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Solvent Extraction of Gallium(III) from Basic Sodium Aluminate Solution by Alkanoyl Oxines

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ABSTRACT

Alkanoyl oxines have been used for the extraction of gallium from basic solution, especially for the selective recovery of gallium in the presence of excess aluminum from Bayer process sodium aluminate liquor. 5-Alkanoyl-8-hydroxyquinolines (R.CO.Ox), where R is the alkyl group $C_{13}H_{27}$ (myristoyl), $C_{15}H_{31}$ (palmitoyl), and $C_{17}H_{35}$ (stearoyl) were synthesized by the Fries rearrangement from the corresponding acid chloride and sodium oxinate using $AlCl_3$ as catalyst. The synthesized alkanoyl oxines were capable of extracting Ga into kerosene or chloroform at a pH around 13; the selectivity of Ga over Al was high at this pH. The extracted Ga could be stripped into the aqueous phase acidified with HCl without significant loss of the ligand. The extractability of Ga was studied as a function of pH, temperature, time, metal concentration, phase separation acid (undecanol) concentration; and the strippability as a function of HCl concentration. Based on these results, a sequential procedure for the selective separation of Ga from alkaline Bayer process liquor has been developed.

Key Words. Solvent extraction; Gallium(III); Recovery; Separation; Aluminum(III); Sodium aluminate solution; Bayer process liquor; 8-Hydroxyquinoline (oxine); 5-Alkanoyl oxines; Myristoyl oxine; Palmitoyl oxine; Stearoyl oxine

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INTRODUCTION

Gallium is used in the modern electronics industry, especially in the manufacture of gallium arsenide laser diodes. Gallium is a scarce element mainly associated with its immediate neighbors in the periodic table, Al, Zn, and Ge. Hence, gallium may be obtained from zinc and aluminum ores.

Sodium aluminate solutions from the Bayer process of alumina production currently constitute the main raw material for the recovery of gallium. The typical composition of an alkaline Bayer leachate is 100–200 mg/L Ga, 40–60 g/L Al, and 150–240 g/L Na_2O. Thus, selective procedures for Ga recovery are required (1, 2).

Direct electrolysis or amalgamation techniques suffer from high costs, preliminary operations, and environmental risks caused by large stocks of mercury (3–5). Liquid–liquid extraction by the use of 8-hydroxyquinoline (oxine) derivatives is a promising technique for the recovery of Ga from aluminate liquor provided that the problems of stripping efficiency and ligand recovery are solved.

Although oxine and acetyl acetone are good extractants for the recovery of Ga from basic solution (6, 7), these substances may only serve as analytical reagents for Ga extraction since they are too soluble in the aqueous phase. In order to minimize the loss of the extractant, a substituted hydroxyquinoline, 7-dodecenyl-8-hydroxyquinoline, commonly known Kelex 100, has been synthesized (2) and patented (8) for the selective extraction of Ga.

Gallium(III) is extracted into the organic phase as $Ga(Ox)_3$ up to pH 11.7. However, from relatively stronger basic solutions and by using alkylated oxines as extractants, the ion-association complexes (or mixed hydroxo species) of $[Ga(Ox)_2(OH)_2]^-Na^+$ or $Na^+[Ga(OH)_3]OH^-$ tend to be kinetic intermediates in the extraction of gallium oxinate (9). The overall Ga extraction equilibrium in NaOH solution using Kelex 100 has been expressed by a cation-exchange reaction (9):

$$Ga(OH)_4^-(aq) + 3HOx(org) \rightleftharpoons Ga(Ox)_3(org) + OH^-(aq) + 3H_2O$$

Although the selectivity of Kelex 100 in Ga/Al separations from strongly alkaline solution is good, the rate of phase transfer is low, and several modifiers, such as long-chain fatty alcohols (decanol, 2-ethyl hexanol, etc.) and long-chain carboxylic acids, have to be added in order to obtain a high transfer rate (10) and to prevent third-phase formation (1). This enhanced transfer rate has been attributed to the formation of a microemulsion structure in the organic phase by the surfactant-type functioning of modifiers (11, 12).

Koide et al. (13) used oxine-type surfactants (5-alkanoyl-8-quinolinol, R_nOx) as ion-flotation collectors. Selective Ga flotation from an Al (100 ppm)–Ga (20 ppm) mixture was observed by using R_8Ox alone or $R_{12}Ox$ along with *N*-alkyl pyridinium bromides in the pH region 10.0–13.3. However, in a strongly alkaline region, the floatability was lower than the extractability of Ga.

In the present study the alkyl chain of the alkanoyl oxines was extended to higher carbon numbers for the purpose of maintaining the chelating ability of oxine while limiting its aqueous phase solubility.

EXPERIMENTAL

Reagents and Solutions

Oxine (8-hydroxyquinoline), myristic acid, palmitic acid, stearic acid, thionyl chloride (for synthesis), undecanol, nitrobenzene, chloroform, carbon sulfide, anhydrous aluminum chloride, sodium carbonate, sodium hydroxide, nitric acid, hydrochloric acid (extra pure), gallium (LAB), and aluminum foil (GR) were purchased from E. Merck.

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. Sodium tetrahydroxogallate(III) and aluminate solutions were prepared by dissolving suitable aliquots of the corresponding stock solutions in NaOH of the desired concentration. A 1% hydroxyquinoline solution was prepared in EtOH. The dilute and concentrated alkanoyl oxine solutions in EtOH and $CHCl_3$ were prepared in 1 and 10% concentrations, respectively. Bayer process sodium aluminate liquor was obtained from the Seydişehir Aluminum Plant located in Konya, Turkey.

Syntheses

5-Alkanoyl-8-hydroxyquinolines were prepared by the Fries rearrangement (14) using two different synthesis routes.

