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Fatty and Resinic Acids Extraction from Crude Tall Oil

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ABSTRACT

The separation of fatty and resinic acidic fractions from crude tall-oil soap solutions with *n*-heptane by the technique of dissociation extraction is discussed. The theory of the overall process is supported by a systematic study developed to cover the high selectivity demonstrated in the differential solubility and the aptness between fatty and diterpenic acids to both liquids phases. To study the main factors affecting those liquid–liquid extraction systems and the amphiphilic behavior of such molecules involved, sodium salts aqueous solutions of crude tall oil and synthetic mixtures as molecular acidic models were used.

Key Words. Crude tall oil; Fatty acids; Resinic acids; Micelles; Extractants; Dissociation extraction

INTRODUCTION

Crude tall oil (CTO), the major by-product in kraft pulp mills from coniferous wood species in cellulose production, represents an important source of long-chain fatty and resinic acids (1, 2). Since the 1940s several studies concerning the refining and fractionation of fatty and resinic acids (3–7) have been proposed but with no conclusive results (8) or any other technology that could replace traditional distillation under high vacuum (9). However, perhaps this is not the ideal way to treat such high molecular weight, low-priced materials because it leads to considerable pitch formation and a high level of energy consumption (10).

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Although several authors have suggested methods to improve good selectivity and easy recovery, these technologies have very high costs and operational difficulties for CTO fractionation. Therefore, it seemed appropriate to study the separation of CTO acids by the liquid–liquid extraction technique using a neutral solvent or combined with an adequate carrier. Moreover, if enough specificity could be achieved at the concentrations used in industry, such a process could become economically acceptable.

Some attention has been given in recent years to ion pair extraction (11–22) of organic acids and complex ions from aqueous solutions using water-insoluble carriers (amines, phosphine oxides, etc.), especially in hydrometallurgy (23). The extraction that would enhance selectivity originates in the difference of pk_a or solubility between two main classes of acids in aqueous solutions that were studied before as sodium abietate and oleate in water at 60°C for CTO molecular acidic models (24). The presence of an amine in small concentration could also discriminate in favor of the more acidic class, as was previously described (25).

For optimum design of an extraction process, it is necessary to develop a method for selecting a solvent that gives high distribution coefficients and enough selectivity (26). However, considering a complex mixture of several components as fatty and resinic acids in CTO, the selectivity concept can only be used for the total if it is assumed that synergistic effects are negligible and the main acidic fractions constitute two distinct classes with different enough characteristics.

According to Somasundaran et al. (27), the amphiphilic characteristics of anionic surfactants, even below the critical micellar concentration (CMC), promote premicellar behavior which indicated the formation of low-molecular weight aggregates such as dimers and ionomolecular complexes in aqueous solutions. In most of those studies, doubly charged dimers have been considered to be a dominant form of the premicellar aggregates. Considering anionic surfactants as sodium salts of fatty (HF) and resinic acids (HR) in aqueous solution, there are mainly species to be considered in the system: HF, HR, F^-, R^-, F_2^{2-}, R_2^{2-}, H_2O, H^+, and OH^-. Multimers such as trimers and tetramers have not been considered in this treatment at this stage because of the reduced probability of their formation resulting from the increased electrostatic repulsion between charged heads which must now be placed closer to one another. Neglecting activity coefficients, the following bulk chemical equilibria and the corresponding equilibrium constants can be written for this system as dissociation constants of both acids:

$$\begin{aligned} &HF \Leftrightarrow H^+ + F^-, && k_a(F) = [H^+][F^-]/[HF] \\ &HR \Leftrightarrow H^+ + R^-, && k_a(R) = [H^+][R^-]/[HR] \end{aligned} \qquad (1)$$

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Simultaneously, stable complexes as anionic (F_2^{2-} and R_2^{2-}) and acidic dimers (HF_2^- and HR_2^-) are formed between dissociated and undissociated species of each acid. Due to the low probability of association among both different molecular structures, linear and cyclic, those complexes should also be considered because association promotes high influence in the small solubility of the corresponding undissociated acidic forms in soap systems, neglecting activity coefficients, as

$$\begin{aligned} 2F^- &\Leftrightarrow F_2^{2-}, & k_d(F) &= [F_2^{2-}]/[F^-]^2 \\ 2R^- &\Leftrightarrow R_2^{2-}, & k_d(R) &= [R_2^{2-}]/[R^-]^2 \end{aligned} \tag{2}$$

$$\begin{aligned} F^- + HF &\Leftrightarrow HF_2^-, & k_{ad}(F) &= [HF_2^-]/[F^-][HF] \\ R^- + HR &\Leftrightarrow HR_2^-, & k_{ad}(R) &= [HR_2^-]/[R^-][HR] \end{aligned} \tag{3}$$

From Eqs. (1), (2), and (3), the overall equilibria and equilibrium constants established in such aqueous phase systems for fatty and resinic acids are given respectively by

$$\begin{gathered} F_2^{2-} + H_2O \Leftrightarrow OH^- + HF_2^- \\ K_F = k_w/k_h(F) = k_a(F)k_d(F)/k_{ad}(F) = [H^+][F_2^{2-}]/[HF_2^-] \end{gathered} \tag{4}$$

and

$$\begin{gathered} R_2^{2-} + H_2O \Leftrightarrow OH^- + HR_2^- \\ K_R = k_w/k_h(R) = k_a(R)k_d(R)/k_{ad}(R) = [H^+][R_2^{2-}]/[HR_2^-] \end{gathered} \tag{5}$$

which represent the main hydrolysis reactions among different dimeric complexes formed for each acidic specie, assuming k_w to be an ion-product of water and a constant water concentration.

