



Extraction Equilibrium of Gallium(III) from Nitric Acid Solutions by Di(2-ethylhexyl)phosphoric Acid Dissolved in Kerosene

HUNG-SHENG TSAI and TEH-HUA TSAI*

Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 10608, Taiwan

*Corresponding author: Tel : +886 2 27712171; Ext-2543; E-mail: divo.tsai@msa.hinet.net

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The solvent extraction of gallium(III) from aqueous nitric acid medium with di(2-ethylhexyl)phosphoric acid (D2EHPA) dissolved in kerosene at 25 °C has been studied. The extraction equilibrium data between the organic phase and the aqueous phase were used in the graphical and numerical analysis. The results showed that the stoichiometry of the extraction reaction and the compositions of gallium-D2EHPA complexes in organic phase. The extraction equilibrium constant of $\overline{\text{GaR}_3}$ in the organic phase has been determined. The results of gallium(III) extraction indicated that the distribution ratios increased when either the pH value of the aqueous phase and/or the concentration of D2EHPA in the organic phase increased. Finally, considering gallium and nitrate ions will form complex reactions, the distribution of gallium ions and their complexes were examined.

Key Words: Extraction, Equilibrium, Gallium, Di(2-ethylhexyl)phosphoric acid.

INTRODUCTION

Gallium is widely applied in electronics and technology industry. For example, gallium arsenic (AsGa), indium gallium nitride (GaInN), aluminium gallium indium phosphide (AlGaInP), aluminium gallium arsenide (AlGaAs) as gallium metal chemical compounds are used in the manufacturing of the light-emitting diodes (LEDs). Nevertheless, gallium metal is rare in the earth. Therefore, the development of gallium recovery technology for electronics industry from wastewater and waste material will be an urgent need to meet the ever increased demands. Solvent extraction is a vital technology in the development of gallium recovery technology and is a key step in hydrometallurgy¹⁻³.

Acidic organophosphorus compounds as important extractants have been used for extraction of gallium⁴⁻⁷. The solvent extraction of gallium from nitrate solution with di(2-ethylhexyl)phosphoric acid (abbreviated as D2EHPA or simply HR), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A), di(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) and di(2-ethylhexyl)phosphinic acid (PIA-8) dissolved in toluene⁸⁻¹⁰ or kerosene¹¹. It was found that the complexes of D2EHPA and PC-88A were both $\text{GaR}_3(\text{HR})$ and the complexes of Cyanex 272 and PIA-8 were both GaR_3 . The complexes compositions of gallium, $\text{GaR}_3(\text{HR})_3$, were also observed by other researchers using several acidic organophosphorus compounds as extractants in toluene from chloride

medium¹² or sulphate medium¹³. The extraction equilibrium of gallium from a sulphuric acid solution by using D2EHPA, PC-88A, diisodecylphosphoric acid (DIDPA) and diisostearylphosphoric acid (DISPA) in toluene or *n*-heptane was observed by Kondo and Matsumoto¹⁴ and gallium can be extracted using D2EHPA and PC-88A in kerosene from chloride solution¹⁵; and gallium extraction with PC-88A dissolved in *n*-heptane from sulphate medium¹⁶. These studies obtained complexes compositions.

Di(2-ethylhexyl)phosphoric acid (D2EHPA) is an effective acidic extractant of organophosphorus compounds in the hydrometallurgy process for the separation and purification of metals because of its high selectivity for metals, extremely low solubility in acidic aqueous solutions and chemical stability^{17,18}. Using D2EHPA to extract the system of $\text{UO}_2\text{-SO}_4$ ¹⁹, the results indicated that the different diluents on the order of the extraction distribution ratio was kerosene > *n*-hexane > cyclohexane > carbon tetrachloride > toluene > benzene > trichloromethane. Therefore, D2EHPA as the extractant and kerosene as the diluent were used in this work.

This work used D2EHPA dissolved in kerosene to extract gallium(III) from aqueous nitric acid medium at 25.0 ± 0.2 °C. The extraction equilibrium data of organic/aqueous solutions was obtained in various D2EHPA concentrations, various pH values of the aqueous phase and various concentrations of gallium ions. The compositions of the complexes were

identified by graphical and slope analysis and then verified by the numerical analysis. Applying both graphical and numerical analysis, the reliability of the experimental result was enhanced. The extraction equilibrium constants of graphical and calculated values were obtained.

