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# Extraction of Gallium(III) by 1-{[2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl}-1H-1,2,4-Triazole from Hydrochloric Acid Solutions

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**Abstract**—The extraction of gallium(III) with 1-{[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl}-1H-1,2,4-triazole from hydrochloric acid solutions into toluene was studied. It was found that gallium(III) was efficiently extracted from 5–10 M solutions of HCl by the anion-exchange mechanism. The following metal extraction order was determined in the above aqueous phase acidity range: Ga(III) > In(III) > Al(III). The concentration constants and the thermodynamic parameters of the reaction of gallium(III) extraction from 6 M solutions of HCl at 25°C were calculated.

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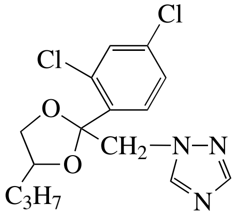
1-[[2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole or Propiconazole (S) is a commonly used systemic fungicide [1]. The availability of this reagent, its low water solubility (0.1 g/L), and weakly basic properties (p$K_a$ = 1.09) [1], as well as the ability of 1,2,4-triazole and its derivatives to form complexes with transition metals [2], are responsible for interest expressed by researchers in the extraction properties of this reagent toward noble metals in hydrochloric acid solutions [3–6]. It was found that this reagent extracted the acid metal complexes $AuCl_4^-$, $PdCl_4^{2-}$, $PtCl_6^{2-}$ (toluene as a diluent) [3], $IrCl_6^{2-}$ [4], and $[RuCl_4(H_2O)_2]^-$ [5] (toluene and 15% decanol) by the anion-exchange mechanism. It extracted rhodium(III) as the ion associates $SH^+[RhCl_4(H_2O)S]^-$ (*p*-xylene and 15% decanol) from 4 M HCl solutions [6]. With the use of $^1H$ and $^{13}C$ NMR spectroscopy, it was found that, in the cation of the extracted ion associates, the reagent is protonated at a nitrogen atom in the 4-position. The ability of the reagent to extract quantitatively the anionic complexes of noble metals from strongly acidic solutions allowed us to hypothesize that it can be efficiently used for the extraction of rare metals that form anionic species in hydrochloric acid solutions.

The aim of this work was to study the extraction of Ga(III) with 1-{[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl}-1H-1,2,4-triazole in toluene from hydrochloric acid solutions.

## EXPERIMENTAL

1-{[2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl}-1H-1,2,4-triazole (molecular, 342.2; $T_m$ = 58°C; purity, no less than 98%) has the following structural formula:



The identity and purity of the reagent were determined using elemental analysis, potentiometric titration in anhydrous acetic acid, thin-layer chromatography, and gas–liquid chromatography. According to $^{13}C$ NMR-spectroscopic data, the reagent was a mixture containing 55–65% *cis*- and 35–45% *trans*-diastereoisomers [3].

The stock solution of the reagent in toluene with a concentration of 0.1 mol/L was prepared from an accurately weighed amount, and the working solutions were prepared by diluting the stock solution with toluene of chemically pure grade.

The stock solutions of Ga(III) and In(III) (0.1 mol/L) in 2 M HCl were prepared by dissolving the weighed portions of corresponding oxides $M_2O_3$ (with a purity of no less than 99.9%) in a solution of HCl (1 : 4) under weak heating followed by adjusting the acidity and volume of the solution to required values. The stock solution of Al(III) (0.1 mol/L) in 2 M HCl was prepared by dissolving a weighed portion of reagent-grade $AlCl_3 \cdot 6H_2O$ in a solution with a required HCl content. The working solutions containing 0.001–0.030 mol/L Ga(III) and 0.005 mol/L In(III) or Al(III) were prepared by diluting the stock solutions with the solutions of HCl.

The concentrations of In(III) and Al(III) in solutions were determined by complexometric titration with a PAN indicator in the presence of a Cu(II) complexonate [7] and by back titration with a solution of $ZnSO_4$ with a xylenol orange indicator [8], respectively. The stock solution of Ga(III) was standardized complexometrically with a PAN indicator [9]. The concentrations of Ca(III) in working solutions, raffinates, and back extracts were determined by a spectrophotometric method with xylenol orange at pH 1.8 (hydrochloric acid buffer solution of HCl–KCl) [10] on a Specord M40 spectrophotometer in 2-cm glass cells. Before analysis, an aliquot of the working solution or raffinate containing Ga(III) and more than 1 mol/L HCl was evaporated in a water bath to wet salts to remove hydrochloric acid. Then, the residue was dissolved in a 0.01 M solution of HCl.

