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Liquid–Liquid Extraction of Gallium(III) with LIX 26

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ABSTRACT

A method for the extraction of gallium(III) with LIX 26 in n-decanol as a moderator has been studied. The extraction of gallium(III) was found to be quantitative with 10 vol% LIX 26 (alkyl substituted 8-hydroxyquinoline) as extractant, 10 vol% n-decanol as modifier and kerosene as diluent. At 1:1 organic to aqueous phase ratio at 30°C, 99% of gallium was recovered in 30 min. The effect of various parameters such as LIX 26 concentration, n-decanol concentration, time to achieve equilibrium, variation of pH, and temperature on the extraction of gallium(III) were also studied. The stoichiometry of the extracted species of gallium(III) was determined.

The extraction of gallium(III) proceeds through a cation exchange mechanism and the extracted species is in the GaL_3 form. The equilibrium constant and thermodynamic functions Enthalpy (ΔH), Entropy (ΔS), and Free Energy (ΔG) in the extraction of gallium(III) with LIX 26 have been evaluated. The extraction reaction was an exothermic process.

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Key Words: Gallium(III); Extraction; LIX 26; Thermodynamic parameters; Kerosene; n-decanol.

INTRODUCTION

Gallium has significant commercial importance because gallium arsenide is used for manufacturing fast computer chips. The metal is also used for optoelectronics, semiconductor lasers, solar cells, and microwave devices.[1–3] It is also used for high-temperature thermometers because of its linear expansion at high temperature. Gallium is present in bauxite ore in trace amounts and is leached during extraction of aluminum by the Bayer process.[4]

Selective extraction of gallium from the Bayer process liquor was first reported by Leveque and Helegorsky using 8.5 vol% of Kelex 100 (a 7-alkyl substituted-8 hydroxyquinoline) (Sherex Chemicals, U.S.A.) in combination with 10 vol% of n-decanol and 81.5 vol% of kerosene, which were used as a modifier and diluent, respectively.[5] Studies conducted by Borgess and Masson[6] on the solvent extraction of gallium from a weak Brazilian Bayer process liquor containing 110 mg/L Ga, 16–25 g/L Al_2O_3, and 108–120 g/L of Na_2O using 10 vol% Kelex 100, 5 vol% Versatic 10, 8 vol% n-decanol, and 77 vol% kerosene, showed 90% recovery of gallium in 2 min. The solvent extraction of gallium using 12 vol%, Kelex 100, 12 vol% isodecanol and kerosene from a concentrated Bayer process liquor containing 190 ± 20 mg/L resulted in 80% recovery in 3 hr.[7] Extraction of gallium from the Bayer process liquor into the organic phase consisting of 14 vol% Kelex 100, 10 vol% iso-decanol, and 76 vol% of kerosene was found to be 89.7% in a 4-hr period.[8] Further investigations have been reported in the literature on the extraction of gallium from alkali solution using Kelex 100.[9–11]

Gallium is extracted with OPAP (octyl phenyl acid phosphate) by cation exchange. The extraction is well described by four simultaneous reactions, leading to formation of four metal extractant complexes.[12] The equilibrium constant and thermodynamic functions Enthalpy (ΔH), Entropy (ΔS), and Free Energy (ΔG) in the extraction of gallium(III) with PC-88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) have been evaluated. The extraction reaction was an endothermic process.[13] Gallium can be separated from high concentrations of aluminum, iron, nickel, titanium, vanadium, copper, zinc, sulfate, fluoride, and chloride by extraction with a commercial polyether type of polyurethane foam (PUF) from 3 M sulfuric acid and 3 M sodium chloride mediums, with at least 92% efficiency. Gallium stripping was fast and quantitative with ethanol solution.[14] Gallium(III) has been extracted with Cyanex 921 (tri-n-octylphosphineoxide) in toluene in the pH range 4.5–6.0 and stripped with 2 M HNO_3. The effects of pH, equilibration period, diluents, diverse ions, and stripping agents on the extraction of gallium(III) have been studied. The equilibrium constant and the thermodynamic parameters ΔH, ΔS, and ΔG have been evaluated. The method has been extended for binary and multicomponent separation of gallium(III).[15]

It has been found from literature that alkyl-substituted-8-hydroxyquinoline chelating reagents are good extractant for gallium extraction in higher pH range. The present work has been undertaken considering almost similar structure of LIX 26 with the structure of alkyl-substituted-8-hydroxyquinoline having higher molecular weight. A systematic study of the extraction of gallium(III) with 10 vol% LIX 26, 10 vol% n-decanol as modifier and kerosene as diluent at different temperatures has been conducted. The various parameters, such as effect of pH, concentration of LIX 26 and n-decanol, and different thermodynamic parameters, have been studied.