EXPERIMENTAL

The di(2-ethylhexyl)phosphoric acid (D2EHPA) was supplied by Daihachi Chemical Industry Co. Ltd., Osaka, Japan. Potentiometric titration was performed using NaOH in an ethanol-water medium to verify its 95 % purity. According to the D2EHPA purification procedure²⁰, the precipitates from a copper-D2EHPA complex were separated from toluene and acetone solutions and then dissolved in a toluene and 4 kmol/m³ sulphuric acid solution. After the purification, the purity of D2EHPA could be as high as 99.5 %. The kerosene, provided by Chinese Petroleum Co., Taiwan, R.O.C., as a diluent was washed three times with 98 % sulphuric acid at 1/5 volume of that of the kerosene and then washed using distilled water until the solution became neutral¹⁹. The stock gallium solution of 0.5 kmol/m³ was prepared by dissolving metal (99.99 % purity) in nitric acid and diluted with distilled water. Prior to conducting the extraction experiments, an appropriate amount of stock solution was mixed with distilled water and 0.5 kmol/m³ nitric acid solution to prepare solutions with various pH and metal concentrations. All the other inorganic chemicals used in this work were analytical reagent grade and provided by Shimadzu's Pure Chemical Industry, Ltd., Osaka, Japan.

Procedure: The concentration of gallium ion in the initial aqueous solutions ranged from 0.02-0.15 kmol/m³. The organic solutions contained 0.10-2.00 kmol/m³ of monomeric D2EHPA in kerosene. An equal volume of the organic solution and the aqueous solution, 20 mL, were mixed in a glass flask using ground glass stoppers. Then, the mixture solution was shaken vigorously by a mechanical shaker at 25.0 ± 0.2 °C for 0.5 h. The preliminary experiments indicated that the solvent extraction process reached equilibrium within 15 min. The mixture solution was placed in the thermostat at 25.0 ± 0.2 °C for more than 12 h before performing a two-phase separation.

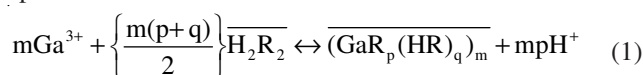
Following the phase separation, the gallium in the organic phase was stripped with 4 kmol/m³ of hydrochloric acid solution and the concentration of gallium was measured in an acidic solution using a GBC SenseAA atomic absorption spectrophotometer (AAS) at a wavelength of 303.9 nm. The equilibrium hydrogen ion concentration was measured using a pH meter and the gallium concentration in the aqueous phase was measured using AAS. The gallium metal mass balance during the extraction and stripping procedure must be maintained at ± 2 %.

RESULTS AND DISCUSSION

Extraction equilibrium of gallium: According to the potential-pH equilibrium diagram for gallium-water system at 25 °C²¹, when the pH value was below 2.74, the gallium ions in an aqueous solution were primarily in the form of Ga³⁺. However, when the pH value was between 1 and 3, gallium ions in the aqueous phase were also present in the form of

Ga(OH)²⁺ and Ga(OH)⁺. Therefore, to avoid interactions between Ga³⁺ and Ga(OH)²⁺, this work maintained a pH value less than 1 during the aqueous phase to maintain the stability of the system.

The metal-D2EHPA complexes would form polymeric species when the metal load of the D2EHPA in the organic phase near its saturation. In the presence of free D2EHPA molecules and ethylene glycol, these polymers would be depolymerized²². Therefore, under assumption that the extraction of gallium(III) with D2EHPA causes the formation of a *m*-merized complex, the extraction reaction could be expressed as



The stoichiometric extraction equilibrium constant could be expressed as

$$K_{\text{mpq}} = \frac{[\overline{(\text{GaR}_p(\text{HR})_q)_m}][\text{H}^+]^{\text{mp}}}{[\text{Ga}^{3+}]^m[\overline{\text{H}_2\text{R}_2}]^{m(p+q)/2}} \quad (2)$$

Concentration with bar signified that the species are in the organic phase.

