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Modifier and Surfactant Dependence of Gallium Extraction by Alkanoyl Oxinates from Basic Solutions

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ABSTRACT

The recently developed method of Ga extraction from basic aluminate solution (pH 13) using an alkanoyl oxine, i.e., myristoyl (M.Ox), palmitoyl (P.Ox), and stearoyl oxine (S.Ox), solution in chloroform has been improved by incorporating 2-hexanone as a modifier and cetyl trimethyl ammonium bromide (CTAB) as a surfactant into the extraction system. 2-Hexanone synergistically enhanced the extraction rate and Ga yield as its volume percentage was increased from 5 to 20% in the organic phase. Other oxygen-donor modifiers such as methyl isobutyl ketone (MIBK) and 1-hexanol, were not as effective as 2-hexanone. By using 10% (by volume) of 2-hexanone in chloroform solution, the order of Ga extraction efficiency for alkanoyl oxinates was M.Ox > P.Ox > S.Ox, i.e., extraction increased with decreasing length of the alkyl group of oxine. The ketone-added system showed satisfactory aluminum tolerance at pH 13, and enabled the shifting of the extraction pH to slightly higher values, which is beneficial for the process economies of Ga recovery from Bayer aluminate liquor. Use of CTAB as a cationic surfactant reduced the equilibration time and increased the Ga yield; the most pronounced effect occurred around its critical micelle concentration, indicative of micellar catalysis via interfacial mechanisms.

Key Words. Solvent extraction; Gallium(III) recovery; Synergistic extraction; 2-Hexanone; Surfactants; CTAB; Basic aluminate solution; Bayer process liquor; Oxine (8-hydroxyquinoline); 5-Alkanoyl oxines; Myristoyl oxine; Palmitoyl oxine; Stearoyl oxine

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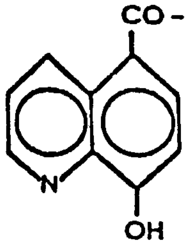
INTRODUCTION

Gallium, a valuable element widely used in the electronics industry, is usually associated with aluminum in nature. Thus, during the Bayer processing of bauxite, gallium needs to be recovered from an alkaline solution containing relatively high amounts of aluminum. Direct electrolysis, amalgamation, and liquid–liquid extraction techniques have been employed for this purpose, the first two suffering from high costs and environmental risks, e.g., from large stocks of mercury. Kelex 100, the trade name for the chemical 7-dodecenyl-8-hydroxyquinoline, has been used as a selective agent for Ga recovery by liquid–liquid extraction (1). Koide et al. (2) used oxine-type compounds (5-alkanoyl-8-quinolinol, R_nOx) as ion-flotation collectors. Recently, Apak and Filik (3) synthesized 5-alkanoyl-8-hydroxyquinolines as Ga extractants, and thus extended the alkyl chain of these types of compounds to higher carbon numbers to maintain the extracting ability of the parent oxine while decreasing its aqueous phase solubility in basic medium. Myristoyl, palmitoyl, and stearoyl oxines, abbreviated as M.Ox, P.Ox, and S.Ox, respectively, of the structural formula



[where R = $C_{13}H_{27}$ (M.Ox.), $C_{15}H_{31}$ (P.Ox), and $C_{17}H_{35}$ (S.Ox)] have been synthesized by a modified route based on the Fries rearrangement (4), and their structures were confirmed by elemental analysis and IR spectroscopy (5). Although this study showed that Ga could be selectively extracted by a $CHCl_3$ solution of these reagents from a basic solution of pH 13 containing up to 20-fold of aluminum, the extraction was rather slow, requiring a time period of 60 minutes at 40°C. Therefore, an investigation of possible synergistic effects on the extraction system was undertaken with special emphasis on shortening the equilibration time to render the developed process economically more applicable to the basic Bayer aluminate liquor, because with slow kinetics the retention time in the extraction stages would have to be greater than for a system involving faster kinetics (6).

In most extraction processes involving metal–chelate complexes, the formation of the chelate compound has been shown to be the rate-determining step (6). The extraction of some coordinatively unsaturated chelates (i.e., the coordination number of the central atom has not been satisfied) has been demonstrated to be synergistically affected by certain Lewis bases, like the Kelex 100–carboxylic acid systems (7).

Ketone-type modifiers as components of the organic phase have been reported to improve dramatically the rate of Ga extraction with Kelex 100 (8). Thus it was decided to examine the stoichiometry of the extracted chelates (Ga-alkanoyl oxinates) from basic medium in regard to coordinative saturation, and the possible synergistic effects of the ketone and alcohol modifiers as oxygen-donors on Ga extraction. As Fourre and Bauer (9) attributed faster Ga extraction in the presence of surfactants to interfacial mechanisms operating between the aqueous phase and microemulsions, possible micellar catalysis with a cationic surfactant such as CTAB was also investigated.

EXPERIMENTS AND RESULTS

Reagents and Solutions

Oxine (8-hydroxyquinoline), myristic acid, palmitic acid, stearic acid, thionyl chloride (for synthesis), nitrobenzene, chloroform, anhydrous aluminum chloride, 2-hexanone, MIBK, 1-hexanol, triton X-100, sodium lauryl sulfate, cetyl trimethyl ammonium bromide (CTAB), sodium carbonate, sodium bicarbonate, sodium hydroxide, calcium hydroxide, anhydrous sodium sulfate, nitric acid, perchloric acid, sulfuric acid, hydrochloric acid (extra pure), gallium (LAB), and aluminum foil (GR) were purchased from E. Merck. The reagents were of analytical grade purity unless otherwise stated.

