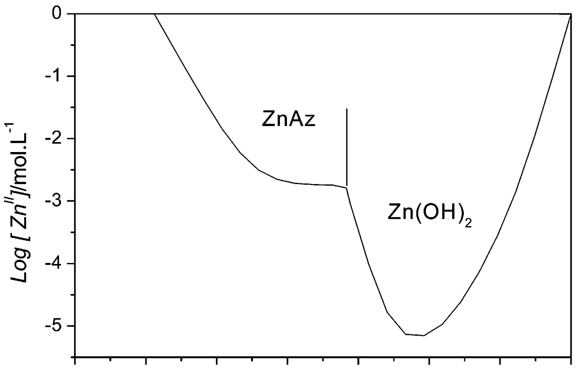

Figure 4. Conditional solubility of zinc azelate as a function of pH.

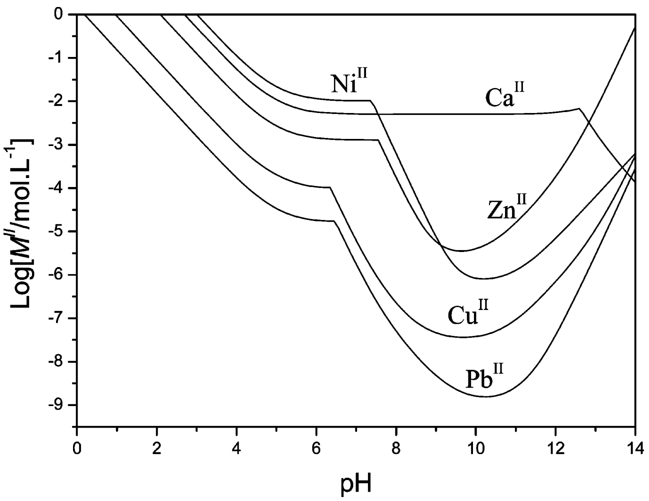

Figure 5. Conditional solubility of divalent metallic azelates as a function of pH. ▲, CuAz; ●, CaAz; ▼, NiAz; ■, ZnAz; ★, PbAz.

Table 4. Theoretical Feasibility of Selective Precipitation for Cations Mixture M_1-M_2

M_1-M_2 mixture	max value of $\log([M_2]/[M_1])$	max pH value	theor residual concn of $M_1/(\mathrm{mg \cdot L^{-1}})$
$\mathrm{Pb}^{2+} + \mathrm{Cu}^{2+}$	0.79	6.4	3.6 $\mathrm{mg \cdot L^{-1}}$
$\mathrm{Pb}^{2+} + \mathrm{Zn}^{2+}$	1.89		
$\mathrm{Pb}^{2+} + \mathrm{Ca}^{2+}$	2.49		
$\mathrm{Pb}^{2+} + \mathrm{Ni}^{2+}$	2.79		
$\mathrm{Cu}^{2+} + \mathrm{Zn}^{2+}$	1.12	6.3	6.5
$\mathrm{Cu}^{2+} + \mathrm{Ca}^{2+}$	1.72		
$\mathrm{Cu}^{2+} + \mathrm{Ni}^{2+}$	2.03		
$\mathrm{Zn}^{2+} + \mathrm{Ca}^{2+}$	0.60	7.6	84.8 $\mathrm{mg \cdot L^{-1}}$
$\mathrm{Zn}^{2+} + \mathrm{Ni}^{2+}$	0.90	7.3	84.8 $\mathrm{mg \cdot L^{-1}}$
$\mathrm{Ca}^{2+} + \mathrm{Ni}^{2+}$	0.30	7.3	410.3 $\mathrm{mg \cdot L^{-1}}$

is then calculated (column 2), and the corresponding pH value is given in column 3. The last column indicates the theoretical residual concentration of M_1 in the solution after precipitation of M_1Az.

Conclusion

This work is devoted to the measurement of the solubility of calcium, copper, nickel, lead, and zinc azelates. Metallic azelates have been synthesized from sodium azelate and metallic cation solutions. Their stoichiometry has been controlled using pH titration and chemical analysis. The solubilities have been determined in pure water at 20 °C, and the solubility products were calculated. The values of K_{sp} for $\mathrm{Pb(CH_2)_7(COO)_2}$, $\mathrm{Cu(CH_2)_7(COO)_2}$, $\mathrm{Zn(CH_2)_7(COO)_2}$, $\mathrm{Ca(CH_2)_7(COO)_2}$, and $\mathrm{Ni(CH_2)_7(COO)_2}$ are respectively $2.48 \cdot 10^{-10}$, $8.91 \cdot 10^{-9}$, $1.50 \cdot 10^{-6}$, $2.55 \cdot 10^{-6}$, and $1.06 \cdot 10^{-4}$. The superimposing of solubility curves, drawn with MINEQL+ software, can be used to predict the feasibility of the separation of two given cations. From a theoretical point of view, sodium azelate could be used to perform the following separations: $\mathrm{Pb}^{2+} + \mathrm{Ca}^{2+}$, $\mathrm{Pb}^{2+} + \mathrm{Ni}^{2+}$, and $\mathrm{Cu}^{2+} + \mathrm{Ni}^{2+}$.