Because of such considerations, as well as amphiphilic characteristics involved in soap solutions, the best way to study the separation of fatty from resinic acids in mixing systems such as those in CTO should be *dissociation extraction*. Such a process showed very good results when applied to difficult separation systems like closely isomeric phenols recovery, penicillin purification (28), etc., as well as low price requirements. The basis of the new method described for fatty and diterpenic acids separation from CTO involves the use of an aqueous solution with a strong base in an amount less than that equivalent to the total acid. So the overall equilibriums involved for each class of acids may be broken down simply by contact with an organic solvent having a stronger affinity for one of them. Thus, if the mixture is partially neutralized by caustic soda, there will be competition between both classes of organic acids for reaction with the strong base. Using the dissociation extraction concept for CTO

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sodium salts aqueous systems, the main fatty and resinic acids involved, oleic [$k_a(\mathrm{O}) = 5.0$ (20°C)] and abietic [$k_a(\mathrm{Ab}) = 6.4$ (25°C)], respectively, of which the former is weaker and presents a higher solubility in soap solutions (29, 30), could be challenged. Such aspects obviously seems to promote significant effectiveness in the extraction process. The main equilibriums in aqueous solutions (Eqs. 4 and 5) should show differences in their affinity for each acidic class, as well as in their relative stability for the formation of complexes, which obviously influences the overall extraction mechanism.

In the general theory of dissociation extraction previously developed (31–36), considering the separation of mixing systems containing fatty (HF) and resinic acids (HR), the remaining equilibrium conditions involved, neglecting activity coefficients, are the distribution coefficients of both undissociated forms between aqueous and organic layers as

$$\begin{aligned} k_d(\mathrm{F}) &= [\mathrm{HF}]_o/[\mathrm{HF}_2^-] \\ k_d(\mathrm{R}) &= [\mathrm{HR}]_o/[\mathrm{HR}_2^-] \end{aligned} \tag{6}$$

and the overall distribution coefficients defined as

$$\begin{aligned} D_\mathrm{F} &= [\mathrm{HF}]_o/([\mathrm{HF}_2^-] + [\mathrm{F}_2^{2-}]) \\ D_\mathrm{R} &= [\mathrm{HR}]_o/([\mathrm{HR}_2^-] + [\mathrm{R}_2^{2-}]) \end{aligned} \tag{7}$$

The following expressions could be achieved from Eqs. (6) and (7) for fatty and resinic acids:

$$\begin{aligned} D_\mathrm{F} &= k_d(\mathrm{F})[\mathrm{HF}_2^-]/([\mathrm{HF}_2^-] + [\mathrm{F}_2^{2-}]) \\ D_\mathrm{R} &= k_d(\mathrm{R})[\mathrm{HR}_2^-]/([\mathrm{HR}_2^-] + [\mathrm{R}_2^{2-}]) \end{aligned} \tag{8}$$

and the reverse expressions obtained from Eqs. (4), (5), and (8) should be expressed as

$$\begin{aligned} D_\mathrm{F}^{-1} &= k_d(\mathrm{F})^{-1} + K_\mathrm{F}/k_\mathrm{d}(\mathrm{F})[\mathrm{H}^+]^{-1} \\ D_\mathrm{R}^{-1} &= k_d(\mathrm{R})^{-1} + K_\mathrm{R}/k_\mathrm{d}(\mathrm{R})[\mathrm{H}^+]^{-1} \end{aligned} \tag{9}$$

According with Puttemans et al. (37), plots of D_F^{-1} and D_R^{-1} versus $[\mathrm{H}^+]^{-1}$ from Expressions (9) should be linear if they are pH-dependent. The intercepts and slopes calculated by linear regression are, respectively, both distribution coefficients [$k_d(\mathrm{F})$ and $k_d(\mathrm{R})$] and overall equilibrium constants (K_F and K_R) for fatty and resinic acidic fractions in such aqueous systems.

The effectiveness of dissociation extraction can conveniently be expressed as the separation factor or selectivity [β(F,R)]. The differential solubility involved between fatty and resinic acids fractions is expressed

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by the following relation from the ratio of Eqs. (9) as

$$\beta(\mathrm{F,R}) = D_{\mathrm{F}}/D_{\mathrm{R}} = k_d(\mathrm{F})/k_{\mathrm{d}}(\mathrm{R})([\mathrm{H}^+] + K_{\mathrm{R}})/([\mathrm{H}^+] + K_{\mathrm{F}}) \quad (10)$$

This expression is acceptable if the total concentration assumed for both classes of fatty and resinic acids in aqueous solution is lower than the overall CMC and if the distribution coefficients are assumed to be constant (38). Any mathematical approach applied to such systems should involve all aspects of Relation (10) including the main parameters involved, while at the same time the theoretical selectivities between fatty and resinic acids separation should be simplified from the high compositional complexity which represents sodium salts of CTO in aqueous solutions.