5-Alkanoyl-8-hydroxyquinolines, i.e., myristoyl oxine (M.Ox), palmitoyl oxine (P.Ox), and stearoyl oxine (S.Ox), were synthesized in the department laboratories as described previously (4, 5).

Gallium(III) and aluminum(III) stock solutions were prepared by dissolving the metal in dilute nitric acid with some HCl, evaporating to expel nitrogen oxide fumes, and diluting to volume with 1% HCl. Working solutions of Ga and Al were prepared from the stock solutions. Sodium tetrahydroxogallate(III) and aluminate(III) solutions were prepared by dissolving suitable aliquots of the corresponding stock solutions in NaOH of the desired concentration. A 1% (w/v) hydroxyquinoline solution was prepared in EtOH. The alkanoyl oxine solutions were prepared in $CHCl_3$ in two different concentrations: the 1% (w/v) concentrated solution corresponded to a molarity of 2.82×10^{-2}, 2.61×10^{-2}, and 2.43×10^{-2} M for M.Ox, P.Ox, and S.Ox, respectively, while the dilute solution contained each alkanoyl oxine at 4.0×10^{-3} M. The pH adjustments of the solutions were made using 3 M HCl and 3 M NaOH solutions. The dilute (~0.1 M) NaOH solution used for dilution of $[Ga(OH)_4]^-$ solutions of pH 13 prior to extraction was prepared by partial neutralization of 3 M NaOH solution with HCl to pH 13. Thus, this solution contained NaOH as well as excessive NaCl. The stripping of the $CHCl_3$ extracts of gallium alkanoyl oxinates into the aqueous phase was made with 6 M HCl as described previously (5). The wet-ashing of the organic extracts after evaporation was made with H_2SO_4 and $HClO_4$.

Instruments

A Hitachi 220 A UV-Vis spectrophotometer equipped with quartz cuvettes was used for spectrophotometric Ga and Al measurements in the organic extracts as well as in the stripped aqueous phases. The metal determinations were confirmed by N_2O-acetylene flame AAS using a Perkin-Elmer 300 atomic absorption spectrometer. The pH values of the solutions were measured with a Metrohm E-512 pH-meter using a full range (pH: 0–14) Metrohm AG-type "U" glass electrode capable of measuring the strongly alkaline region (pH > 13) with a maximum deviation of 0.15 units. The electrode was calibrated against a 0.025 M $NaHCO_3$–0.025 M Na_2CO_3 buffer (pH 10.062 at 20°C) and a saturated $Ca(OH)_2$ solution (pH 12.627 at 20°C) prior to measurements.

Extraction and Spectrophotometric Determination of Gallium

Gallium determinations in the organic extracts were made by both wet ashing (H_2SO_4–$HClO_4$) of the evaporated organic extracts followed by oxine/$CHCl_3$ extraction of the aqueous solution at pH 7 using Moeller et al.'s spectrophotometric procedure (10) ($\epsilon_{392} = 6.5 \times 10^3$ L·mol^{-1}·cm^{-1}), and by stripping of the Ga-alkanoyl oxinate containing extracts by 6 M aqueous HCl, followed by neutralization of the aqueous phase to pH 7 and application of the standard procedure (10) using a calibration curve (5).

Stoichiometry of the Extracted Species

The stoichiometries of the extracted gallium alkanoyl oxinates were found by the mole-ratio method (11). For this purpose, 1 mL aliquots of the pH 13 $[Ga(OH)_4]^-$ solution ($C_{Ga} = 4.0 \times 10^{-3}$ M) were transferred to 10 test tubes and diluted to 6 mL with dilute NaOH (0.1 M) solution of pH 13. To each tube, 0.5–5.0 mL aliquots (with 0.5 mL increments) of 4.0×10^{-3} M alkanoyl oxine solution in $CHCl_3$ were added; the organic phases were diluted to 6 mL with $CHCl_3$. The tubes were stoppered and extracted in a thermostatic (t = 40°C) shaker for 1 hour. The organic extracts were separated, dessicated with anhydrous Na_2SO_4, and filtered through a blue-band Whatman filter paper. The Ga contents of the organic phases were determined by the standard spectrophotometric procedure (10) after evaporation and wet-ashing. The results, plotted on a curve drawn as A_{392nm} vs alkanoyl oxine/Ga mole ratio (Fig. 1), show that the stoichiometry of the extracted gallium palmitoyl oxinate is 1:2, i.e., one Ga^{3+} is chelated to two alkanoyl oxinate molecules.