Route 1

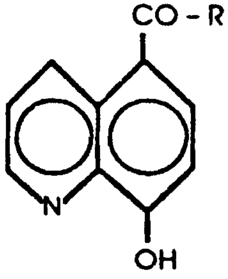
A modified procedure of Banthorpe's synthesis (15) was followed. The acid chlorides of myristic acid ($C_{13}H_{27}COOH$), palmitic acid ($C_{15}H_{31}COOH$), and stearic acid ($C_{17}H_{35}COOH$) were prepared by refluxing an excess of thionyl chloride ($SOCl_2$) with the acid on a water bath and distilling off the unreacted $SOCl_2$. A mixture containing 0.05 mole of the acid chloride and 0.05 mole of sodium oxinate was homogenized in a flask on a water bath at 70°C. After cooling, 50 mL nitrobenzene was added. A slight excess of the stoichiometric amount (1 : 1 mole/mole oxine) of anhydrous $AlCl_3$ was added slowly with continuous stirring while the mixture was cooled to 5°C. The flask was refluxed on an oil bath to 85–110°C for 24 hours. When the evolution of HCl gas ceased, the reaction mixture was cooled and 6 M HCl solution was carefully added to it. Nitrobenzene was removed by steam distillation, and the residual mass was poured into 2 L dilute acid, resulting in the separation of orange-brown crystals of R_nOx, where R_n is the *n*-carbon atom containing the alkanoyl group. The product was thoroughly washed with water, neutralized with a 5% Na_2CO_3 solution, rewashed, and finally crystallized twice from methanol.

Route 2

Route 1 was followed with the exception that CS_2 was used instead of nitrobenzene (16). The intermediary product following $AlCl_3$ reaction was heated on an oil bath to 85–110°C for 24 hours without the need of refluxing. The final product was crystallized from MeOH.

There are precautions that should be taken in the above syntheses. The initial reaction with acid chloride in both cases should be carried out with Na-oxinate and not oxine itself. Even traces of $SOCl_2$ residues should be avoided in Route 1. Anhydrous $AlCl_3$ should be added to the homogenized mixture of the acid chloride and sodium oxinate, and not directly on the acid chloride. The products were tested for their deep green color reaction with $FeCl_3$.

It is known that in the Fries rearrangement of the alkanoic acid Ox ester (15, 17), the acyl group usually migrates to the *p*-position with respect to the –OH group of oxine at the relatively low temperatures employed in the syntheses. The structures of the synthesized 5-alkanoyl oxines were confirmed by elemental analysis and IR spectroscopy.



where R = $C_{13}H_{27}$ (M.Ox), $C_{15}H_{31}$ (P.Ox), and $C_{17}H_{35}$ (S.Ox).

Characterization of Alkanoyl Oxines

The elemental analysis results of the synthesized alkanoyl oxines were as follows. Percentages expected: Carbon: 77.75, 78.33, and 78.83%; hydrogen: 9.30, 9.66, and 9.98%; nitrogen: 3.94, 3.66, and 3.41% for myristoyl ($C_{13}H_{27}CO$–), palmitoyl ($C_{15}H_{31}CO$–) and stearoyl ($C_{17}H_{35}CO$–) oxines, respectively.

Percentages found: Carbon: 77.40, 78.73, and 78.80%; hydrogen: 9.58, 9.76, and 10.00%; nitrogen: 4.01, 3.65 and 3.40% for myristoyl, palmitoyl, and stearoyl oxines, respectively.

The characteristic IR bands of the alkanoyl oxines (R_nOx, where R_n = $C_{13}H_{27}CO$, $C_{15}H_{31}CO$, and $C_{17}H_{35}CO$) appeared at the following wavenumbers: $\nu_{C=O}$ = 1670 cm^{-1}, ν_{OH} (phenol) = 2950 cm^{-1}, $\nu_{C=C,\,C=N}$ = 1510, 1570, and 1620 cm^{-1}, and ν_{CH} in $Ar.CO.CH_2R$ = 1370 cm^{-1}.

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. Some metal determinations were confirmed by AAS using a Perkin-Elmer 300 flame atomic absorption spectrometer. The IR spectra of the synthesized oxine derivatives were recorded with a Perkin-Elmer 599 model infrared spectrometer. The pH values of the solutions were measured with a Metrohm E-512 pH-meter.

Extraction and Spectrophotometric Determination of Gallium

Gallium(III) oxinate, $Ga(Ox)_3$, was extracted into $CHCl_3$ at pH 7, and its absorbance was measured against the reagent blank at 392 nm, enabling the spectrophotometric determination of Ga(III) according to the procedure of Moeller et al. (18). The molar absorptivity of gallium oxinate was $\epsilon = 6.5 \times 10^3 L{\cdot}mol^{-1}{\cdot}cm^{-1}$.

The extractability of Ga and Al oxinates and alkanoyl oxinates from the aqueous phase at various pH values was tested by the following procedure: 2 mL of a-1000 ppm stock solution of Ga(III) or Al(III) was diluted to approximately 50 mL with H_2O and made alkaline with NaOH. The resulting sodium tetrahydroxogallate(III) and aluminate(III) solution was adjusted to the desired pH by the aid of HCl and NaOH, then diluted to 100 mL with H_2O in a volumetric flask. To 5 mL of this 20 ppm Ga (or Al) solution, 2 mL of 1% alkanoyl oxine solution in $CHCl_3$, followed by 7 more mL of $CHCl_3$, were added, and extraction was carried out in a thermostatic bath kept at 40°C for 60 minutes. The organic extract was separated, stripped with 6 M HCl, and Ga (or Al) determination was made in the aqueous phase by using Moeller's method (18) and AA spectrophotometry.

The effect of different parameters (other than pH) on the extraction equilibrium was tested by the use of a 20-ppm Ga solution at pH 13. Thus, the extractabilities of gallium alkanoyl oxinates were investigated as functions of temperature, time, Al(III) concentration, and undecanol (phase-separation aid) concentration.

The partition coefficients of the alkanoyl oxine ligands in the chloroform–water system were measured by contacting equal volumes of 0.25% alkanoyl oxine in $CHCl_3$ and water between pH 10 and 13, followed by spectrophotometric determination of the residual oxine in $CHCl_3$ at 370 nm.

The effect of HCl concentration on the stripping equilibrium of Ga(III) alkanoyl oxinate from the organic extract was studied by using an equal volume (7:7 mL) of HCl of the desired molarity. Gallium was stripped from an organic phase previously equilibrated with a pH 13 Ga solution.