The distribution ratio of gallium was defined as

$$D_{\text{Ga}} = \frac{[\overline{\text{Ga(III)}}]}{[\text{Ga(III)}]} \quad (3)$$

Substitute eqn. 2 into 3 to obtain 4.

$$D_{\text{Ga}} = \frac{m[\overline{(\text{GaR}_p(\text{HR})_q)_m}]}{[\text{Ga}^{3+}]} = mK_{\text{mpq}}[\text{Ga}^{3+}]^{m-1}[\overline{\text{H}_2\text{R}_2}]^{m(p+q)/2}[\text{H}^+]^{-\text{mp}} \quad (4)$$

when D2EHPA presented at a low distribution ratio and its concentration in the organic phase varied insignificantly, $[\text{Ga}^{3+}]^{m-1}[\overline{\text{H}_2\text{R}_2}]^{m(p+q)/2}$ remained almost unchanged. Therefore, mp can be determined from the slope by plotting log D_{Ga} vs. pH. Fig. 1 showed the impact of the pH on the distribution ratio when extracting gallium(III) with various concentrations of D2EHPA from the nitric acid aqueous solutions. The slope of the straight lines was 3, that is mp = 3. Therefore, eqn. 4 can be simplified to

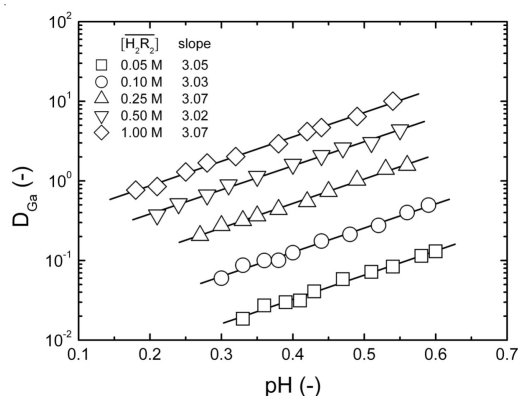


Fig. 1. Relationships of log D_{Ga} vs. pH at equilibrium with various D2EHPA concentrations in kerosene at 25 °C. $[\text{Ga}^{3+}] = 0.02\text{-}0.15 \text{ kmol/m}^3$. (□) $[\overline{\text{H}_2\text{R}_2}] = 0.05 \text{ kmol/m}^3$, slope = 3.05; (○) $[\overline{\text{H}_2\text{R}_2}] = 0.10 \text{ kmol/m}^3$, slope = 3.03; (△) $[\overline{\text{H}_2\text{R}_2}] = 0.25 \text{ kmol/m}^3$, slope = 3.07; (▽) $[\overline{\text{H}_2\text{R}_2}] = 0.50 \text{ kmol/m}^3$, slope = 3.02; (◇) $[\overline{\text{H}_2\text{R}_2}] = 1.00 \text{ kmol/m}^3$, slope = 3.07

$$\overline{[\text{Ga(III)}][\text{H}^+]^3} = mK_{\text{mpq}}[\text{Ga}^{3+}]^m \overline{[\text{H}_2\text{R}_2]}^{m(p+q)/2} \quad (5)$$

When the D2EHPA concentration in the organic phase remained unchanged, the aggregation degree of complexes of gallium(III) and D2EHPA in the organic phase, m , can be identified by plotting $\log \overline{[\text{Ga(III)}][\text{H}^+]^3}$ vs. $\log [\text{Ga}^{3+}]$. As shown in Fig. 2, the slope of the straight lines was 1, that was $m = 1$, which also proof the previous assumption that gallium(III) and D2EHPA will not polymerize. Therefore, $p = 3$ and eqns. 2 and 4 become