EXPERIMENTAL

Reagents and Solvents

All solvents and reagents used were commercially pure grade of more than 99% purity (GC). A CTO sample from the Portuguese Pulp and Paper Industry (Portucel SA, Rodão) with the characteristics shown in Table 1 was used according to ASTM D 803 (39).

Commercial oleic acid [Merck: Art. 471, 75% (GC)] was used without further purification. Resinic acids from Portuguese commercial colophony (WW) was purified to >99% (GC) with di-isobutylamine (Aldrich), in analogy to the Harris and Sanderson purification method for abietic acid (40). It was stored in the dark under dry nitrogen to prevent isomerization and oxidation. The acid number obtained after purification decreased to 178.9, according to ASTM D 465 (41).

Dibuthylphtalate [Merck: Art. 800919, better than 99.5% purity (GC)] was used as an internal standard in chloroform (2 mg/cm^3) for GC analysis.

Diazomethane was obtained from *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide dissolved in diethyl ether (5%) by reaction with potassium hydroxide in ethanolic aqueous solution. By using bubbling nitrogen gas, fresh

TABLE 1
Characteristics of the
Portuguese CTO Sample

Acid number	156.6
Saponification number	179.4
Unsaponifiable matter	13.1%
Water content	1.5%
Fatty acids	37.5%
Resinic acids	49.4%

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diazomethane was obtained. It esterified the carboxylic acids samples, as recommended in ASTM D 3008 (42).

Tri-*n*-octylamine (TOA), tri-iso-octylamine (TIOA), tri-*n*-octylphosphine oxide (TOPO), and di-*n*-octylamine (DOA) were used as extractants (Aldrich, with better than 99% purity) dissolved in *n*-heptane (0.01 M).

Methodology

Accurately weighed samples of CTO, oleic acid (O), resinic acids (R), and several molar proportions of oleic plus resinic acids [O + R (2:1), O + R (1:1), and O + R (1:2)], as synthetic mixtures for CTO molecular acidic models, were suspended in water, and a 1% excess of 0.1 M sodium hydroxide was added. The samples were subjected to ultrasonic waves at room temperature until clear solutions were obtained. The correct pH values (Orion model 420 A) were attained by small additions of 0.01 M hydrochloric acid. The samples were diluted with water to the desired concentration below CMC. To study the concentration effect in the overall extraction of fatty and resinic acids, sodium salts aqueous solutions from the 0.5–5 g/dm^3 CTO concentration range were used. For experiments involving the effect of ionic strength, sodium chloride of final concentrations 0.1, 0.2, and 0.3 M were added, to three equimolar synthetic mixtures [O + R (1:1)] of sodium salts aqueous solutions at different pH values (9.2, 10.2, and 11.2), respectively.

Equal volumes (10 cm^3) of samples in aqueous solutions previously prepared and *n*-heptane alone or with dissolved extractants (DOA, TIOA, TOA, and TOPH) were mixed in separatory flasks (25 cm^3), shaken for 20 minutes, and left standing for 2 hours in a thermostat at 30°C before samples of each phase were taken and quantified.

All results were the average of experiments run in triplicate.

Analytical Procedure

Organic phases (2 cm^3) were evaporated under nitrogen, diluted in diethyl ether/methanol (9:1), and esterified with gaseous freshly prepared diazomethane. Aqueous phases (5 cm^3) were previously acidified with hydrochloric acid (pH $<$ 1), extracted with 5 cm^3 of diethyl ether/methanol (9:1), and finally also esterified with diazomethane (2 cm^3). Dibutylphthalate solution (1 cm^3) was added as an internal standard to the methylated samples after nitrogen evaporation.

A Hewlett-Packard 5890 A gas chromatograph, equipped with a flame ionization detector [FID: air/hydrogen (high grade)] and a capillary inlet system with a glass liner tube (HP part 18740-60840) using the parameters shown in Table 2, was used for quantification (43). The data were reported

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TABLE 2
Conditions and Parameters Used in GC Analytical Method [43]

Column	Fused silica capillary (HP-5); 25 m; 0.20 mm i.d.; 0.33 μm film thickness; 5% diphenyl, 95% dimethyl polysiloxane liquid phase (crosslinked)
Injection	1 μL (Hamilton 710 N syringe); "hot needle technique"
Carrier gas	Nitrogen (high grade); linear flow 20 cm/s
Split ratio	1:100
Injector temperature	260°C
Detector temperature	260°C
Oven temperature	220°C isothermal

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in a HP-3396 electronic integrator and calibration plots were made. Oleic and/or linoleic acids were quantified in the fatty fraction. Abietic, dehydroabietic, isopimaric, palustric, pimaric, neoabietic, and sandaracopimaric acids were quantified in the resinic fraction.