EXPERIMENTAL

Reagents

The extractant LIX 26 (alkyl-substituted-8-hydroxyquinoline) supplied by Henkel Corporation (U.S.A.) was used without any further purification. An accurately weighed amount of gallium metal (purity 99.99%, Koch-light Limited, England) was dissolved in minimum amount of aqua regia and diluted with double distilled water.[16] The commercial grade kerosene by Indian Oil, India was triple distilled under vacuum. All inorganic reagents used in this study were of analytical grade.

Procedures

An aliquot of gallium(III) was taken for all experimental studies and equilibrated with LIX 26 in kerosene after adjusting the pH of the aqueous solution. Experiments were conducted by preparing the organic phase of the required composition and mixing it thoroughly in a (1-L) five-neck flat bottom flask using a mechanical stirrer at 1000 ± 10 rpm. The flask was immersed in a water bath controlled by a Beckmann thermometer to maintain uniform temperature ± 1°C. Gallium concentrations were determined by flame atomic absorption spectrometry (using acetylene as fuel and nitrous oxides as oxidant)

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in aqueous phase before and after extraction, and the respective concentration in the organic phase were calculated from the difference.

All the instruments used in the investigation were calibrated by using standard quality ensurance practices. The relative standard deviations of the experimental results are kept within 1.5%. Unknown samples were measured by using Perkin Elmer AAS (model no. 2380) with standard solutions.

RESULTS AND DISCUSSION

Effect of Gallium Concentration

The nature of extracted species of gallium by LIX 26 in kerosene and n-decanol as a moderator was investigated by varying the initial concentration of the gallium solution in aqueous phase. It was observed that the distribution constant (K_D) was independent of the gallium concentration, which is a clear indication that the extracted species is mononuclear.

Effect of Extractant Concentration

The volume percentage of LIX 26 in kerosene was varied from 5 to 20 vol%. From the data it was found that with increase in volume percentage of LIX 26 the extraction of gallium(III) increases (Fig. 1). The results indicated that the optimum concentration of LIX 26 was 10 vol% for nearly complete extraction of gallium by a single-stage operation. From the above experiment it was also investigated that three ligands react with one gallium(III) ion by the plot of $\log K_D$ *vs.* log [LIX 26], ([LIX 26] = volume percentage of LIX 26), with slope 2.89 which is close to 3 (Fig. 1A).

Effect of Shaking Time

For the purpose of examination of the effect of shaking time for formation of complex and subsequent extraction into organic phase, experiments were carried out with various shaking times of aqueous and organic contents. It was observed that the gallium was completely extracted within 30 min of shaking (Fig. 2).