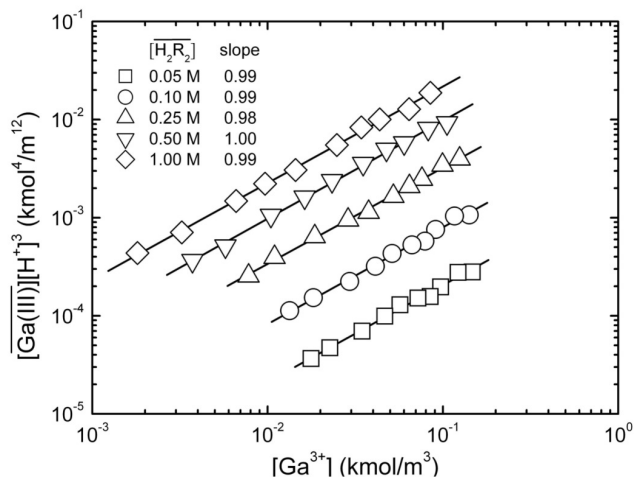


Fig. 2. Log-plots of $\overline{[\text{Ga(III)}][\text{H}^+]^3}$ vs. $[\text{Ga}^{3+}]$ at equilibrium with various D2EHPA concentrations in kerosene at 25 °C. $[\text{Ga}^{3+}]_i = 0.02\text{--}0.15$ kmol/m³. (◻) $[\text{H}_2\text{R}_2] = 0.05$ kmol/m³, slope = 0.99; (○) $[\text{H}_2\text{R}_2] = 0.10$ kmol/m³, slope = 0.99; (△) $[\text{H}_2\text{R}_2] = 0.25$ kmol/m³, slope = 0.98; (▽) $[\text{H}_2\text{R}_2] = 0.50$ kmol/m³, slope = 1.00; (◇) $[\text{H}_2\text{R}_2] = 1.00$ kmol/m³, slope = 0.99

$$K_{3q} = \frac{\overline{[\text{GaR}_3(\text{HR})_q][\text{H}^+]^3}}{[\text{Ga}^{3+}]\overline{[\text{H}_2\text{R}_2]}^{(3+q)/2}} \quad (6)$$

and
$$D_{\text{Ga}} = K_{3q} \overline{[\text{H}_2\text{R}_2]}^{(3+q)/2} [\text{H}^+]^{-3} \quad (7)$$

Reorganize eqn. 7 to obtain

$$\log D_{\text{Ga}} = \log K_{3q} + \left\{ \frac{(3+q)}{2} \right\} \log \overline{[\text{H}_2\text{R}_2]} + 3\text{pH} \quad (8)$$

Next, assume that only species of the type $\overline{\text{GaR}_3(\text{HR})_q}$ were formed during the organic phase. Thus, plotting $\log (D_{\text{Ga}}[\text{H}^+]^3)$ vs. $\log \overline{[\text{H}_2\text{R}_2]}$ and the intercept and slope of the straight line were K_{3q} and $(3+q)/2$.

As shown in Fig. 3, the slope of the straight line was 1.54 and $q = 0.08$. Because q had a considerably small value, it can be assumed that $q = 0$. The type of species in the organic phase was $\overline{\text{GaR}_3}$; therefore, eqn. 3 can be expressed as

$$D_{\text{Ga}} = \frac{\overline{[\text{GaR}_3]}}{[\text{Ga}^{3+}]} \quad (9)$$

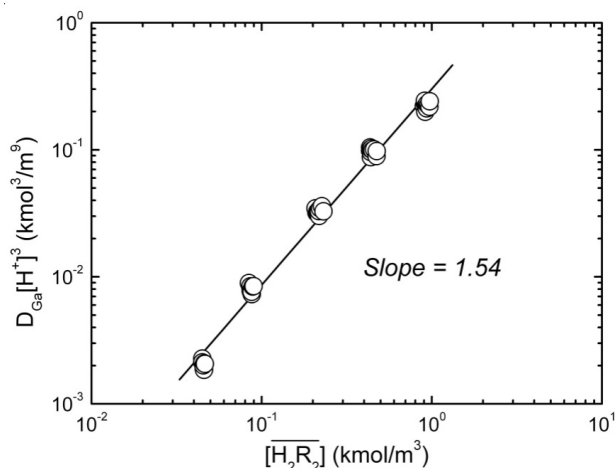


Fig. 3. Log-plots of $D_{\text{Ga}}[\text{H}^+]^3$ vs. $\overline{[\text{H}_2\text{R}_2]}$ at equilibrium with various D2EHPA concentrations in kerosene at 25 °C. $[\text{Ga}^{3+}]_i = 0.02\text{--}0.15$ kmol/m³, slope = 1.54

By using eqns. 6 and 9, the equation can be expressed as

$$D_{\text{Ga}}[\text{H}^+]^3 = K_{30} \overline{[\text{H}_2\text{R}_2]}^{3/2} \quad (10)$$

or
$$D_{\text{Ga}} = K_{30} \frac{\overline{[\text{H}_2\text{R}_2]}^{3/2}}{[\text{H}^+]^3} \quad (11)$$

Plot $\log D_{\text{Ga}}$ vs. $\log \overline{[\text{H}_2\text{R}_2]}^{3/2} [\text{H}^+]^{-3}$. When the slope is 1, the intercept was $\log K_{30}$. As shown in Fig. 4, the intercept for the straight line is -0.55 , that was $K_{30} = 0.28$ (kmol/m³)^{3/2}.