RESULTS AND DISCUSSION

Effect of pH

The hydrogen ion concentration seems to be the most important parameter in fatty and resinic acids solubility when they are dissolved in dilute aqueous solutions of sodium soap. According with Palonen et al. (24), above CMC the solubility of undissociated acidic forms known as acid soap increased by incorporation into micelles, and below that critical point they have higher stability when dimer species are formed (44).

In Fig. 1 can be seen the overall extraction with *n*-heptane is a function of the pH of fatty (a) and resinic (b) acids from the several sodium salts aqueous systems studied under the conditions used (45). The results demonstrate that advantage was taken of the low solubility of free fatty acids in the soap formed at pH values lower than the titration value and, as expected, decreases with decreasing pH while increasing the overall extraction. According to the shape of the graphical plots (a and b), and in accordance with the hydrophobicity level of both acidic fractions, the dissociation extraction process seems to give a high selectivity index for fatty acids separation out of resinic acids in synthetic mixtures as well as in CTO sodium salts aqueous solutions. Figure 2 shows some change in the selectivity values for all pH values studied between 9.2 and 11.2.

According with Puttemans et al. (37), the hydrogen ion concentration effect seems to be confirmed by linear representations of plots of D_F^{-1}

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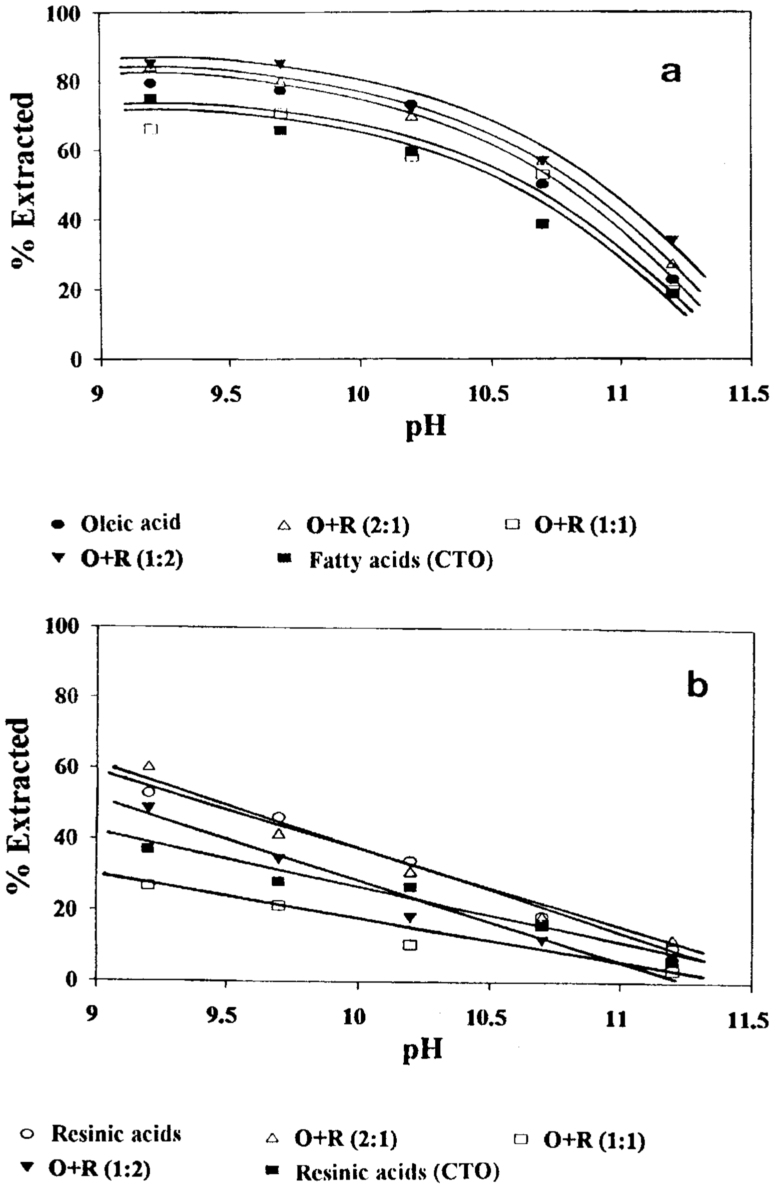

FIG. 1 Extraction of fatty (a) and resinic (b) acids from several sodium salts aqueous systems below CMC with *n*-heptane as a function of pH evaluation (T = 30°C) [45].