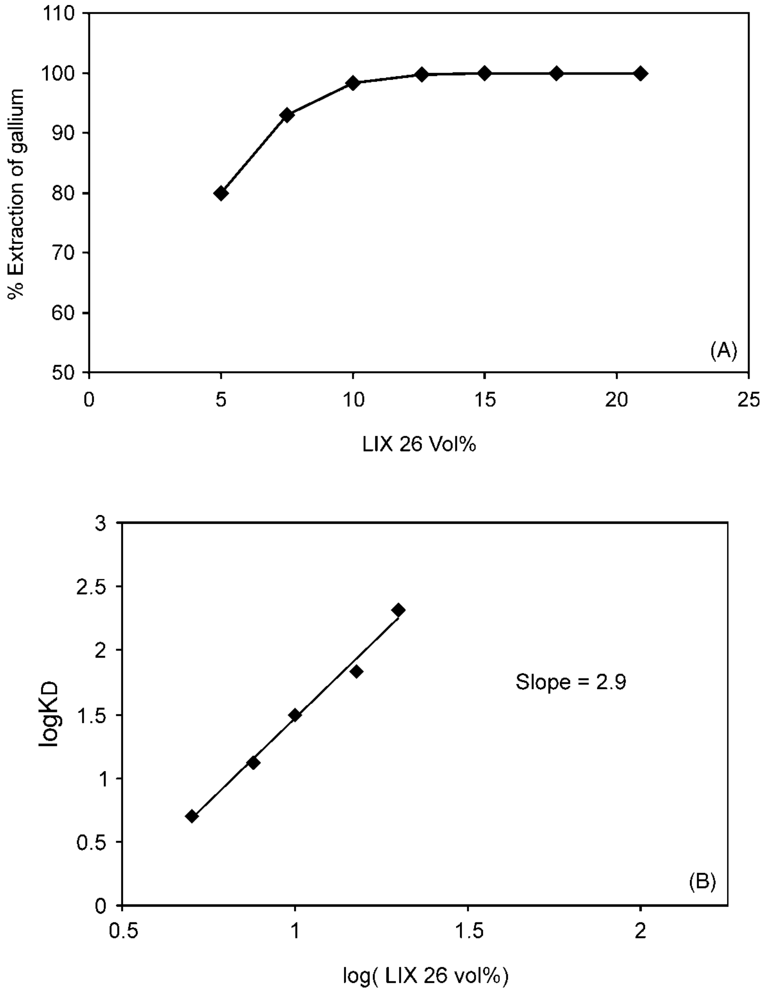

Figure 1. (A) Plot of % extraction in organic phase *vs.* LIX 26 volume percentage in kerosene. Initial concentration of metal 500 ppm, t(mixing) = 30 min. O\A ratio 1. (B) Plot of log K_D *vs.* log (LIX 26 vol%).

Effect of pH on Extraction

The extraction of gallium(III) was performed at different pH of the aqueous solution. The saturation loading of the solvent was attained at $O/A = 1$ with

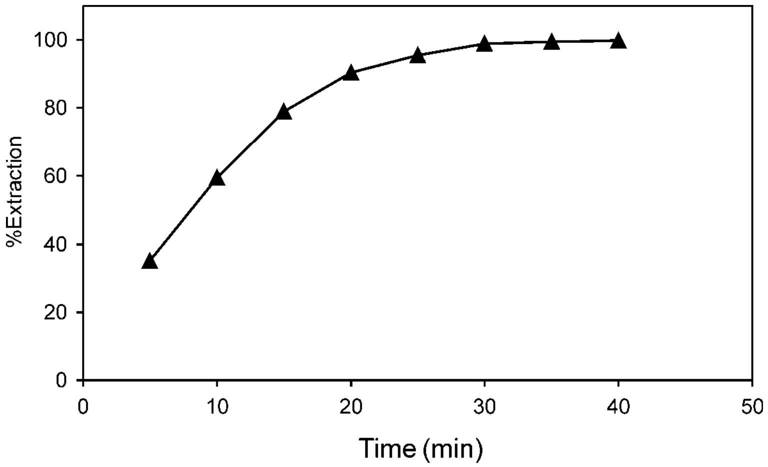

Figure 2. Plot of % extraction *vs.* time (min). Organic phase: 5 vol% LIX 26 in kerosene. Initial concentration of metal 500 ppm, O\A ratio 1.

aqueous solution of a fixed concentration of gallium(III), and the results are presented in Fig. 3. It was shown that increasing the pH of the aqueous medium recovery percentage of gallium(III) increases.

At constant extractant concentration of 10 vol% predicted value LIX 26 in kerosene and n-decanol as a moderator, a plot of log K_D against pH is linear with slope 3.03 for gallium(III), which is in good agreement with the predicted value of 3. This finding confirmed that three protons were released during a cation exchange reaction.

Hence, the probable extracted gallium-LIX 26 is GaL_3 (L = LIX 26), and the overall cation exchange extraction reaction may be expressed as follows

$$Ga^{+3}(aq) + 3LH_{org} = (GaL_3)_{org} + 3H^+(aq) \tag{1}$$

where LH = LIX 26

$$\text{Therefore,}\quad \log K_D = \log K_{ex} + 3\log LH + 3pH \tag{2}$$

where K_{ex} = equilibrium constant.

From the plot, log K_D *vs.* pH (Fig. 3A) intercept is also calculated and incorporated in Eq. (2). The log K_{ex} equal to -9.40 is obtained. The negative sign indicates the very low molar concentration of LH.