Gallium(III) Extraction from a Synthetic and Real Sodium Aluminate Solution

The extractability of Ga(III) and Al(III) alkanoyl oxinates from a pH 13 aqueous solution was studied as a function of metal concentration in the range of 25–250 ppm Ga and 500–6000 ppm Al with the purpose of estimating the purity of the recovered Ga. The extractant was a 10% solution of the alkanoyl oxine in $CHCl_3$. The contact period of the aqueous and organic phases was 60 minutes at 40°C.

Two synthetic Na-aluminate solutions at pH 13 were prepared containing 300 ppm and 700 ppm Al and equimolar (70 ppm) Ga. These solutions were subjected to five successive stages of extraction and stripping in order to determine Ga recoveries with a certain level of Al contamination. The extractant and stripping solutions were 10% alkanoyl oxine and 6 M HCl, respectively.

The alkaline sodium aluminate solution (Bayer process liquor) obtained from the Seydişehir Aluminum Plant contained 171 mg Ga/L, 27 g Al/L, and 87 g Na/L. Carbon dioxide was bubbled through this liquor until turbidity was noticeable. The precipitate was allowed to settle, filtered off, and the pH of the filtrate was measured as 13.50. The filtrate was diluted with an equal volume of water to decrease the pH to the value required for extraction, i.e., pH 13.0. Five successive stages of extraction and stripping were carried out by the conventional procedure using 10% alkanoyl oxine/$CHCl_3$ and 6 M HCl solutions, respectively. The purity of the extraction-recovered Ga was recorded.

RESULTS AND DISCUSSION

The extractability of 20 ppm solutions of Ga(III) and Al(III) from an aqueous solution of varying pH using 1% oxine (8-hydroxyquinoline) in $CHCl_3$ is shown in Fig. 1. It can be seen from Fig. 1 that Al-oxinate is not extracted at pH 13 while Ga-oxinate is extracted appreciably at this pH. However, the loss of sodium oxinate in the aqueous phase would not

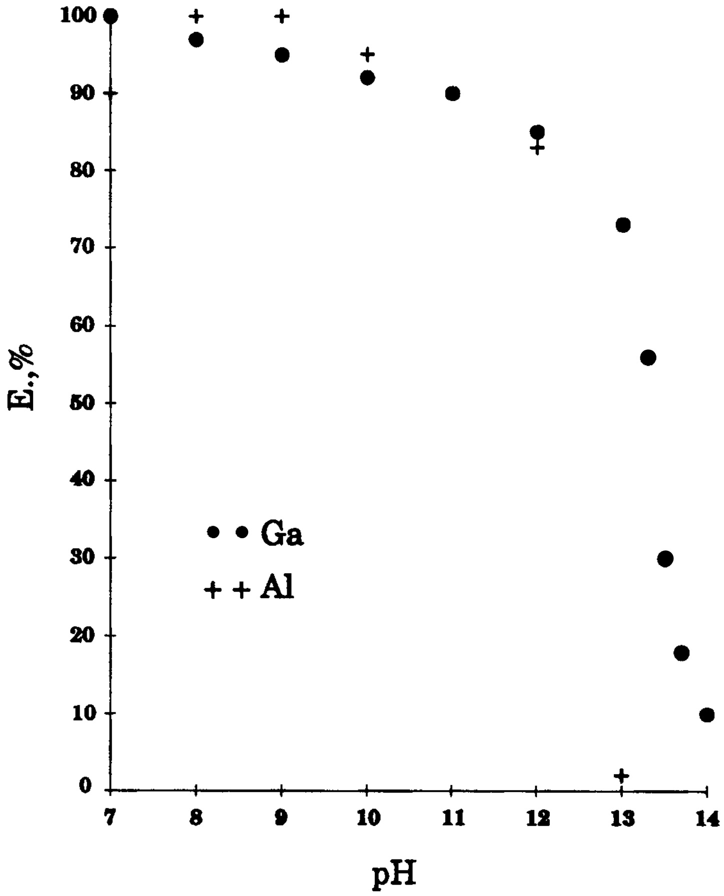


FIG. 1 The extractability of Ga and Al oxinates with $CHCl_3$ as a function of pH (*E*, %: Percentage ratio of extracted metal concentration to total metal concentration).

allow an economical process for Ga recovery. The data in Fig. 1 refute Lacroix's prediction (19) of the quantitative extractability of Ga-oxinate at any pH above 2, and they support Moeller's findings (18) of decreased Ga extraction above pH 7. If Ga extraction were to be expressed merely by the formation of a neutral chelate:

$$\mathrm{Ga^{3+}(aq)} + n\mathrm{HOX(org)} \rightleftarrows \mathrm{M(Ox)}_n\mathrm{(org)} + n\mathrm{H^+(aq)}$$

then the distribution coefficient of Ga would be

$$D_{\mathrm{Ga}} = \frac{P_c K_c[\mathrm{HOx}](\mathrm{org})}{P_r^n K_r^n[\mathrm{H^+}]^n}$$

or

$$\log D_{\mathrm{Ga}} = \mathrm{constant} + \log[\mathrm{HOx}](\mathrm{org}) + n\mathrm{pH}$$

where P_c and K_c are the partition coefficient and formation constant of the chelate complex, respectively, and P_r and K_r are the partition coefficient and association constant (reciprocal of acidity constant) of the free oxine, HOx, respectively (20). In other words, the logarithm of the distribution coefficient of Ga would have been proportional to the aqueous phase pH, as Lacroix (19) had predicted for the extraction of Ga-oxinate. However, this is not the case because the predominant Ga species in aqueous solution in alkaline medium is $\mathrm{Ga(OH)_4^-}$ [or $\mathrm{Al(OH)_4^-}$ in the case aluminum (21)], and the major extraction equilibrium would be expressed by the equation

$$\mathrm{Ga(OH)_4^-} + 3\mathrm{HOx(org)} \rightleftarrows \mathrm{Ga(Ox)_3(org)} + \mathrm{OH^-} + 3\mathrm{H_2O}$$

which would favor the reactants at high pH, i.e., the equilibrium would shift to the left in alkaline medium. In that case, the distribution coefficient of gallium, D_{Ga}, could be approximated by

$$D_{\mathrm{Ga}} = \frac{[\mathrm{Ga(Ox)_3}](\mathrm{org})}{[\mathrm{Ga(Ox)_3}](\mathrm{aq}) + [\mathrm{Ga(OH)_4^-}](\mathrm{aq})}$$