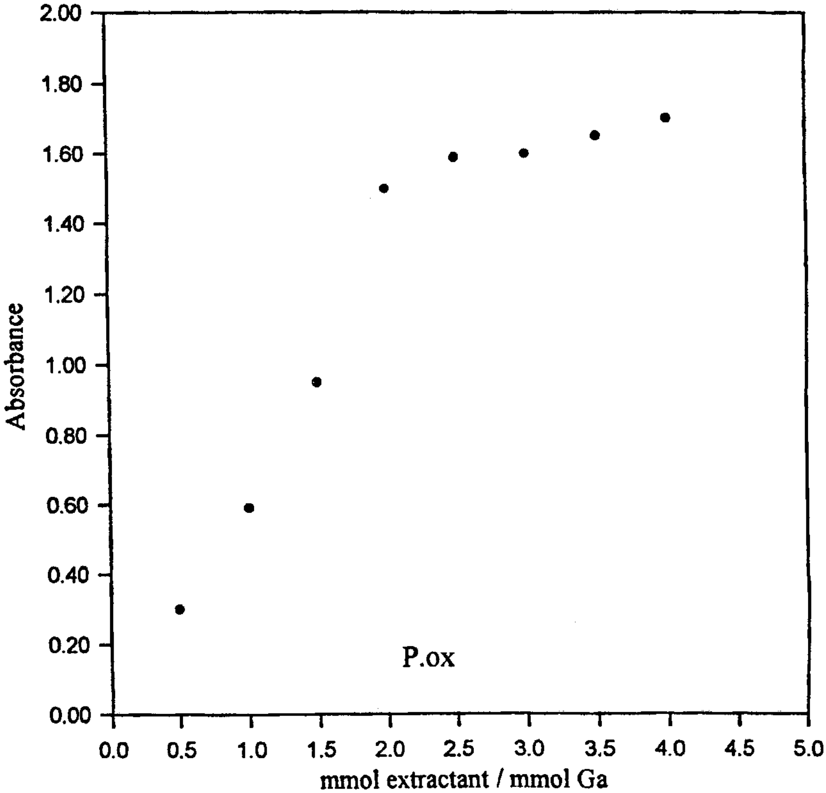


FIG. 1 Finding the stoichiometry of the extracted Ga-palmitoyl oxinate by the mole-ratio method.

Effect of Oxygen-Donor Solvents and Their Concentration (standard procedure)

One milliliter aliquots of 4.0 × 10^{-3} M $[Ga(OH)_4]^-$ solution at pH 13 were transferred to a series of test tubes with ground joints, and the aqueous phases were diluted to 6 mL with dilute NaOH (0.1 M) solution such that the pH was kept at 13. Two milliliters of alkanoyl oxine solution (1% in $CHCl_3$) were added to each tube, followed by v mL of the O-donor solvent (2-hexanone, MIBK, and 1-hexanol), and $(4 - v)$ mL of $CHCl_3$ such that the aqueous-to-organic ratio was 1:1 (6 mL to 6 mL). While studying the effectiveness of organic solvents, i.e., relative rate enhancement in the extraction (Figs. 2–4), the O-donor modifier solvents (both

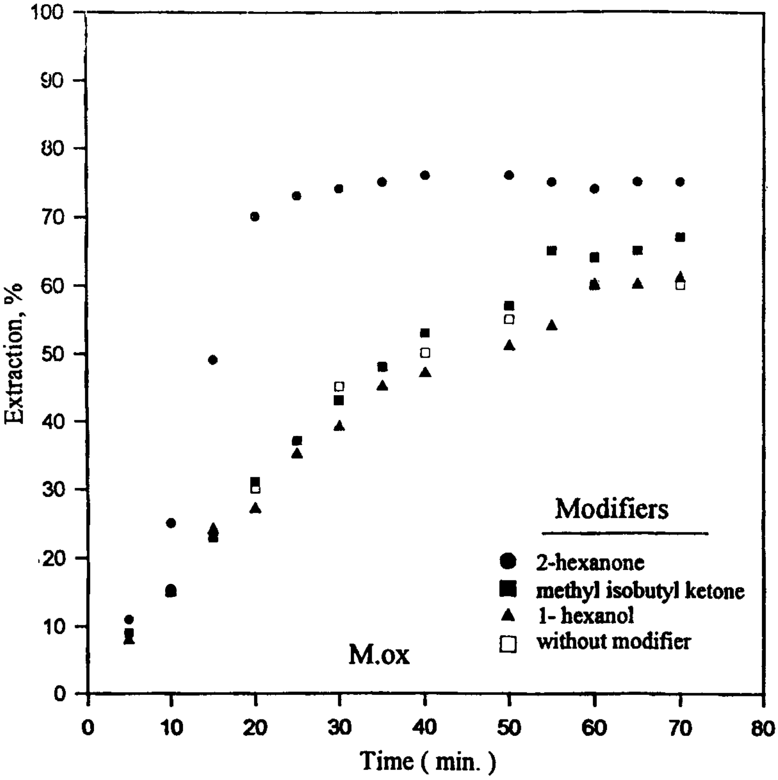


FIG. 2 Effect of oxygen-donor solvents on the extraction of gallium myristoyl oxinate into $CHCl_3$ (modifier: 10% by volume).