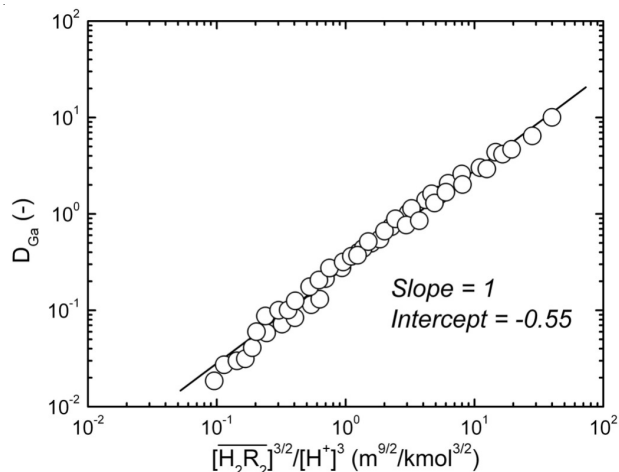


Fig. 4. Log-plots of D_{Ga} vs. $\overline{[\text{H}_2\text{R}_2]}^{3/2} [\text{H}^+]^{-3}$ at equilibrium with various D2EHPA concentrations in kerosene at 25 °C. $[\text{Ga}^{3+}]_i = 0.02\text{--}0.15$ kmol/m³

Reconfirmation of extraction equilibrium formation by computer treatment: To verify the complexes compositions and equilibrium constants of the extraction equilibrium, this work used the LETAGROP-DISTR program to perform a numerical treatment on data of the four-component system^{1,2,23}. The numerical analysis was performed to verify the results of graphical analysis.

For the calculation process, to enable the computer to search for the optimal equilibrium constants, the minimized sum of the squared errors was defined as

$$U = \sum (\log D_{\text{calc}} - \log D_{\text{exp}})^2 \quad (12)$$

where D_{calc} and D_{exp} were the distribution ratios of gallium by program-calculated and experimentally measured, respectively. The solute concentrations inputted into the program included H_2R_2 , NO_3^- , Ga^{3+} and pH, to solve the mass balance equations. The acquired best model was the result with minimization of the function U . The lowest mean standard deviation $\sigma(\log D)$ was then defined as

$$\sigma(\log D) = \left(\frac{U}{N_p} \right)^{1/2} \quad (13)$$

where N_p represents the degree of freedom, *i.e.*, the number data points.

The equilibrium constants of D2EHPA between the aqueous phase and organic phase were required for the program, as shown in Table-1. In Fig. 5, the program-calculated U_{min} shown that the optimal value for q was 0. Therefore, the optimal (p, q) was $(3, 0)$, which meant that the complex composition was $\overline{\text{GaR}_3}$. This result was consistent with that obtained from graphical treatment, where the calculated equilibrium constant was $\log K_{30} = -0.55 \pm 0.03$ (the error provided corresponds to $3\sigma(\log K)$). Subsequently, the equilibrium constants of the graphical and computer calculation were showed in Table-2. The results show that the calculated value was consistent with the graphical treatment value.

Reaction	Constant
$\text{HR} \leftrightarrow \text{H}^+ + \text{R}^-$	$\text{p}K_a = 1.49$
$\text{HR} \leftrightarrow \overline{\text{HR}}$	$\log K_d = 3.20$
$2\text{HR} \leftrightarrow \text{H}_2\text{R}_2$	$\log K_2 = 4.50$

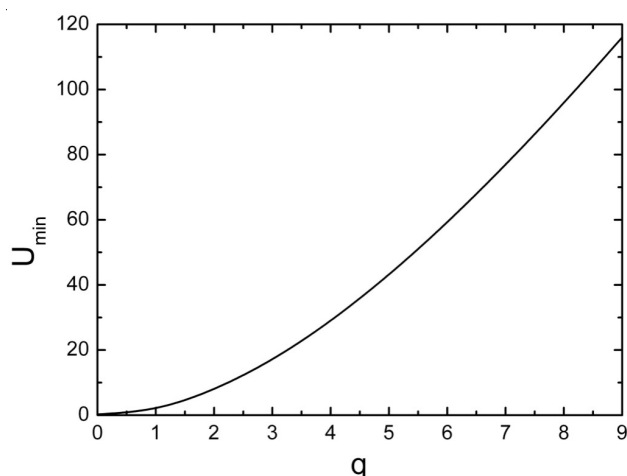


Fig. 5. Relationships between U_{min} of gallium and number of free monomeric D2EHPA involved in the extracted species (q)