Extraction was performed in thermostated glass cells at the aqueous to organic phases volume ratio of 1 : 1 with intense stirring using MM 2A magnetic stirrers. The temperature was maintained to within ±0.2°C using a U4 thermostat.

The IR spectra of the reagent, its hydrochloride, and the extracted complex of Ga(III) in thin films were measured on a Specord M80 spectrophotometer in the region of 600–250 $cm^{-1}$.

## RESULTS AND DISCUSSION

The equilibration time of Ga(III) extraction from 4–10 M solutions of HCl was no longer than 2 min regardless of the initial concentrations of Ga(III) and the reagent; the phase separation time was 1–2 min. The main regularities of Ga(III) extraction at 20–25°C were studied at the phase contact time $\tau = 5$ min. Gallium(III) was efficiently back extracted from the extracts with 0.01–0.1 M solutions of HCl; in this case, the degree of back extraction decreased from 98.4 to 93.4% in accordance with an increase in the acidity of the back extractant. The equilibration time of back extraction was 3 min.

To determine optimum conditions for the extraction of Ga(III) and the selectivity of the extractant, we studied the dependence of the extraction efficiency of Ga(III), In(III), and Al(III) on the acidity of the aqueous phase (Fig. 1). We found that Ga(III) was efficiently extracted in the region of >4 M HCl; in this case, its recovery increased to a maximum at 8 mol/L HCl and then insignificantly decreased as the acidity of solution was increased to 10 mol/L. This was likely due to a shift of the hypothetical anion-exchange equilibrium of Ga(III) extraction to the left at high concentrations of chloride ions:

$$SHCl_{org} + GaCl^{-}_{4aq} \rightleftharpoons SHGaCl_{4org} + Cl^{-}_{aq}. \quad (1)$$

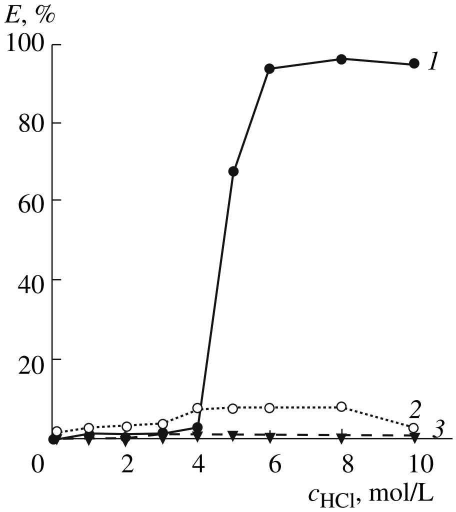


**Fig. 1.** Dependence of the extraction efficiency of (*1*) gallium(III) ($c_{Ga}$ = 0.002 mol/L; $c_S$ = 0.006 mol/L; $\tau$= 5 min), (*2*) indium(III) ($c_{In}$ = 0.005 mol/L; $c_S$ = 0.015 mol/L; $\tau$ = 30 min), and (*3*) aluminum(III) ($c_{Al}$ = 0.005 mol/L; $c_S$ = 0.015 mol/L; $\tau$ = 30 min) on the acidity of the aqueous phase at 20°C.

The dependence of the extraction of Ga(III) by the reagent on the acidity of the aqueous phase was analogous to the dependence of the extraction of Ga(III) by weakly basic extractants—Primene 81-R branched primary amines in toluene [11] and 1-hexyl-3-methylpyrazol-5-one (HMP) in chloroform [12]—from hydrochloric acid solutions. In this case, the extractability of the test reagent in the optimum acidity range was much higher than that of the above extractants. For the quantitative extraction of Ga(III), the concentration of HMP in the organic phase should be more than ten times higher than the concentration of Ga(III) in the aqueous phase. At a ratio of 1 : 7 between the initial concentrations of Ga(III) and Primene 81-R in the aqueous and organic phases, respectively, and an aqueous phase acidity of 8 mol/L HCl, the distribution coefficient of Ga(III) was ~5.6. The test reagent extracted Ga(III) from a 8 M solution of HCl with the distribution coefficient $D = 27.6$ (96.5% recovery) at a ratio of 1 : 3 between the initial concentrations of Ga(III) and the reagent in the aqueous and organic phases, respectively (Fig. 1).