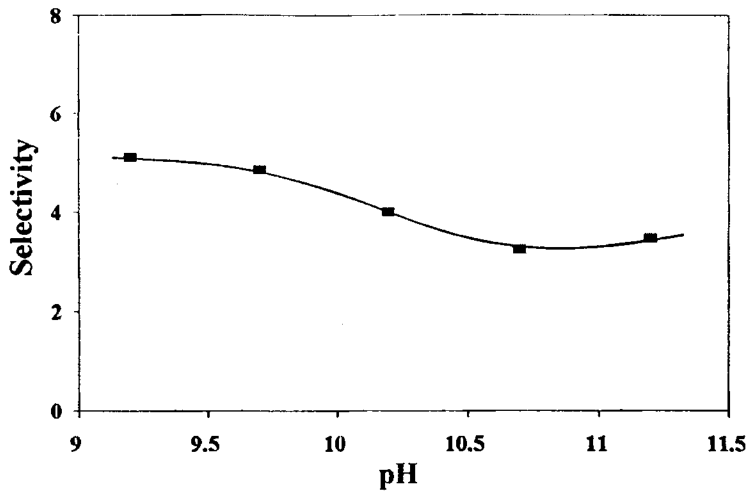

FIG. 2 Selectivity obtained between fatty and resinic acids from several CTO sodium salts aqueous solutions extracted with *n*-heptane as a function of pH evaluation (T = 30°C; [CTO] = 1.116 g/dm^3) [45].

and D_R^{-1} versus $[H^+]^{-1}$ from Expressions (9) as previously described. Good correlation coefficients were achieved (r_F and r_R), and they clearly show pH dependence in the extraction process for all systems studied. The parameters presented in Table 3, obtained from the intercepts and slopes by linear regression (least squares), could be used to estimate the distribution coefficients [k_d(F) and k_d(R)] and the overall equilibrium con-

TABLE 3

Parameters Obtained from Linear Regression of the D_F^{-1} and D_R^{-1} versus $[H^+]^{-1}$ Plots for Fatty and Resinic Acids Extractions from Several Soap Systems Studied, Shown in Fig. 1 [45]

System	X_R	k_d(F)	$K_F/10^{-10}$	r_F	k_d(R)	$K_R/10^{-10}$	r_R
O	0	7.82	1.60	0.9940	—	—	—
O + R (2:1)	0.31	7.23	1.10	0.9927	0.73	0.27	0.9261
O + R (1:1)	0.50	4.00	0.94	0.9621	0.40	0.59	0.9096
O + R (1:2)	0.64	5.82	0.66	0.9974	0.42	0.28	0.9140
R	1	—	—	—	0.91	0.47	0.9874
CTO	0.74[a]	3.07	0.78	0.9993	0.64	0.53	0.9943

[a] Considering only oleic plus linoleic as the fatty acid fraction.

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stants (K_F and K_R) for both acidic classes involved in sodium salts aqueous systems.

The data confirm that fatty acids have a higher solubility in the organic phase than do resinic acids, and so they have very superior distribution coefficient values in all systems studied. In accordance with the substantial difference observed in the dissociation constants between the main fatty and resinic acid involved (oleic and abietic, respectively), K_F always has higher values than K_R.

The overall competition between both class of acids in all systems studied was shown to be controlled by the aqueous solubility because a substantial difference in the coefficient distribution values was obtained. However, a small variation was observed when the resinic molar fraction (X_R) was increased, but there was simultaneous proportionality for fatty and resinic acids.

A far better confirmation of the theory developed for the dissociation extraction process could be a comparison between the experimental and predicted selectivities for all systems studied using the regression lines method as an approach to identifying systematic errors (46). Figure 3 shown the plotted results and the corresponding regression line (45); the graph fits the expected and obtained selectivities with good correlation.

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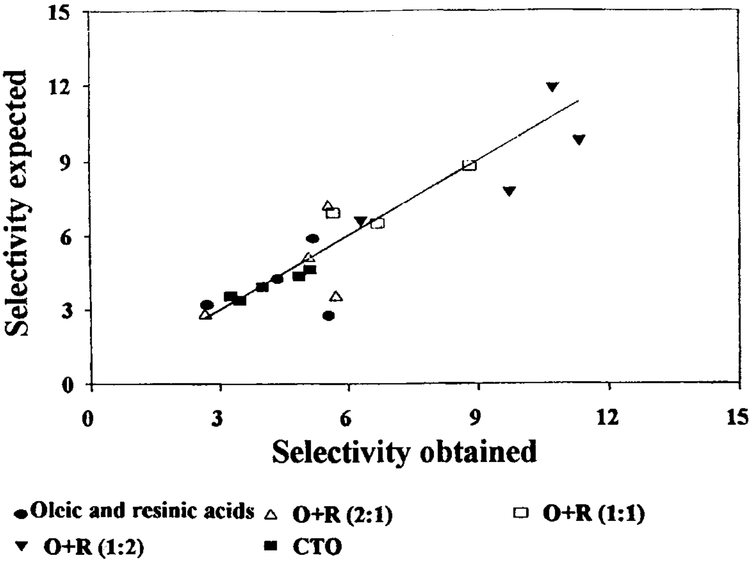

FIG. 3 Regression line of the expected and obtained selectivities between fatty and resinic acids extractions from several systems by the experimental data shown in Fig. 1 [45].