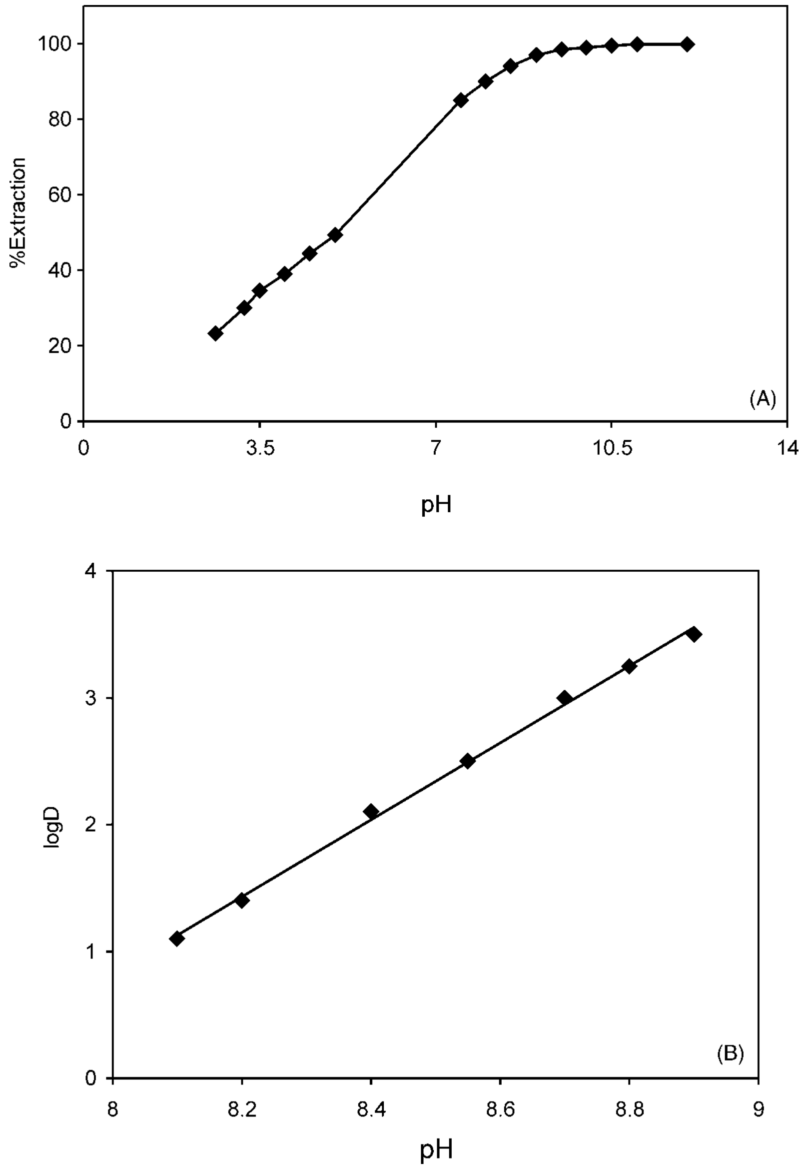

Figure 3. (A) Plot of % extraction *vs.* pH. Initial metal concentration 500 ppm. Organic phase: 10 vol% LIX 26 in kerosene. t(mixing) = 30 min. O\A ratio 1. (B) Plot of log K_D *vs.* pH.

Effect of Temperature on Extraction of Gallium(III)

The extraction of gallium(III) from aqueous solution adjusted to pH 9.2 using 5 vol% LIX 26 in kerosene and n-decanol as a moderator at varying temperatures between 303 and 343K has been studied and results are shown in Table 1. It is found that the distribution constant (K_D) decreases with rise in temperature.

The change of the distribution constant (K_D) with temperature is expressed by Van't Hoff equation. The plot of $\log K_D$ *vs.* (1/T) K^{-1} is linear and with slope 2.54 and enthalpy change of the extraction reaction carried out at constant pH 9.2 was found to be as $\Delta H = -48.6\,\mathrm{kJ\,mol^{-1}}$, which means it is an exothermic reaction. The free energy change ΔG and enthalpy change (ΔH) and entropy change (ΔS) were calculated from the following equations.

$$\Delta G = -2.303RT \log K_D \quad \text{and} \quad \Delta S = (\Delta H - \Delta G)/T$$

The negative values of free energy (ΔG) imply that reaction is spontaneous, and the extraction of gallium with LIX 26 in kerosene and n-decanol as a moderator is favored on lowering of temperature.