which may be reduced to

$$D_{\mathrm{Ga}} = \frac{P_c}{1 + \dfrac{\beta_4[\mathrm{OH^-}]^4}{K_c[\mathrm{Ox^-}]^3}}$$

where β_4 and K_c are the cumulative formation constants of the tetrahydroxogallate(III) and tris-oxinatogallium(III) species, respectively. Since

$$[\mathrm{Ox^-}] = \frac{[\mathrm{HOx}](\mathrm{org})[\mathrm{OH^-}]}{P_r K_r K_w} \qquad (K_w = K_{\mathrm{water}} = [\mathrm{H^+}][\mathrm{OH^-}])$$

by substituting and reorganizing terms, it may be deduced that

$$D_{\mathrm{Ga}} = \frac{P_c K_c [\mathrm{HOx}]^3(\mathrm{org})}{P_r^3 K_r^3 K_w^3 \beta_4 [\mathrm{OH}^-]}$$

the distribution coefficient of gallium(III) should be inversely proportional to the OH^- ion concentration. This presents an oversimplified scheme of gallium extraction in alkaline medium where the only species extracted by the organic solvent is $Ga(Ox)_3$, and the predominant aqueous species are $Ga(Ox)_3$ and $Ga(OH)_4^-$. When the complete hydrolytic equilibria is envisioned, the respective complexes of $Ga(OH)_6^{3-}$ ($\log \beta_6 = 40.3$) and

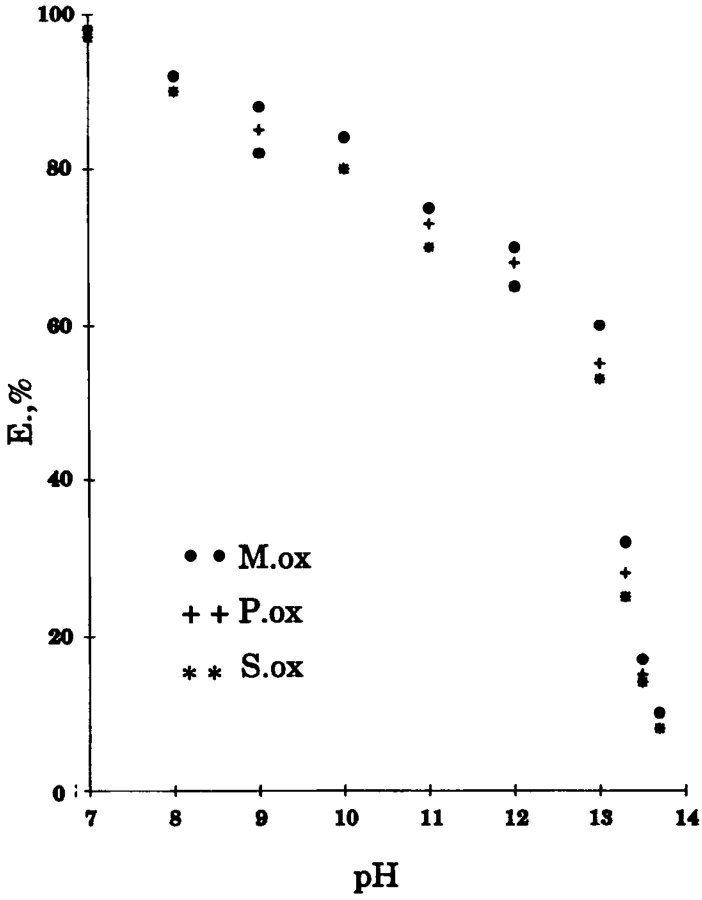


FIG. 2 The extractability of Ga alkanoyl oxinates as a function of the aqueous phase pH (M.Ox, P.Ox, and S.Ox are 5-myristoyl, palmitoyl, and stearoyl oxines, respectively).

$Ga(Ox)_3$ (log K_c = 40.8) are of comparable strength, necessitating the usage of a concentrated solution of the oxine derivative to shift the extraction equilibria to the right at elevated pH.

The Ga and Al curves in Fig. 1 suggest that Ga may be selectively recovered as the oxinate complex from an alkaline solution of suitable pH in the presence of Al. Thus the alkanoyl oxines have been synthesized as potential commercial extractants for the selective separation of Ga from Al without any significant loss of the ligand in the aqueous phase.

The Ga extraction efficiencies of the alkanoyl oxines are shown in Fig. 2. The significant extraction yield of gallium alkanoyl oxinate observed at pH 13.0 (53–60%) falls to 8–10% at pH 13.7 depending on the alkyl

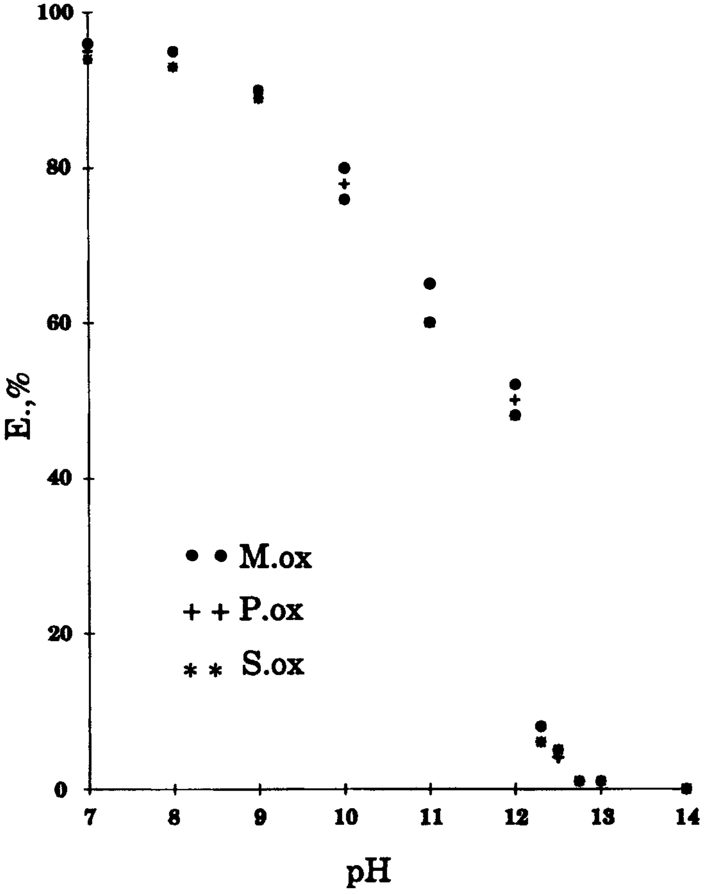


FIG. 3 The extractability of Al alkanoyl oxinates as a function of the aqueous phase pH.

group R. Similar curves were drawn for aluminum alkanoyl oxinate (Fig. 3), showing that there is negligible extraction of Al at pH ≥ 13.