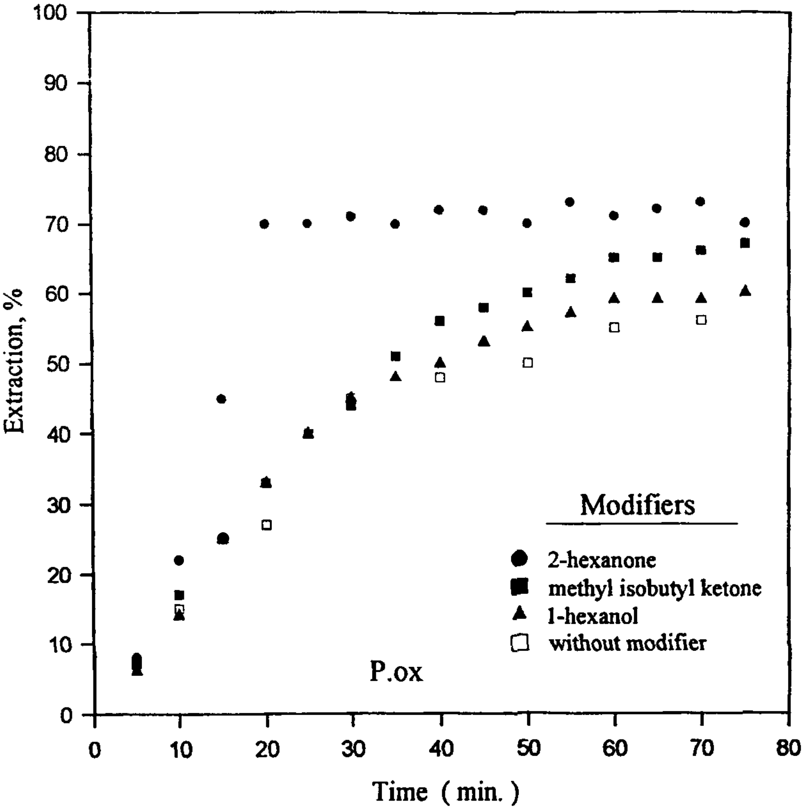


FIG. 3 Effect of oxygen-donor solvents on the extraction of gallium palmitoyl oxinate into $CHCl_3$ (modifier: 10% by volume).

alcohol and ketone) were taken in a fixed (10%) volume ratio of the organic phase. Once the modifier with the best performance, i.e., 2-hexanone, was selected, varying volume ratios of the latter (5, 10, 15, 20%) as a percentage of the organic phase were employed for observing the extraction–time relationship of each Ga alkanoyl oxinate (Figs. 5–7). The mixture of phases was shaken for varying periods of time with intermittent inversion at 40°C in an orbital shaker/thermostatic water bath at a shaking rate of 80 rpm. The organic phases were separated from the aqueous phases in separating funnels, dried with anhydrous Na_2SO_4, and the complexes were stripped to an aqueous phase using 6 M HCl. The HCl phases were neutralized to pH 7.0, and Ga analyses in the aqueous phase were

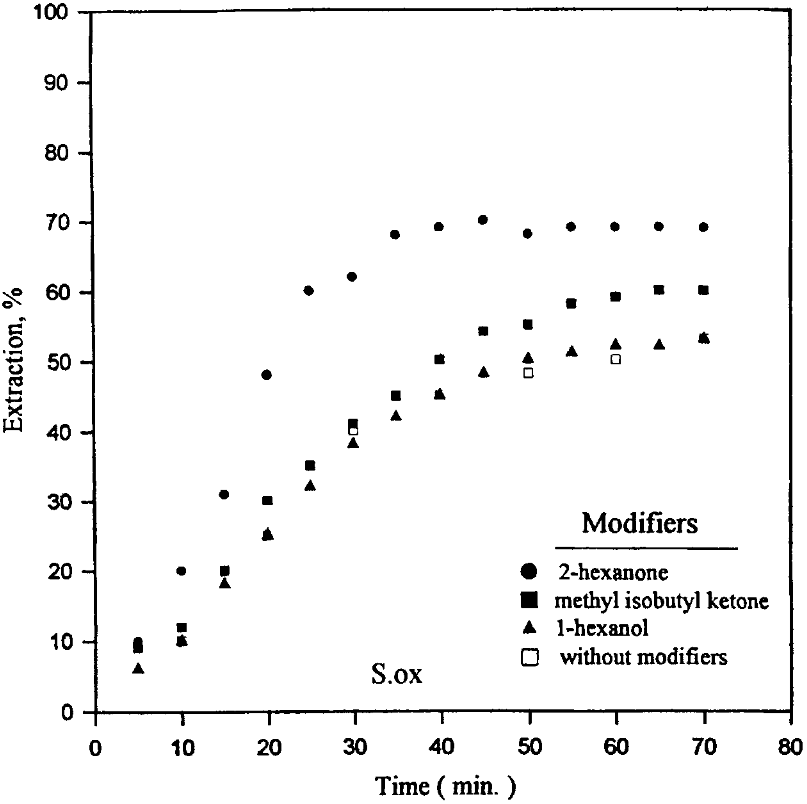


FIG. 4 Effect of oxygen-donor solvents on the extraction of gallium stearoyl oxinate into $CHCl_3$ (modifier: 10% by volume).

performed with the aid of the 8-hydroxyquinoline spectrophotometric procedure (10).

The reported extraction percentages (E) could easily be converted to the corresponding distribution ratios (D_{Ga}) by the following relationship:

$$D_{Ga} = \frac{E}{(100 - E)} \frac{V_{aq}}{V_{org}}$$

where (V_{aq}/V_{org}) is the aqueous-to-organic volume ratio.