The parameters from the regression line, obtained by least squares (a = 0.5818, b = 0.9161, r = 0.8173, s_a = 1.1170, and s_b = 0.1021), clearly shows no evidence of systematic differences between both results. The s_a and s_b values can be used to estimate confidence limits for the intercept and slope in the usual way with 95% significance (which are given by $a \pm 2.3457$ and $b \pm 0.2144$, respectively) at the desired confidence level of $N - 2$ degrees of freedom for all systems studied, using the t-distribution. From the plot obtained in Figure 3 and statistical results, it is clear that the calculated slope and intercept do not differ significantly from ideal values of 1 and 0, respectively. It is therefore evident that the correlation coefficient obtained is of less importance in the present context and suggests reasonable precision as demonstrated by the small scatter of the observed results. Other factors as well as synergetic effects, could be involved in the overall extraction.

The mass transfer competition and the degree of hydrophobicity between fatty and resinic acids in both liquid layers shows that the dissociation extraction process is quite satisfactory for CTO fractionation. It is also clear that the difference in solubilities shown by both acid fractions in CTO and molecular acidic models as soap systems promotes effectiveness in the overall extraction process. From the data obtained, a pH value of 9.2 was chosen to evaluate the other main parameters studied in the extraction of fatty and resinic acids from CTO sodium salts aqueous systems.

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Effect of Solvent Classes

Fatty and resinic acids in sodium soap aqueous solutions should show different affinities for several organic solvent classes due to many factors, including intermolecular forces, structure, and polarity (47). Figure 4 presents selectivity values of the extraction of fatty and resinic acids from CTO soap solutions as obtained in different solvents in the conditions used (25, 45). The results show that the overall distribution coefficients are quite similar for all the solvents used ($2 < D_F < 5$ and $0.5 < D_R < 2.5$) except for ethers and α-pinene for which superior values were obtained ($D_F > 12$ and $D_R > 3$). Nonetheless, selectivity is better for paraffinic solvents which have a higher solubility for fatty than for resinic acids.

The data obtained in the pH study also indicate that resinic acids present more hydrophilic characteristics than do fatty acids in soap aqueous systems, especially because double bonds and the diterpenic structure strongly influence the extraction yield and even change the organic phase polarity, as demonstrated by the use of aromatic solvents.

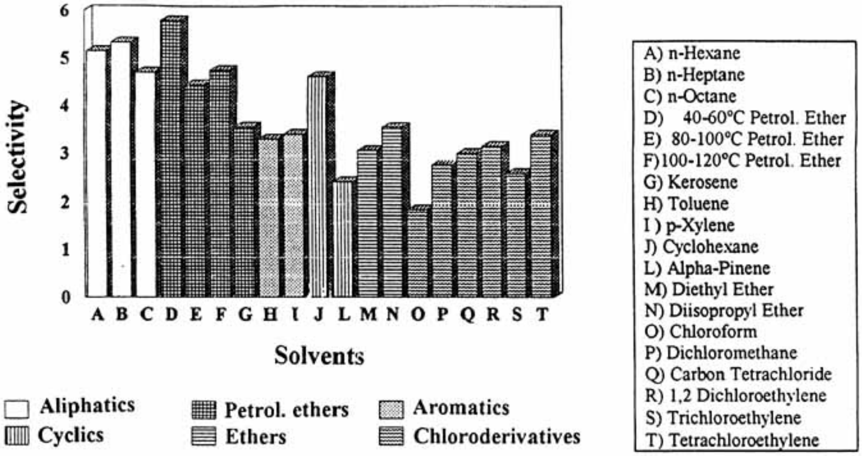

FIG. 4 Selectivity obtained between fatty and resinic acids from several CTO sodium salts aqueous solutions extracted with several solvents (T = 30°C; [CTO] = 0.730 g/dm^3; pH 9.2) [25, 45].

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From the selectivity studies and practical considerations, *n*-heptane was chosen to evaluate the other main parameters studied in the extraction of fatty and resinic acids from CTO sodium salts aqueous solutions.

Effect of Extractants

Because the overall pk_a for each acidic fraction from CTO presents significative differences, the addition of an adequate carrier into the organic medium could promote much better selectivities in the extraction process. Figure 5 shown the selectivity evaluation of fatty and diterpenic acids from CTO sodium salts aqueous solutions as a function of four extractants in *n*-heptane as well as in *n*-heptane alone in the conditions used (45). It is clear that the separation factor decreases substantially when either extractants with basic (DOA, TOA, and TIOA) or solvation characteristics (TOPO) are used. This observation seems to confirm the strong influence in the overall mass transfer process of both acids as promoted by an increase of the organic layer polarity by using phosphines. On the other hand, the occurrence of ion pair formation when using amines following protonation (37) should also significantly influence the extraction of resinic acids fraction from aqueous solutions of CTO soap. Indeed, the overall selectivity decreases because in contrast with fatty acids extraction which has been demonstrated to be much more controlled by the