Literature Cited

(1) Bossert, R. G. The metallic soaps. *J. Chem. Educ.* **1950**, *37*, 10–15.

(2) Karleskind, A. *Manuel des Corps Gras*; Lavoisier: 1992.

(3) Rocca, E.; Steinmetz, J. Inhibition of lead corrosion with satured linear aliphatic chain monocarboxylates of sodium. *Corros. Sci.* **2001**, *43*, 891–902.

(4) Muller, B.; Förster, I.; Kläger, W. Corrosion inhibition of zinc pigments in aqueous alkaline media by polymers. *Prog. Org. Coat.* **1997**, *31*, 229–233.

(5) Rapin, C. Etude de l'inhibition de la corrosion aqueuse du cuivre. Ph.D. Thesis, University of Nancy, France, 1994.

(6) Beucler-Bour, V. Etude d'une famille d'inhibiteurs organiques de la corrosion de l'acier. Ph.D. Thesis, University of Nancy, France, 1993.

(7) Sin'kova, L. A. Some characteristics of flotation extraction of cadmium ions collected with aliphatic acid potassium soaps. *Kolloidn Zh.* **1992**, *54*, 119–122.

(8) Choi, S. J.; Kim, K. H. The improvement of the removal efficiency of foam flotation by the synergistic effect of mixed surfactant solutions. *Environ. Technol.* **1998**, *19*, 1151–1156.

(9) Sreenivasarao, K.; Doyle, F. M. Solubility products of selected metal ions and anionic C_{12} surfactants. *Sep. Purif. Technol.* **1997**, *12*, 157–164.

(10) Husein, M. M.; Vera, J. H.; Weber, M. E. Removal of lead from aqueous solutions with sodium caprate. *Sep. Sci. Technol.* **1998**, *33*, 1889–1904.

(11) Preston, J. S.; Du Preez, A. C. Separation of nickel and calcium by solvent extraction using mixtures of carboxylic acids and alkylpyridines. *Hydrometallurgy* **2000**, *58*, 239–250.

(12) Akanni, M. S.; Okoh, E. K.; Burrows, H. D.; Ellis, H. A. The thermal behaviour of divalent and higher valent metal soaps: a review. *Thermochim. Acta* **1992**, *208*, 1–41.

(13) Peneliau, F.; Meux, E.; Lecuire, J. M. *Hydroplus no. 128*, *Hydrosciences*, **2002**.

(14) Goebel C. G. Method of making azelaic acid. Patent 2,813,113, 1957.

(15) Process for production of a purified grade of azelaic acid by treatment with ozone during purification. Patent 3,402,108, 1968.

(16) Zimmermann, F.; Meux, E.; Mieloszynski, J. L.; Lecuire, J. M.; Oget, N. Ruthenium catalysed oxidation without $\mathrm{CCl_4}$ of oleic acid, other monoenic fatty acids and alkenes. *Tetrahedron Lett.* **2005**, *46*, 3201–3203.

(17) Santacesaria, E.; Sorrentino, A.; Rainone, F.; Di Serio, M.; Speranza, F. Oxidative cleavage of the double bond of monoenic fatty chains in two step: a new promising route to azelaic acid and other industrial products. *Ind. Eng. Chem. Res.* **2000**, *39*, 2766–2771.

(18) Bäumer, U.-S.; Schäfer, H. J. Cleavage of olefinic double bonds by mediated anodic oxidation. *Electrochim. Acta* **2003**, *48*, 489–495.

(19) Baumann, H.; Bühler, M.; Fochem, H.; Hirsinger, F.; Zoebelein, H.; Falbe, J. Natural fats and oils—renewable raw materials for the chemical industry. *Angew. chem. Int. Ed. Engl.* **1988**, *27*, 41–62.

(20) Hill, K. Fats and oils as oleochemical raw materials. *Pure Appl. Chem.* **2000**, *72*, 1255–1264.

(21) Box, G. E. P.; Hunter, W. G.; Hunter, J. S. *Statistics for Experimenters*; Wiley: New York, 1978.

(22) Draper, N. R.; Smith, H. *Applied Regression Analysis*, 2nd ed.; Wiley: New York, 1981.

(23) Ringböm, A. *Complexation in Analytical Chemistry*; Wiley: New York, 1963.

(24) Martell, A. E.; Motekaitis, R. J. *Determination and Use of Stability Constants,* 2nd ed.; VCH Publishers: New York, 1992.

(25) Schecher, W. D.; McAvoy, D. C. *MINEQL+ A Chemical Equilibrium Modeling System Version 4.5*; Environmental Research Software: Hallowell, ME, 2001.

Received for review January 6, 2005. Accepted September 11, 2005. This work is financially supported by the ADEME (the French Environment and Energy Management Agency) and the Regional Council of Lorraine.

JE050008U