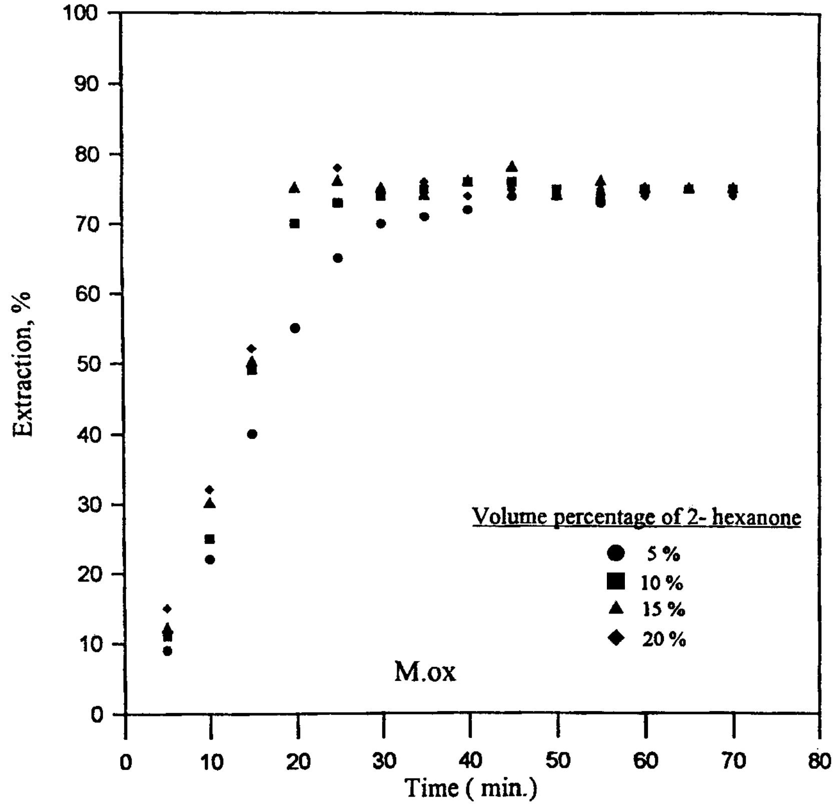


FIG. 5 Effect of the volume percentage of 2-hexanone on the extraction of gallium myristoyl oxinate.

Effect of pH on the 2-Hexanone/Chloroform Extraction System

The standard procedure using 10% 2-hexanone in $CHCl_3$ as the extracting solvent was repeated (40°C temperature and 30 minutes time) with the only exception that the aqueous phase was adjusted to the desired pH value close around 13. The results are given in Table 1A. The extraction (distribution ratio) vs pH data were collected between pH 13.00 and 13.50 with smaller pH increments (0.05 units) for Ga-palmitoyl oxinate with the purpose of clarifying the acidity dependence of extraction (Table 1B).

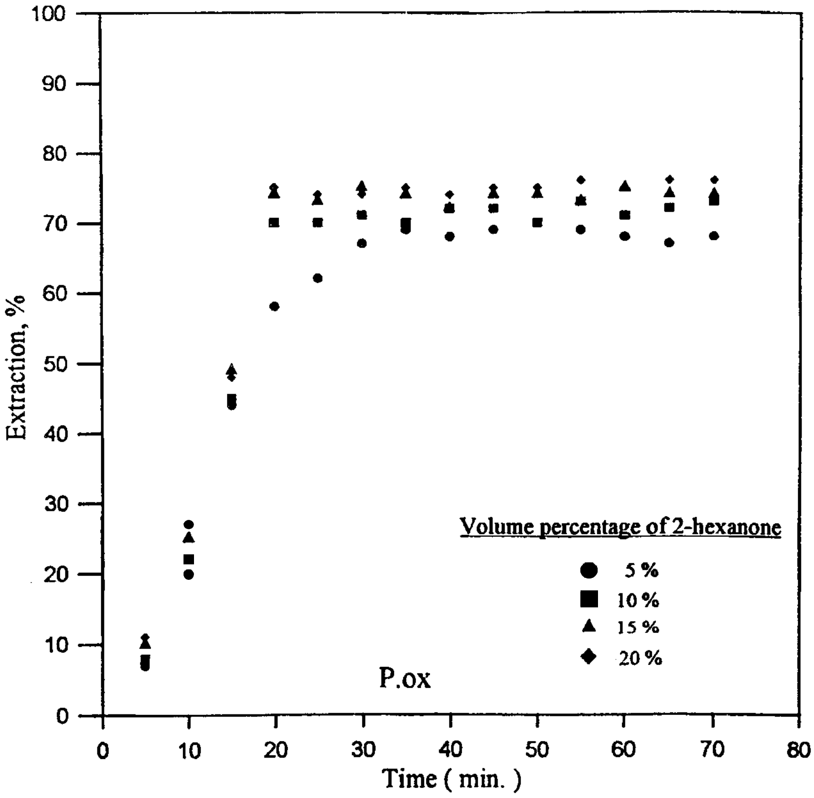


FIG. 6 Effect of the volume percentage of 2-hexanone on the extraction of gallium palmitoyl oxinate.

TABLE 1A
The pH Dependence of the Gallium Alkanoyl Oxinate/2-Hexanone (10% by volume)/Chloroform Extraction System

	Extraction, %, by alkanoyl oxine extractants		
pH	M.Ox	P.Ox	S.Ox
13.3	42	38	32
13.0	73	72	68
12.5	81	80	78