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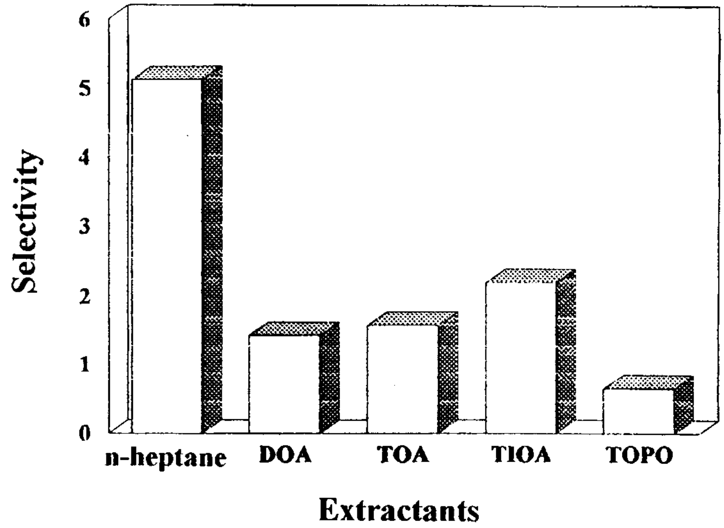

FIG. 5 Selectivity obtained between fatty and resinic acids from CTO sodium salts aqueous solutions extracted with *n*-heptane alone and with several extractants in *n*-heptane (0.01 M), (T = 30°C; [CTO] = 0.980 g/dm^3; pH 9.2) [45].

hydrophobicity characteristics of the organic layer, resinic acids have a much better solubility in the aqueous phase but lose substantial hydrophilic behavior in the presence of organic reactants.

Based on these experiments, *n*-heptane alone was chosen to evaluate the other main parameters studied in the extraction of fatty and resinic acids from CTO sodium salts aqueous solutions.

Effect of CTO Concentration

The amphiphilic behavior of sodium salts from fatty and resinic acids in aqueous solutions could have great influence on the dissociation extraction process. Figure 6 shown fatty and resinic acids extraction evaluation as a function of CTO concentration under the conditions used (45). It can be easily recognised that up to nearly 2 g/dm^3, fatty and resinic acids extraction changes substantially and proportionally with the CTO concentration. Aqueous solutions with concentrations higher than 5 g/dm^3 showed difficult phase separation due to persistent foaming.

Micellar aggregates are also involved in the extraction process up to such a concentration. A simple explanation of this change is that the increased solubility of the free undissociated acidic forms incorporated in-

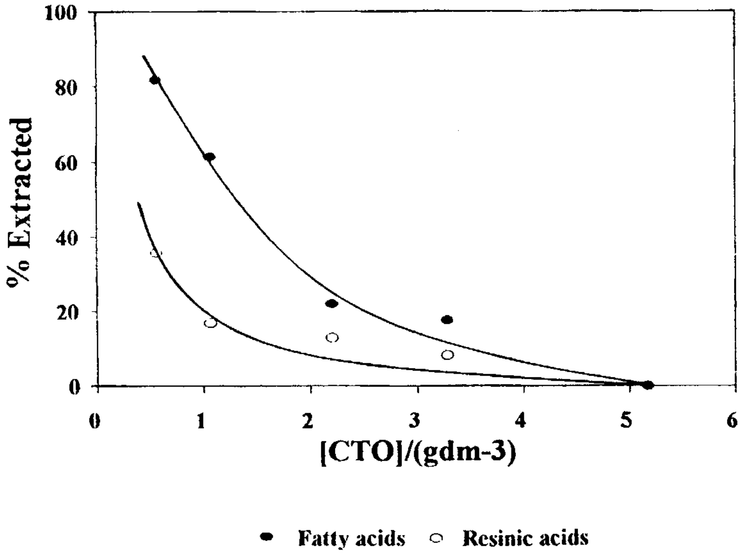

FIG. 6 Extraction of fatty and resinic acids with *n*-heptane as a function of CTO concentration evaluation from sodium salts aqueous solutions (T = 30°C; pH 9.2) [25, 45].

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side the micelles formed when the concentration is above the CMC promote higher solubility of fatty and resinic acidic species in the aqueous layer and, of course, lower the extraction yield.

Light-scattering measurements (45) showed the existence of a double phase behavior with a corresponding transition at approximately 2 g/dm^3 for CTO sodium salts in aqueous systems. This is consistent with data obtained in our experiments. These observations are in accordance with Ödberg et al. (48) who demonstrated that micellar associations of such amphiphilic molecules are usually formed as sodium oleate and abietate in synthetic mixtures for the CTO molecular acidic model.

From the extraction percentages and practical considerations, concentrations of CTO below 2 g/dm^3 were chosen to evaluate the other main parameters studied in the extraction of fatty and resinic acids from CTO sodium salts aqueous systems.

Effect of Ionic Strength

Ionic strength is of significative importance in amphiphilic/water systems. According with several authors (49), the addition of a strong electrolyte screens the repulsion and promotes micelle formation, i.e., the CMC for ionic surfactants is dramatically lowered when the ionic strength increased because of the growth of electrostatic repulsion.