In the optimal model, the mass balance equation of H_2R_2 was

$$[\overline{\text{H}_2\text{R}_2}]_t = [\overline{\text{H}_2\text{R}_2}] + \frac{1}{2} K_2^{-1/2} [\overline{\text{H}_2\text{R}_2}]^{1/2}$$

Method of calculation	$\log K_{30}$
Conditional constants ^a	
Graphic	-0.55
Numerical	-0.55 ± 0.03^b
Correct for $\text{Ga}(\text{NO}_3)_3$ complex at $(\text{Ga}^{3+}, \text{H}^+)\text{NO}_3^-$ solutions ^c	
Numerical	-0.52 ± 0.03

^aCalculated without regarding nitrate complexing. ^bThe error given corresponds to $3\sigma(\log K)$ and the value after max corresponds to $\log [K + 3\sigma(K)]$. ^cThe optimal values of stability constants from calculation were $\log \beta_1 = -0.84$ max -0.23 and $\log \beta_2 = -1.09$ max -0.55 .

$$+ 1.5K_{30}[\text{Ga}^{3+}][\overline{\text{H}_2\text{R}_2}]^{1.5}[\text{H}^+]^{-3} \quad (14)$$

Complexation of gallium in nitrate solutions: Since gallium and nitrate ions form complex reactions when in contact with each other; therefore, take the consideration of NO_3^- , the stability constants of $\text{Ga}(\text{NO}_3)_2^+$ and $\text{Ga}(\text{NO}_3)_3$ were defined as

$$\beta_1 = \frac{[\text{Ga}(\text{NO}_3)_2^+]}{[\text{Ga}^{3+}][\text{NO}_3^-]} \quad (15)$$

and
$$\beta_2 = \frac{[\text{Ga}(\text{NO}_3)_3]}{[\text{Ga}^{3+}][\text{NO}_3^-]^2} \quad (16)$$

$[\text{NO}_3^-]$ can be calculated using the mass balance equation of the nitrate concentration, as follows

$$[\text{NO}_3^-]_t = [\text{NO}_3^-] + \beta_1[\text{Ga}^{3+}][\text{NO}_3^-] + 2\beta_2[\text{Ga}^{3+}][\text{NO}_3^-]^2 \quad (17)$$

For minimizing the sum of the squared errors calculations, the optimal values of $\log K_{30}$, $\log \beta_1$ and $\log \beta_2$ were obtained and shown in Table-2.

Table-3 displayed the different equilibrium constants used in this study as discussed in literatures.

Fig. 6 showed the distribution of the molar fraction of gallium ion at different D2EHPA concentrations under the effects of the complex reactions of gallium and nitrate ions.

As indicated in the figure, the $\overline{\text{GaR}_3}$ concentration increased as the total concentration of D2EHPA increased; while the concentrations of Ga^{3+} , $\text{Ga}(\text{NO}_3)_2^+$, $\text{Ga}(\text{NO}_3)_3$ decreased. Fig. 6a and 6b shown, under the same gallium ions concentrations, the higher pH value of aqueous phase, the better extraction efficiency of D2EHPA for gallium(III). In other words, it is easier to form GaR_3 in the organic phase. Fig. 6b and 6c indicated the extraction amount of gallium by D2EHPA can be increased by raising the gallium ions concentration in the aqueous phase at the same pH value. However, only at higher D2EHPA concentration, gallium(III) can be extracted totally from the aqueous phase.