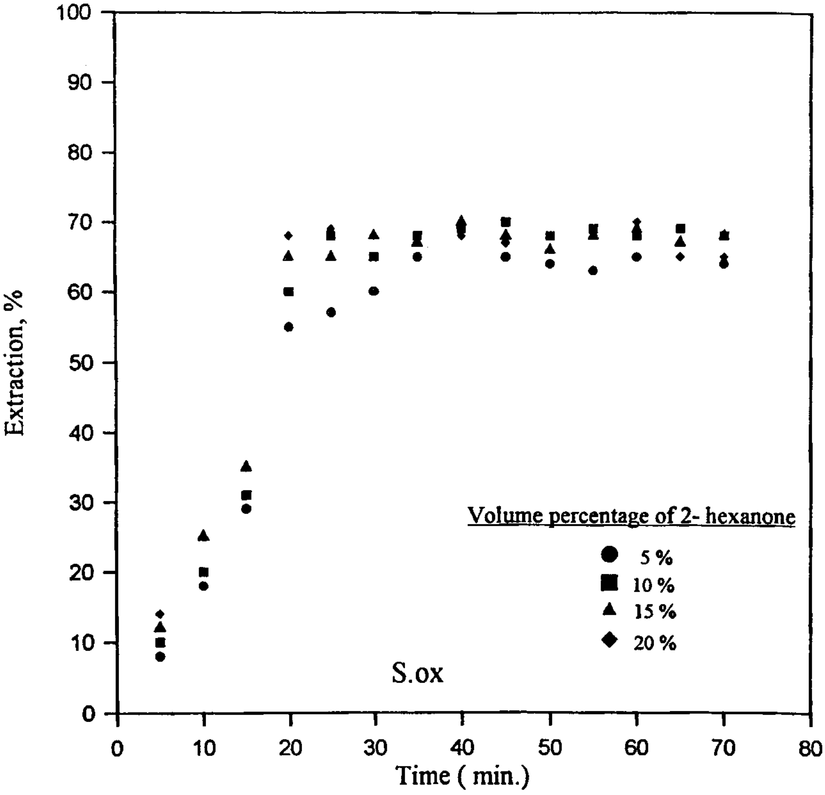


FIG. 7 Effect of the volume percentage of 2-hexanone on the extraction of gallium stearoyl oxinate.

TABLE 1B

Detailed Analysis of pH Dependence of the Gallium Palmitoyl Oxinate/2-Hexanone (10% by volume)/Chloroform Extraction System[a]

Equilibrium pH	Extraction, % (E)	Distribution ratio, D_{Ga}	Log D_{Ga}
13.00	72	2.57	0.410
13.10	68	2.13	0.327
13.20	61	1.56	0.194
13.25	39	0.639	−0.194
13.30	38	0.613	−0.213
13.35	28	0.388	−0.410
13.50	25	0.333	−0.477

[a] Linear equation for data in the table: Log D_{Ga} = −1.93 pH + 25.5, with r = 0.962.

Effect of Aluminum on the 2-Hexanone/Chloroform Extraction System

The standard extraction procedure using 10% 2-hexanone in $CHCl_3$ as the extracting solvent was adapted for Al extraction from a 700 and 1000 ppm solution of pH 13 at 40°C for 30 minutes. Aluminum determinations in the extracts were made by the standard spectrophotometric procedure (10) and confirmed by AAS. The results are given in Table 2.

Effect of Surfactants and Optimal Concentration of CTAB

The effect of surfactants (cationic, CTAB; nonionic, triton X-100; and anionic, sodium lauryl sulfate) on the Ga-alkanoyl oxinate/chloroform extraction system was tested by incorporating 2 mL of the 2.0×10^{-3} M alkaline surfactant solutions (pH 13) into the aqueous phases described in the standard procedure. Preliminary experiments showed that sodium lauryl sulfate did not change the extraction rate, while the rate increase observed with triton X-100 and cetyl trimethyl ammonium bromide (CTAB) were slight and considerable, respectively.

The effect of CTAB was further tested by following the extraction rate from an aqueous solution prepared by adding 2 mL of 2.0×10^{-3} M CTAB to 2 mL of 4.0×10^{-3} M $[Ga(OH)_4]^-$, both solutions at pH 13, and diluting to 7 mL with 0.1 M NaOH. Two milliliters of alkanoyl oxine (1% in $CHCl_3$) followed by addition of 5 mL of $CHCl_3$ were added. The mixture of phases was agitated at 40°C for different periods of time. The organic phases were separated, evaporated, and wet-ashed with the acid mixture, and the Ga contents of the extracts were determined as in the standard procedure. The extraction–time curves in the presence and absence of surfactant are shown in Fig. 8.

TABLE 2
The Concentration Dependence of Aluminum Extraction in the Alkanoyl Oxinate/2-Hexanone (10% by volume)/$CHCl_3$ System

Initial Al concentration, ppm	Extracted Al concentration, ppm, for alkanoyl oxine extractants		
	M.Ox	P.Ox	S.Ox
700	3	4	2
1000	8	8	7

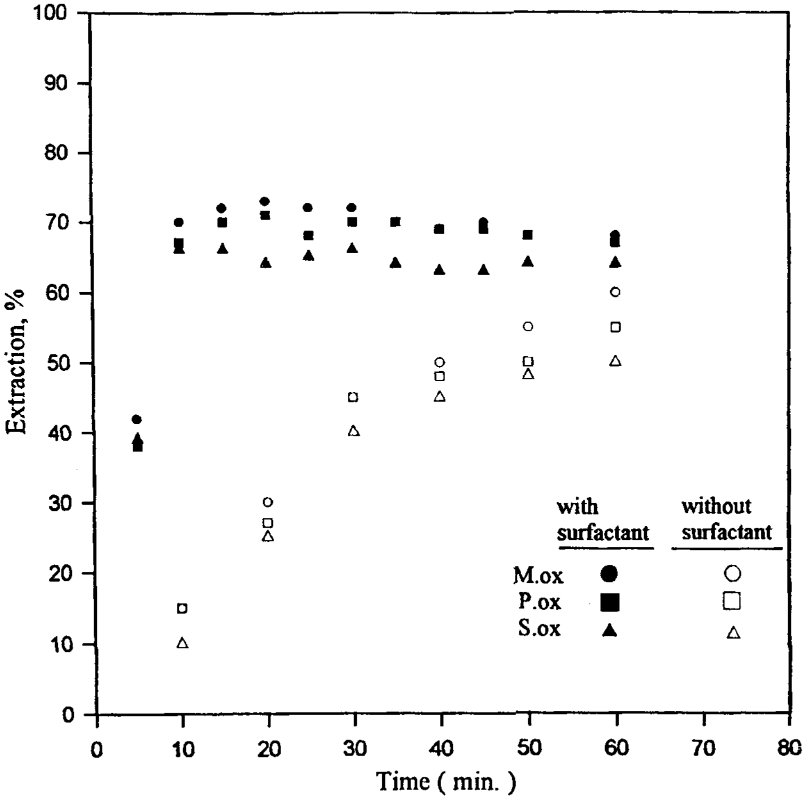


FIG. 8 Percentage extraction against time in the presence and absence of the cationic surfactant CTAB (surfactant concentration: 5.7 × 10^{-4} M).