The distribution coefficient of Ga and Al has been computed by

$$D_M = \Sigma[M](org)/\Sigma[M](aq)$$

Extractability is defined as the percentage ratio of the extracted metal concentration to the total metal concentration:

$$\begin{aligned} E, \% &= \frac{\Sigma[M](org)}{\Sigma[M](total)} \times 100 \\ &= \frac{\Sigma[M](org)}{(\Sigma[M](org) + \Sigma[M](aq))} \times 100 \\ &= \frac{D_M}{(D_M + 1)} \times 100 \end{aligned}$$

The distribution coefficients are depicted in Table 1 as a function of pH. The relative standard deviation of eight replicate determinations of the distribution coefficients varied between 3.77 and 7.25% within the pH range 12.0–13.0. The uncertainties [i.e., ($t_{.95}$ × standard deviation) × (no. of measurements)$^{-1/2}$] in D_{Ga} values in Table 1 between pH 12 and

TABLE 1

The Distribution Coefficients (D_M) of Ga(III) and Al(III) as a Function of pH using $R_nOx/CHCl_3$ as Extractant

	Alkanoyl oxiner					
	M.Ox		P.Ox		S.Ox	
pH	D_{Ga}[a]	D_{Al}	D_{Ga}[a]	D_{Al}	D_{Ga}[a]	D_{Al}
7.0	49	24	49	19	32	17.3
8.0	11.5	19	9	13.3	9	11.5
9.0	7.3	9	5.7	9	4.6	8.1
10.0	5.3	4.0	4.0	3.8	4.0	3.0
11.0	3.0	1.9	2.7	1.6	2.3	1.5
12.0	2.3	1.1	2.2	1.0	1.9	1.0
12.30	2.2	0.09	2.1	0.06	1.8	0.06
12.50	2.0	0.05	2.0	0.04	1.7	0.05
12.75	1.7	0.01	1.7	0.01	1.4	0.01
13.0	1.5	0.01	1.4	0.01	1.3	0.01

[a] The uncentainty at the 95% confidence level between pH 12 and 13 was between ±0.06 and 0.07.

[b] The uncentainty at the 95% confidence level between pH 12 and 13 was between ±0.05 and 0.06.

13 were ±(0.06–0.07) for M.Ox and P.Ox, and ±(0.05–0.06) for S.Ox at the 95% confidence level.

If selectivity (S) is defined as

$$S = D_{\mathrm{Ga}}/D_{\mathrm{Al}}$$

then the preferential extraction of Ga over Al is as shown in Fig. 4 with S = function (pH) plots. There is reasonable selectivity in the extraction system around pH 13, which might enable the recovery of relatively pure Ga from alkaline sodium aluminate solution.

The alkanoyl oxine/$CHCl_3$ extraction of Ga was studied as a function of contact time (Fig. 5) at 40°C, and for temperature (Fig. 6) by contacting

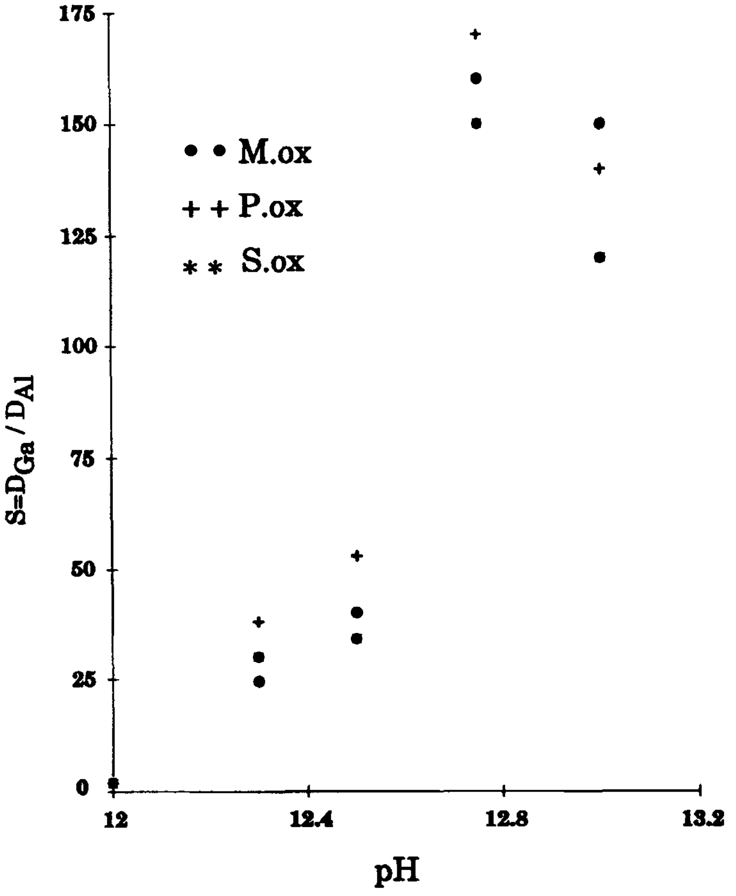


FIG. 4 The preferential extraction (S: selectivity) of Ga over Al as a function of pH.