By studying the extraction evaluation with *n*-heptane of fatty and resinic acids from aqueous soap solutions of equimolar synthetic mixtures [O + R(1 : 1)] as a function of sodium chloride concentration and pH evaluation, a decrease of the selectivity values could be observed as shown in Fig. 7. Because ionic strength promotes great stability in micellar behavior, the undissociated acidic forms incorporated inside the micelles formed decrease the overall extraction process of fatty and resinic acids species by an increase of the solubility in aqueous solution for all pH range, according with Ödberg et al. (47). Such behavior seems to present dispersion characteristics similar to those in microemulsion formation where acidic molecules in an aqueous medium are dispersed into micellar aggregates, as in oil-in-water systems (50).

This study seems to demonstrated that the high affinity of fatty acids to the organic layer is also limited by the aggregation behavior which

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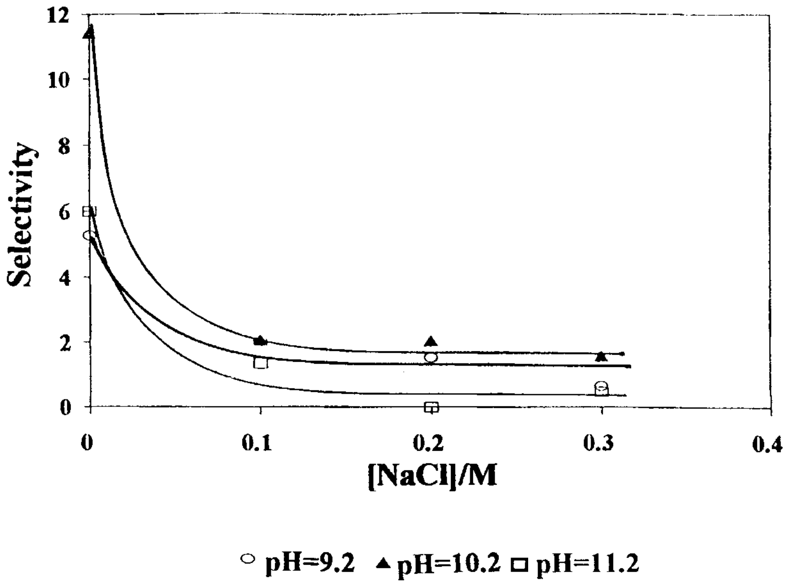

FIG. 7 Selectivity obtained between oleic and resinic acids from equimolar synthetic mixtures [O + R (1 : 1)] of sodium salts aqueous solutions below CMC extracted with *n*-heptane as a function of ionic strength and pH evaluation (T = 30°C) [45].

strongly controls mass transfer, increases the solubility of both classes in the aqueous layer, and consequently decreases the overall selectivity.

CONCLUSIONS

The separation of fatty and resinic acids from CTO sodium salts aqueous solutions with *n*-heptane, known as dissociation extraction, showed good results as well as a high level of overall selectivity.

The theoretical aspects studied demonstrate consistency with the experimental data when the regression lines methodology approach was used. The overall process seems to be strongly dependent on the pH. Careful control of pH is necessary in order to obtain high solubilities and good extraction efficiencies, especially of the fatty acid fraction.

The other main parameters (CTO concentration, solvent class affinity, ionic strength, and extractant dependence) have a much smaller influence on the overall extraction process of fatty and resinic acids from CTO, as well as from synthetic mixtures. The amphiphilic behavior of such soap systems increases the solubility of undissociated acidic species in the aqueous medium by incorporation inside the micellar aggregates when the concentration is higher than the critical point, thereby lowering the overall extraction yield.

The data obtained should promote interest in studying the multistage continuous extraction of fatty and resinic acids from CTO soap systems because they offer economic advantages when compared with the industrial practice of distillation under high vacuum.

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NOTATION

[HF]	fatty acids concentration
[HR]	resinic acids concentration
$[HF_2^-]$	fatty acid dimers concentration
$[HR_2^-]$	resinic acid dimers concentration
$[F^-]$	fatty anion concentration
$[R^-]$	resinic anion concentration
$[F_2^{2-}]$	fatty anionic dimers concentration
$[R_2^{2-}]$	resinic anionic dimers concentration

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$[H^+]$	hydrogen ion concentration
$[OH^-]$	hydroxyl ion concentration
D	overall distribution coefficients
k_d	distribution coefficients
K	overall equilibrium constant of the main species involved in sodium salts aqueous solutions
k_a	dissociation constant
k_ad	association constant for acidic dimeric species
k_d	association constant for anion species
k_h	hydrolysis constant
k_w	ion-product of water
r	correlation coefficient
a	intercept
b	slope
s	standard deviation
X	molar fraction
N-2	degree of freedom
O + R	oleic plus resinic acids
t	t-distribution

Greek Symbols

β	selectivity

Brackets and Subscripts

F	fatty acids
R	resinic acids
F, R	fatty and resinic acids
O	oleic acid
Ab	abietic acid
(1:2)	molar proportion of 1 to 2
(1:1)	molar proportion of 1 to 1
(2:1)	molar proportion of 2 to 1
o	organic phase

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