An increase in the concentration of chloride ions in the aqueous phase makes it possible to considerably increase the extraction of Ga(III) from solutions with an HCl concentration lower than an optimum as a result of an increase in the concentration of the extracted $GaCl^{-}_{4}$ complex (Fig. 2).

In the acidity range of 4–10 mol/L at the same ratio between the initial metal and reagent concentrations, the following metal extractability order was found: Ga(III) (maximum distribution coefficient $D_{max} = 27.6$) >

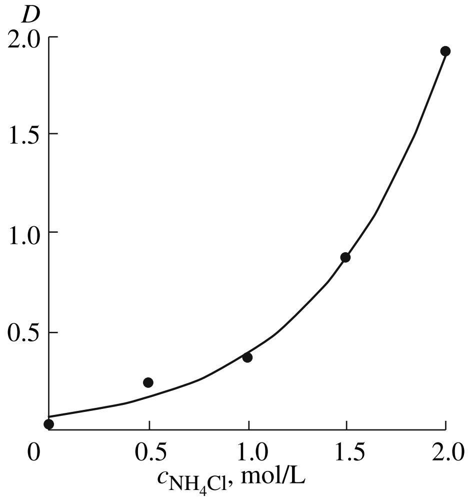


**Fig. 2.** Dependence of the distribution coefficient of Ga(III) on the concentration of $NH_4Cl$ in the aqueous phase at $c_{HCl}$ = 4 mol/L, $c_{Ga}$ = 0.002 mol/L, $c_S$ = 0.006 mol/L, and 20°C.

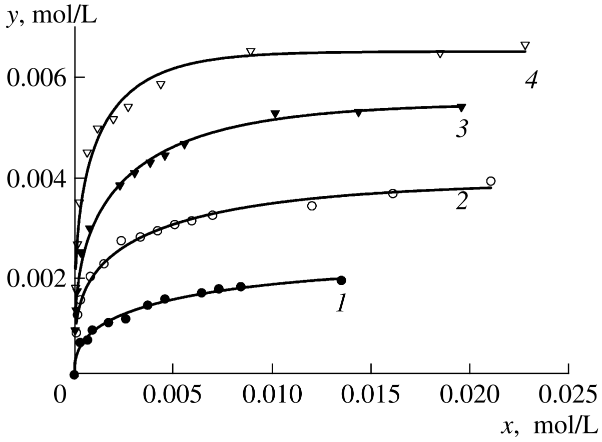


**Fig. 3.** Isotherms of Ga(III) extraction from 6 M solutions of HCl at 25°C and reagent concentrations of (*1*) 0.002, (*2*) 0.004, (*3*) 0.006, and (*4*) 0.008 mol/L.

In(III) ($D_{max}$= 0.1) > Al(III) ($D_{max}$ = 0.01) (Fig. 1). This order corresponds to a decrease in the concentration and an increase in the hydration of anionic complexes like $MCl_4^-$ in the aqueous phase, and it is analogous to an extractability order for weakly basic extractants such as HMP [12] and tertiary amines [13]. In the given range of HCl concentrations, aluminum(III) does not form anionic chloro complexes in detectable amounts; therefore, it was almost not extracted by HMP, amine salts, and the test reagent. Gallium(III) mainly occurs in these solutions as the tetrahedral $GaCl_4^-$ complex of $T_d$ symmetry [14, 15], which is the species extracted with the salts of secondary and tertiary amines and quaternary ammonium bases [16, 17]. The aquachloro complexes $[InCl_4(H_2O)_2]^-$ and $[InCl_5H_2O]^{2-}$ were the predominant In(III) species in the specified acidity range of the aqueous phase [11, 15]. The IR spectra of In(III) extracts containing a tertiary of quaternary amine in a molar ratio of 1 : 1 or 2 : 1 with respect to In(III) suggest that In(III) occurred in the form $InCl_4^-$ in ion associates [16, 18]. Consequently, the transfer of In(III) into the organic phase in the course of extraction with amines was accompanied by the displacement of water molecules from the inner coordination sphere of the aquachloro complex anions of In(III), and this process required an additional input energy. It is also well known that the extractability of aliphatic amines for In(III) decreases with decreasing the basicity of the amine [11]. It is likely that the extractability of the test reagent for In(III) was low for the above reasons. Thus, Ga(III) can be selectively separated from Al(III) and In(III) by extraction with this reagent from hydrochloric acid solutions.