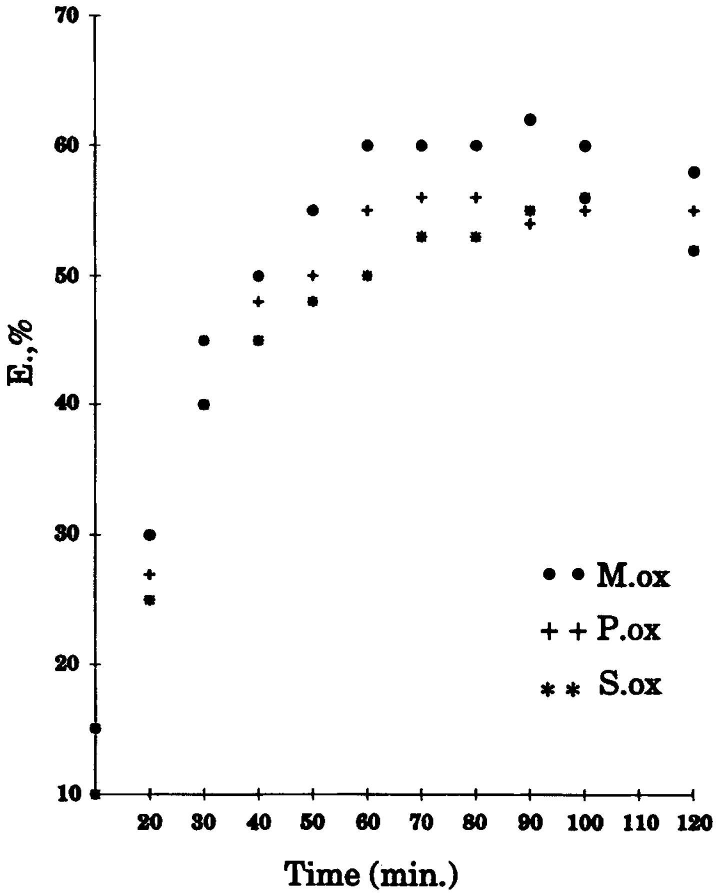


FIG. 5 The time dependence of Ga extraction by alkanoyl oxine in $CHCl_3$.

the phases for 60 minutes, both from an aqueous solution of pH 13. The optimal Ga extraction pH, temperature, and contact time were established as 13.0, 40°C, and 60 minutes, respectively.

All the alkanoyl oxines showed a gradual decrease of partition coefficients from approximately 900 to 830 between pH 10 and 13. Unlike the parent compound, 8-hydroxyquinoline, the loss of oxine derivatives in alkaline aqueous solution was negligible, therefore the ligands were predominantly in the organic phase at pH 13, i.e., the optimal pH for Ga extraction. Maintaining a high concentration of the ligand in the organic phase favors gallium extraction.

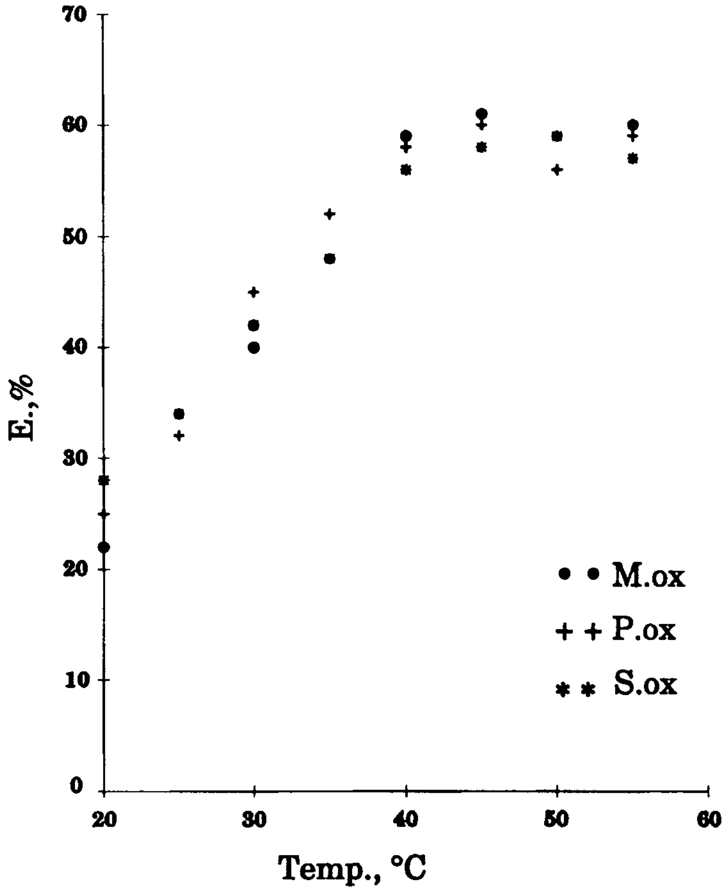


FIG. 6 The temperature dependence of Ga extraction by alkanoyl oxine in $CHCl_3$.

The extraction was not negatively affected to a significant extent by the presence of long-chain fatty alcohols such as undecanol because the phase separation is aided by up to 35% by volume of the alcohol in $CHCl_3$ (Fig. 7). Leveque and Helgorsky (2) have likewise reported a slight decrease of Ga extraction with increasing concentration of *n*-decanol up to a volume percentage of 20% in Kelex 100/kerosene solution. The modifier, e.g., undecanol, aids phase separation and prevents third-phase formation during acidic stripping of the loaded solvent. However, increasing the modifier concentration above a certain level leads to a loss of selectivity toward Ga with respect to Na (2). This may partly be explained by a slight increase in the dielectric constant of the modified solvent, enabling the