To find the effective CTAB concentration yielding maximum extraction, 2-mL aliquots of the 4.0 × 10^{-3} M $[Ga(OH)_4]^-$ solution (pH 13) were transferred to a series of test tubes, and 0.5–3.0 mL of 2.0 × 10^{-3} M CTAB (pH 13) as 0.5-mL increments were added. The contents of the tubes were made to 7 mL with 0.1 M NaOH. Two milliliters of 1% alkanoyl oxine/$CHCl_3$ and 5 mL $CHCl_3$ were added, and the mixture containing equal volumes of aqueous and organic phases was agitated for 15 minutes (equilibration time with CTAB) at 40°C. The organic extracts were separated, evaporated, and wet-ashed. The Ga contents were measured to give the extraction vs volume of CTAB solution curve shown in Fig. 9.

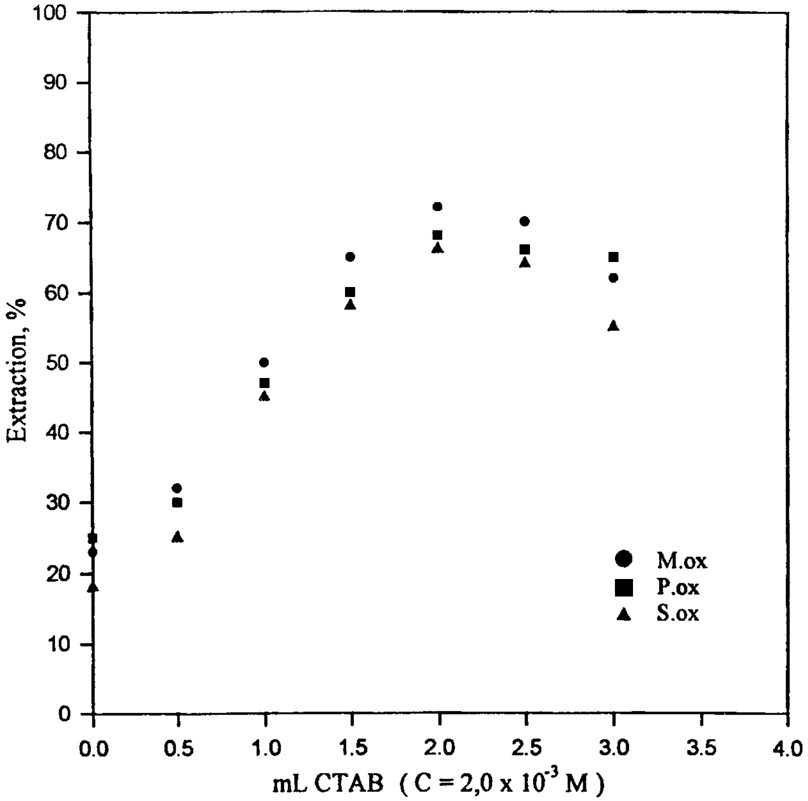


FIG. 9 The dependence of extraction of Ga-alkanoyl oxinates on the volume of 2.0×10^{-3} M CTAB ($V_{aq} = V_{org} = 7$ mL).

DISCUSSION

As the mole-ratio method suggests (Fig. 1), the stoichiometry of the extracted gallium palmitoyl oxinate (as for M.Ox and S.Ox) is 1:2, i.e., one Ga^{3+} ion is chelated to two alkanoyl oxinate molecules. Since coordinatively unsaturated metal complex extractions are open to synergistic interactions with other ligands through adduct formation (12), Ga^{3+} ion with a coordination number of 6 via sp^3d^2 hybridization is capable of accommodating more ligands (Lewis bases) in its coordination sphere when extracted from an alkaline solution (pH 13) as the alkanoyl oxinate chelate. Since the Kelex 100/carboxylic acid systems have exhibited synergism (7), and some ketones have improved Ga extraction with Kelex 100 (8), it was decided to investigate possible synergistic enhancement of the recently developed extraction system for Ga recovery from alkaline solution (3, 5) using alcohols and ketones as Lewis bases for coordinatively saturating gallium. It is apparent that potential synergistic improvements in either extraction rate or recovery efficiency of gallium would be greatly beneficial for the process economies in Ga isolation from the basic aluminate liquor of the Bayer process.

Figures 2–4 show that the order of extraction rate enhancement of modifiers was 2-hexanone $\gg$ MIBK $>$ 1-hexanol. Further, extraction equilibrium was achieved in 30 minutes with 2-hexanone/$CHCl_3$ instead of the 60 minutes required by $CHCl_3$ alone (5). Likewise, alcoholic R·OH as the oxygen donor showed less improvement on the extraction rate of Ga with Kelex 100 than the ketone RR′CO (8), probably due to the stronger Lewis basicity of the ketone.

Aside from the significant rate enhancement, 2-hexanone also exhibited a slight improvement in equilibrium efficiency of extraction at pH 13 when compared to the previously developed extraction system by $CHCl_3$ alone (5); for example, the percentage Ga extraction using M.Ox with hexanone/$CHCl_3$ and pure $CHCl_3$ solvents were 73 and 67% (5), respectively. For a fixed concentration of modifier 2-hexanone (10% by volume), the order of extraction efficiency for alkanoyl oxinates was M.Ox $>$ P.Ox $>$ S.Ox, similar to earlier findings (3, 5) and probably due to increasing steric hinderance in extraction by the longer alkyl chain of the alkanoyl oxine.