The rapid equilibration and easy back extraction of Ga(III) from the organic phase with weakly acidic solutions of HCl suggest the anion-exchange mechanism of Ga(III) extraction by the test reagent from hydrochloric acid solutions. We studied the mechanism of Ga(III) extraction at an aqueous phase acidity of 6 mol/L HCl. In these solutions, Ga(III) occurred as $GaCl_4^-$ [14]. Changes in the $^1H$ and $^{13}C$ NMR spectra of hydrochloric acid extracts obtained at an aqueous phase acidity of 1–4 mol/L indicate that the reagent was incompletely protonated at a nitrogen atom in the 4-position upon contact with solutions of < 4 mol/L HCl [3]. Using two-phase titration of hydrochloric acid extracts with a 0.1 M solution of NaOH in the presence of bromothymol blue, we found that the degree of protonation of the test reagent in contact with 5 and 6 M solutions of HCl was 98 and 100%, respectively.

The solvation number of Ga(III) was 1, as determined using organic phase saturation method (Fig. 3, curves *1*, *2*). The solvation number determined from the initial parts of equilibrium extraction isotherms by the slope method was also close to unity (Fig. 4).

To confirm the composition of $SHGaCl_4$ ion associates formed in the organic phase during the extraction of Ga(III) from 6 M HCl solutions, we obtained the extracted complex of Ga(III) under conditions of the full saturation of the organic phase (initial concentrations, $c_{Ga}$ = 0.3 mol/L and $c_S$ = 0.1 mol/L; volume ratio of the aqueous to organic phases 3 : 2). The solvent (toluene) was separated from the complex by evaporation. The extracted complex was a reddish brown highly viscous liquid. According to elemental analysis data, the Ga(III) content of this complex was 12.56%, which is consistent with the theoretical value (12.57%). The molar ratio between the elements Ga : N : Cl = 1 : 3.2 :

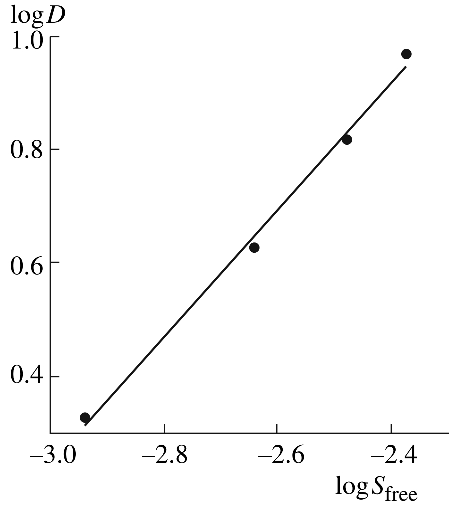


**Fig. 4.** Bilogarithmic dependence of the Ga(III) distribution coefficient on free extractant concentration at $c_{\mathrm{HCl}}$ = 6 mol/L and 25°C. The least-squares estimate of the linear correlation coefficient is $r = 0.994$; $\tan\alpha = 1.11$.

6.0 corresponds to the composition of the ion associate $\mathrm{SHGaCl_4}$. The IR spectrum of the complex exhibited a strong broad absorption band with a maximum at 381 cm$^{-1}$ and a weak absorption band at 346 cm$^{-1}$, which were absent in the spectra of the reagent and its hydrochloride. The intense absorption band can be atributed to $\nu_d$(Ga–Cl) of the tetrahedral $\mathrm{GaCl_4^-}$ complex with $T_d$ symmetry [16, 17, 19], which was observed in the IR spectra of $\mathrm{GaCl_4^-}$ ion associates with aliphatic amine cations [16, 17]. The appearance of a weak absorption band due to $\nu_s$(Ga–Cl), which is inactive in the IR spectra of symmetrical tetrahedral complexes, suggests an insignificant deformation of the $\mathrm{GaCl_4^-}$ ion in the extracted complex [17].