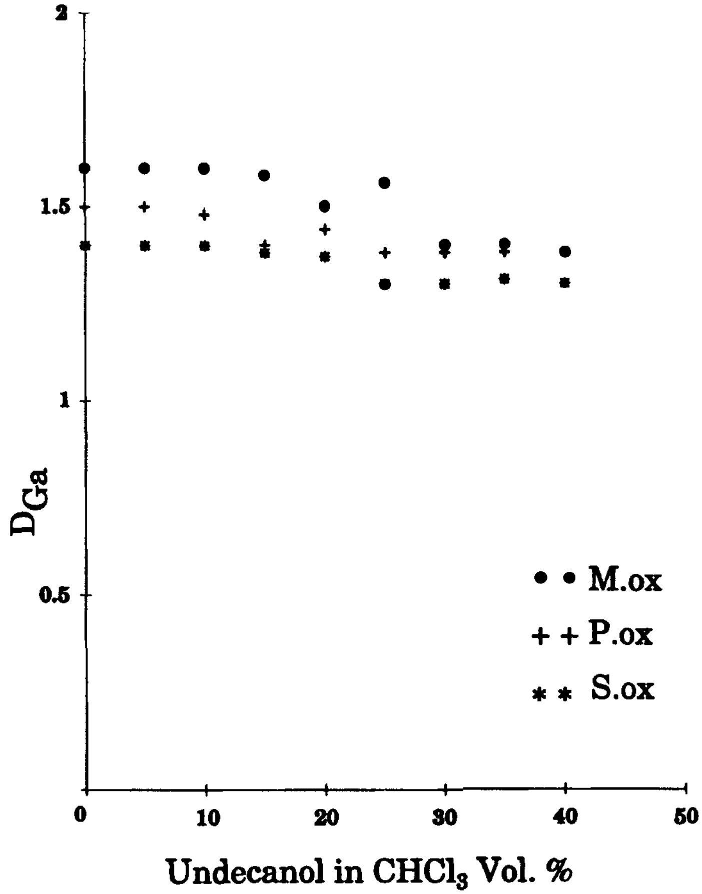


FIG. 7 The distribution coefficient of Ga as a function of undecanol concentration in the extractant solution.

extraction of more ion-pairs. Further, certain association reactions of the extracted species in the organic phase may be suppressed by to the modified solvent, giving rise to a slight decrease of D_{Ga} with increasing undecanol concentration.

The stripping yield of the Ga-alkanoyl oxinate extracted at pH 13 was investigated as a function of the acidity (HCl concentration) of the stripping solution (Fig. 8). It may be observed that almost all Ga extracted at pH 13 using $R_nOx/CHCl_3$ is stripped back into the aqueous phase by 6 M HCl.

The metal concentration dependence of Ga and Al extraction from a pH 13 aqueous solution using alkanoyl oxines (10% solution in chloroform)

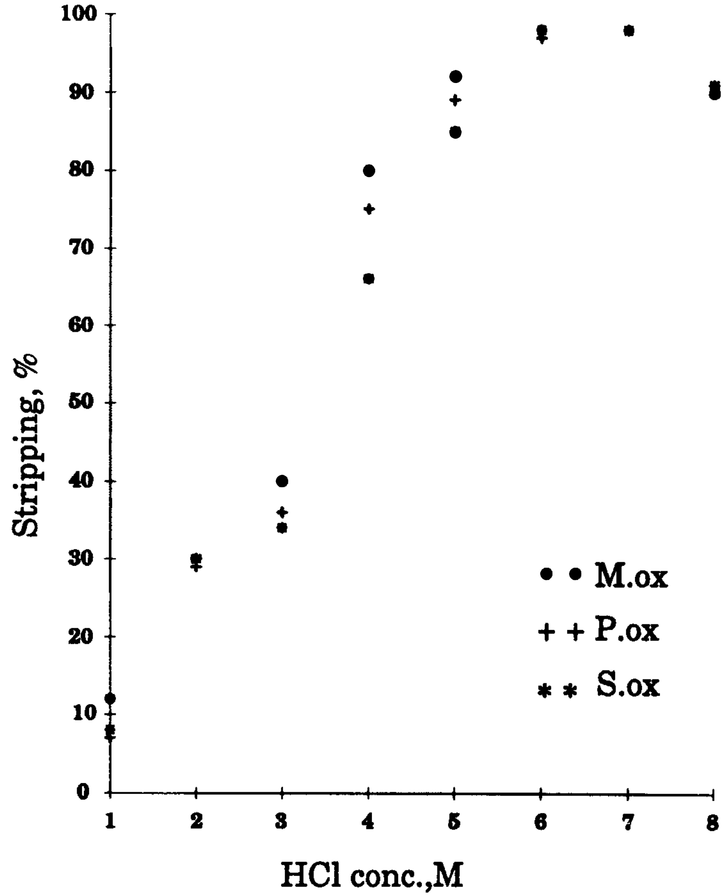


FIG. 8 The stripping yield of the extracted Ga as a function of the aqueous phase HCl concentration.

TABLE 2
Gallium Recoveries of Synthetic Sodium Aluminate Solutions after Five Successive Extraction–Stripping Stages

	M.Ox		P.Ox	
	Solution I	Solution II	Solution I	Solution II
Ga concentration (ppm) in final solution	42.46	43.26	37.49	38.25
Ga recovery, %	61	62	54	55
Al concentration (ppm) in final solution	2.4	2.3	2.5	3.5
Al recovery, %	0.008	0.003	0.008	0.005

is shown in Fig. 9. Chloroform as the solvent of the extractant solution may be substituted for with cheaper kerosene. Thus, if the carbonation process (22) is applied to the Bayer aluminate liquor to partially remove the Al excess accompanying Ga prior to extraction, the purity of the extraction-recovered Ga may be estimated by evaluating the data in Fig. 9.

The Ga recoveries with a certain level of Al contamination from two synthetic sodium aluminate solutions at pH 13 (Solution I, 70 ppm Ga +