In spite of the synergistic interactions, the use of 2-hexanone gave some phase separation problems. 1-Hexanol, similar to the effect of long-chain fatty alcohols like undecanol (5), aided phase separation but did not improve recovery. The synergistic enhancement of 2-hexanone may also be attributed in part to the formation of a microemulsion which may accelerate extractive mass-transfer via quick formation of intermediary unstable species at the interphase (13); a similar synergism has been reported for the $[Ga(OH)_4]^-$–Kelex 100–sodium octanoate extraction system which utilizes an oxine-type extractant and a long-chain carboxylate oxygen-donor (13).

The extraction of Ga-alkanoyl oxinate increased slightly with the volume percentage (5–20%) of 2-hexanone in the organic phase (see Figs. 5–7), which may correspond to shifting the equilibrium of synergic adduct formation to the right.

As a pH of 13 was found to be critical in the extraction of Ga-alkanoyl oxinates by $CHCl_3$ in earlier work (5) and yielded a high selectivity for

Ga over Al, the gallium extraction performance of the 10% 2-hexanone added system needed to be demonstrated around pH 13 and in the presence of Al. The data in Tables 1A, 1B, and 2 show the pH and Al concentration dependence of the extraction system. The alkanoyl oxine-hexanone/chloroform system has a good tolerance of Al at pH 13, and there is considerable Ga extraction even at pH 13.3 with the order M.Ox > P.Ox > S.Ox, indicating a shift in the pH of extractability to higher values. Thus the developed system has better prospects of application to Bayer process aluminate liquor than the alkanoyl oxine/$CHCl_3$ system (5) that requires pH adjustment to 13 using large amounts of carbon dioxide and water of dilution which have an adverse effect on process economies.

Since Ga is transformed from tetrahydroxogallate(III) ion in the aqueous phase to a 1:2 chelate with the acidic extractant in the organic phase, the acid dependence based on the proposed reaction stoichiometry

$$[Ga(OH)_4]^-(aq) + 2(HR\text{-}Ox)(org) \rightleftharpoons [Ga(R\text{-}Ox)_2]^+(org) + 2H_2O + 2OH^-(aq)$$

would be

$$\frac{d \log D_{Ga}}{d\,pH} = -2$$

around pH ≥ 13, which is experimentally reported as −1.93 for Ga-palmitoyl oxinate in Table 1B. Here the $[Ga(R\text{-}Ox)_2]^+$ cationic chelate may form an ion pair with an inorganic anion, e.g., OH^- or Cl^-, present in aqueous solution so as to be extracted. The close agreement between the expected and observed slopes of log D_{Ga} vs pH curve for $13 \leq pH \leq 13.5$ probably shows that two alkanoyl oxine chelating ligands replace the four hydroxyl groups around the Ga(III) ion, releasing two of the latter to the aqueous phase.

Since mixed hydroxo-complexes of the type $[Ga(R'\text{-}Ox)_2)]^- Na^+$, where R'-Ox is the alkylated oxine, may play a role in the extraction of Ga(III) from strongly basic sodium aluminate solution by the use of alkylated hydroxyquinoline (14), it is understandable that a cationic surfactant like CTAB may take part in improving the extraction of some anionic Ga-alkanoyl oxinate mixed complexes (which may coexist in equilibrium with other species) through coulombic interaction of the oppositely charged species. As shown in Fig. 8, CTAB greatly aids extraction kinetics, i.e., the equilibration time is reduced to 15 minutes while slightly increasing the Ga yield in comparison to alkanoyl oxine/$CHCl_3$ alone. The ineffectiveness of sodium lauryl sulfate excludes the possibility of extraction of a cationic species. However, the nonionic triton X-100 improves extraction somewhat, though not as efficiently as CTAB. Further, it is noteworthy that CTAB is most effective at a concentration, i.e., 5.7×10^{-4} M, around its critical micelle concentration, which has been reported as 9.2×10^{-4} M in the literature (15). These observations lead to the possible role of micellar catalysis acting via interfacial mechanisms in operation between the aqueous phase and microemulsions, as suggested (13) for the quaternary ammonium salts of high moleculer weight amines, e.g., CTAB, capable of phase-transfer catalysis.

CONCLUSION

Both the rate and efficiency of extraction of Ga-alkanoyl oxinates, i.e., using myristoyl (M.Ox), palmitoyl (P.Ox), and stearoyl oxine (S.Ox), are significantly improved when either 2-hexanone as modifier or CTAB as surfactant is added to the alkaline aqueous phase $CHCl_3$ extraction system. These extraction aids may act through mechanisms of synergistic adduct formation and micellar catalysis involving the production of microemulsions. For a fixed concentration of the modifier, the order of extraction efficiency by alkanoyl oxinates is M.Ox > P.Ox > S.Ox. By means of the developed method, the pH of extractability of Ga(III) may shift to higher values of better Al tolerance, enabling a more economical process for Ga recovery from basic aluminate solution, e.g., Bayer liquor of alumina manufacture. Thus, the recently developed method of extractive Ga recovery by alkanoyl oxinate/$CHCl_3$ from basic solution (3, 5) has been improved by the incorporation of either 2-hexanone or CTAB into the extraction system, the latter exhibiting the most pronounced effect around its critical micelle concentration.

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