Conclusion

From the experiment results of gallium(III) extraction from aqueous nitric acid medium, it was found that the distribution ratio of gallium(III) between the organic phase and aqueous phase increased when the pH value of the aqueous solution or the D2EHPA concentration of the organic solution

TABLE-3
LITERATURE EQUILIBRIUM CONSTANTS OF $\overline{\text{GaR}}_p(\text{HR})_q$ EXTRACTED BY D2EHPA

Aqueous phase	Temp. (°C)	Diluent	log K_{ps}			Reference
			(3.0)	(3.1)	(3.3)	
NO_3^-	25 ± 0.2	Kerosene	-0.55			This work
1 M (Na, H)NO ₃	30	Toluene		-1.64		8
I = 0.1 M (Na, H)NO ₃	30	Toluene		0.64		10
I = 0.5 M (Na, H)NO ₃	21 ± 1	Kerosene		-0.12		11
SO_4^{2-}	25	Toluene			-1.29	13
SO_4^{2-}	30	n-Heptane		-0.49		14
SO_4^{2-}	30	Toluene		-2.26		14
I = 1 M (Na, H)Cl	25	Kerosene		-0.60		15

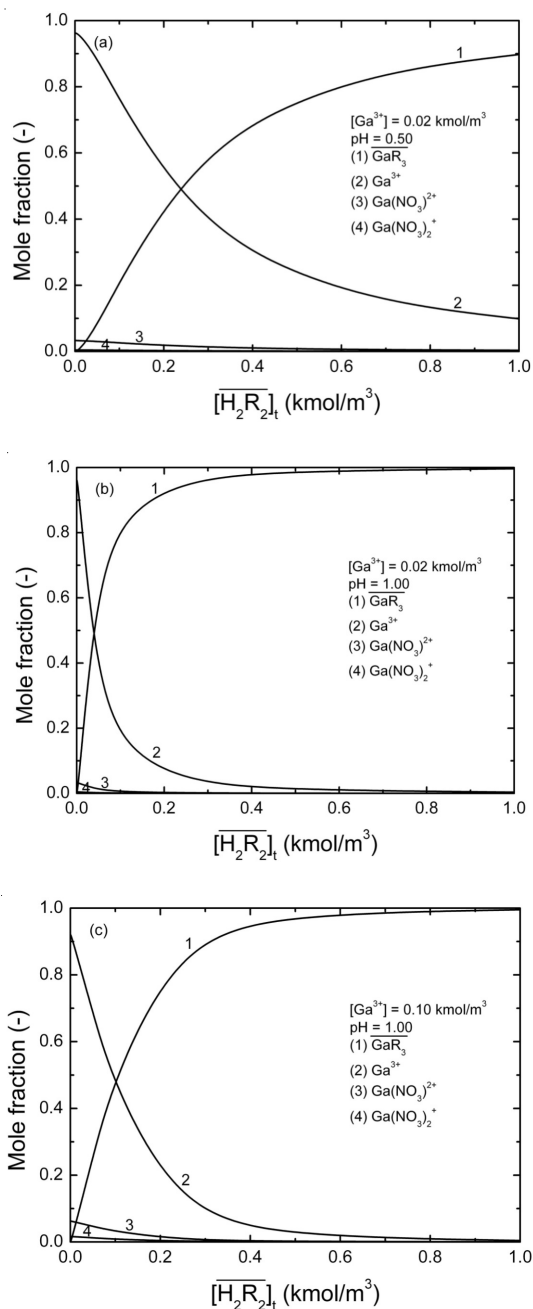


Fig. 6. Mole fractions of gallium ions and their complexes as a function of the total D2EHPA concentration at two different total concentrations of gallium and two pH values. Curves 1, 2, 3 and 4 represent $\overline{\text{GaR}}_3$, Ga^{3+} , $\text{Ga}(\text{NO}_3)_2^+$ and $\text{Ga}(\text{NO}_3)_2^+$, respectively. (a) $[\text{Ga}^{3+}]_0 = 0.02 \text{ kmol/m}^3$, $\text{pH} = 0.50$; (b) $[\text{Ga}^{3+}]_0 = 0.02 \text{ kmol/m}^3$, $\text{pH} = 1.00$; (c) $[\text{Ga}^{3+}]_0 = 0.10 \text{ kmol/m}^3$, $\text{pH} = 1.00$

increased. By graphical and numerical analysis, the type of species in the organic phase was determined to be $\overline{\text{GaR}}_3$, in which the equilibrium constants of graphical and calculated value were $\log K_{30} = -0.55$ and -0.55 ± 0.03 , respectively. As for the complex reactions of gallium and nitrate ions, the $\overline{\text{GaR}}_3$ concentration increased as the total concentration of D2EHPA increased; while the concentrations of Ga^{3+} , $\text{Ga}(\text{NO}_3)_2^+$, $\text{Ga}(\text{NO}_3)_2^+$ decreased.

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