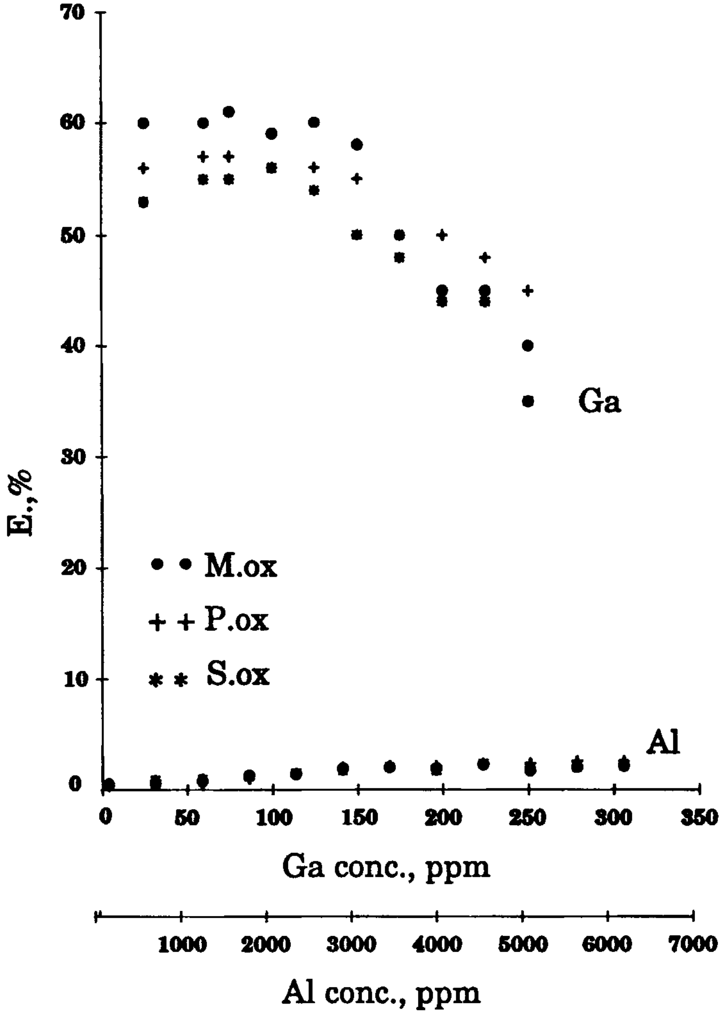


FIG. 9 The metal concentration dependence of Ga and Al extraction from a pH 13 solution using a 10% solution of R_nOx in $CHCl_3$ as extractant.

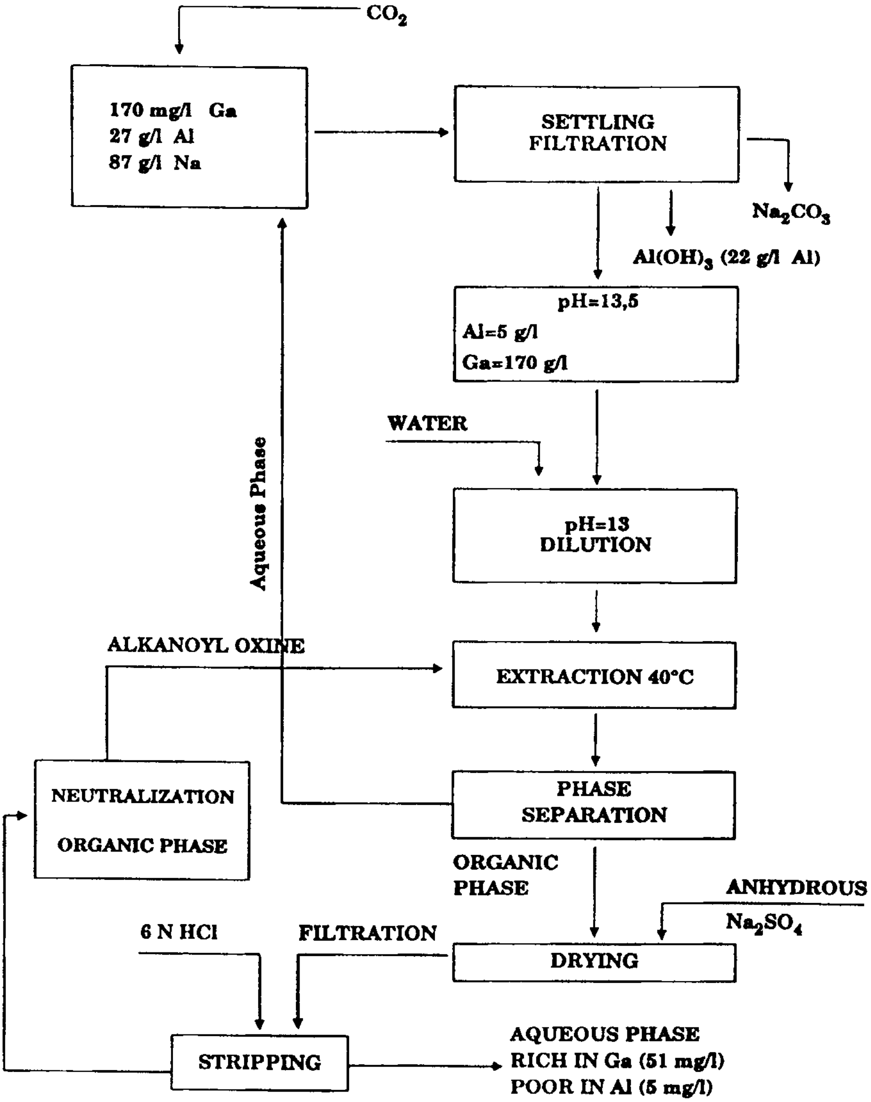


FIG. 10 Gallium recovery from a real sodium aluminate liquor (of the Bayer process) using the recommended procedure sequentially after carbonation.

300 ppm Al; Solution II, 70 ppm Ga + 700 ppm Al) after five successive extraction–stripping stages are listed in Table 2. It is apparent that a gallium product of reasonable purity may be obtained from a synthetic sodium aluminate solution by the recommended procedure applied sequentially.

The real sodium aluminate liquor (Bayer leach solution) supplied from the Seydişehir Aluminum Plant was subjected to the same sequential procedure (consisting of five extraction–stripping stages) after preliminary separation of the excess $Al(OH)_3$ by carbonation (Fig. 10).

The Ga contained in the real aluminate liquor was recovered in 35, 32, and 30% yields (contaminated with 5 ppm aluminum) using the above procedure (see Fig. 10) with M.Ox, P.Ox, and S.Ox, respectively. Myristoyl oxine produced the best results for Ga recovery.

CONCLUSION

The synthesized alkanoyl oxines in chloroform are capable of extracting gallium(III) at a pH around 13 with an optimal contact period of 60 minutes at 40°C. The extracted Ga may be stripped with 6 M HCl solution, and the ligand may be regenerated without significant loss. The selectivity of the extractant for Ga over Al is high at pH 13. Among the synthesized compounds, myristoyl oxine yields the best performance in regard to extraction and stripping. Undecanol in the extractant solution effectively prevents third-phase formation without significant reduction of the distribution coefficient of Ga. More concentrated solutions of alkanoyl oxines may be used for recovering Ga from both synthetic and real sodium aluminate solutions, and kerosene may be substituted for chloroform as the solvent. Following a preliminary separation of excess $Al(OH)_3$, a gallium product of reasonable purity has been isolated from Bayer process liquor by using the recommended procedure sequentially.

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