Effect of n-Decanol on Extraction of Gallium(III)

From the kinetics of extraction it was found that the extraction of gallium(III) increased with increasing n-decanol concentration and also prevented formation of third phase. It was also observed that 10 vol% n-decanol is sufficient for maximum extraction of gallium(III) from aqueous solution.

Table 1. Effect of temperature on extraction of gallium(III).

Temp. (K)	%E	$K_D =$ $[Ga]_o/[Ga]_a$	$\log K_D$	$\frac{1}{T}\times 10^3$ (K^{-1})	ΔG ($\mathrm{kJ\,mol^{-1}}$)	ΔS ($\mathrm{JK^{-1}\,mol^{-1}}$)	ΔH ($\mathrm{kJ\,mol^{-1}}$)
303	90.0	9.3	0.970	3.3	− 3.92	− 147.5	− 48.6
313	88.5	7.6	0.880	3.2	− 3.59	− 143.8	
323	85.5	5.8	0.765	3.1	− 3.27	− 140.3	
333	83.5	4.8	0.680	3.0	− 3.03	− 136.8	

Initial metal concentration 500 ppm. Organic phase: 5 vol% LIX 26, 10 vol% n-decanol in kerosene. O\A ratio 1.

Effect of LIX 26 on Loading Capacity of the Gallium Extraction

It was found that complete loading of gallium(III) could be obtained in one stage by using 10 vol% of LIX 26, 10 vol% n-decanol and kerosene in 30 min, at $O/A = 1$, pH of the solution should be about 8 to ensure complete loading. But extracting with 5 vol% LIX 26 and 10 vol% n-decanol with O/A ratio of unity and fourth stage of extraction may achieve 0.977 g/L.

Separation of Gallium(III) from the Bayer Process Liquor

The solvent extraction of gallium from the Bayer process liquor containing $180 \pm 30\,\mathrm{mg/L}$ of gallium, 420–450 g/L of Na_2O, and 70 g/L of Al_2O_3 was investigated by using 10 vol% of LIX 26, 10 vol% n-decanol as modifier, and kerosene as diluent. At 1:1 organic to aqueous phase ratio and at room temperature, 99% gallium was recovered in 30 min as shown in Table 2. Gallium was extracted from the Bayer process liquor, the organic phase was scrubbed with 6 M HCl at a 1:1 organic to aqueous phase for 10 min and then recycled for a second cycle of extraction where the recoveries in 10 min were found to be 98%, 95%, and 90.5% for the 1st, 2nd, and 3rd cycles, respectively.

Stripping of the loaded organic phase after the third scrub was carried out with 2 M HCl at 1:1 organic to aqueous phase ratio for 10 min. The final strip liquor was found to contain 540 mg/L of gallium.

Comparison Between KELEX 100 and LIX 26

The solvent extraction of gallium using 12 vol% Kelex 100, 12 vol% isodecanol and kerosene from a Bayer process liquor containing 190 ± 20 ppm

Table 2. Gallium extraction form Bayer process of liquor at different temperatures.

Temperature (K)	%Recovery of gallium from Bayer process liquor
303	99
313	95
323	89
333	85

Initial metal concentration 500 ppm. Organic phase: 10 vol% LIX 26, 10 vol% n-decanol as modifier in kerosene. O\A ratio 1.

has resulted in 80% recovery in 3 hr,[7] whereas only 10 vol% LIX 26, 10 vol% n-decanol and kerosene from concentrated Bayer process liquor containing 180 ± 30 ppm has resulted in 99% recovery in alkaline medium in 30 min.

CONCLUSION

From the above results it is observed that gallium(III) is extracted with LIX 26 in kerosene and n-decanol as a moderator by a cation exchange mechanism. The extracted species in the organic phase is GaL_3. The thermodynamic functions enthalpy (ΔH), entropy (ΔS), and free energy (ΔG) in the extraction of gallium(III) with LIX 26 have been evaluated. The extraction reaction is an exothermic process with the extraction percentage increasing on lowering of temperature. By using the proposed process it is possible to separate gallium(III) from accompanying elements such as aluminum (III) and sodium (I) in ores and alloys. Another important feature of the proposed method is that extraction of gallium using only 10 vol% LIX 26, 10 vol% n-decanol and kerosene from a concentrated Bayer process liquor containing 180 ± 30 mg/L has resulted in 99% recovery in alkaline medium in 30 min.

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