The concentration constants of equilibrium for anion-exchange extraction (1) were calculated from the equation

$$K_{\mathrm{ex}} = [\mathrm{SHGaCl_{4org}}][\mathrm{Cl^-_{aq}}]/([\mathrm{GaCl^-_{4aq}}][\mathrm{SHCl_{org}}]), \quad (2)$$

where $[\mathrm{SHGaCl_{4\,org}}] = y$, mol/L is the equilibrium concentration of Ga(III) in the organic phase, as calculated from the difference between the concentrations of Ga(III) in the initial aqueous solution and the raffinate; $[\mathrm{GaCl^-_{4aq}}] = x$, mol/L is the equilibrium concentration of Ga(III) in the aqueous phase; $[\mathrm{Cl^-_{aq}}] = [\mathrm{HCl_{aq}}] - [\mathrm{SHCl_{org}}]$= 6 mol/L is the equilibrium concentration of chloride ions in the aqueous phase (it can be taken equal to the concentration of HCl in the aqueous phase because the equilibrium concentration of the hydrochloric acid salt of the reagent in the organic phase $[\mathrm{SHCl_{org}}]$ is much lower than $[\mathrm{HCl_{aq}}]$); and $[\mathrm{SHCl_{org}}] = [\mathrm{S}]_0 - y$, mol/L, where $[\mathrm{S}]_0$ is the initial reagent concentration in the organic phase.

The final equation for calculating the concentration constants of extraction has the form

$$K_{\mathrm{ex}} = 6y/\{x([\mathrm{S}]_0 - y)\}. \quad (3)$$

The table summarizes the concentration constants of anion-exchange extraction of Ga(III) from 6 M solutions of HCl at 25°C, as calculated from the initial portions of extraction isotherms.

The study of the temperature dependence of the Ga(III) extraction at the range of 10–45°C demonstrated that the concentration constant increased with temperature rise (Fig. 5). Consequently, the extraction is an endothermic process. We evaluated the thermodynamic parameters of the anion-exchange extraction of Ga(III) from 6 M solutions of HCl. The value of $\Delta H = 7.0$ kJ/mol was calculated from the slope of the function $\log K_{\mathrm{ex}}$ =

Concentration constants of Ga(III) extraction with reagent S from 6 M solutions of HCl at 25°C

| Initial reagent concentration, mol/L | Equilibrium Ga(III) concentration, mol/L | | Concentration constant of extraction $K_{\mathrm{ex}} \times 10^{-4}$ |
|---|---|---|---|
| | *x* | *y* | |
| 0.004 | 0.00010 | 0.00095 | 1.79 |
| 0.004 | 0.00016 | 0.00132 | 1.89 |
| 0.004 | 0.00025 | 0.00168 | 1.74 |
| 0.006 | 0.00009 | 0.00139 | 2.00 |
| 0.006 | 0.00014 | 0.00179 | 1.89 |
| 0.006 | 0.00025 | 0.00265 | 1.90 |
| 0.008 | 0.00016 | 0.00274 | 1.95 |
| 0.008 | 0.00027 | 0.00359 | 1.84 |
| 0.008 | 0.00050 | 0.00475 | 1.75 |

Average value of $K_{\mathrm{ex}} = (1.86 \pm 0.07) \times 10^4$

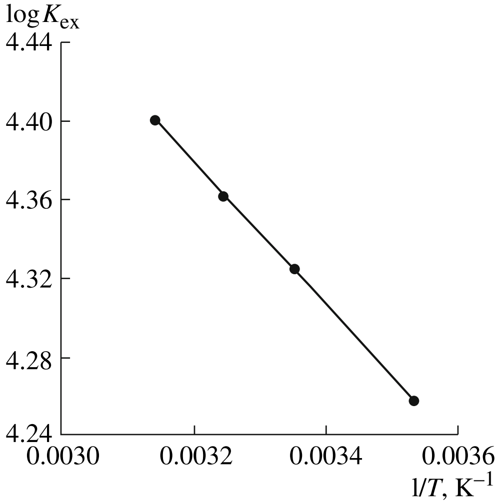


**Fig. 5.** The temperature dependence of the concentration constant of Ga(III) extraction at $c_{HCl}$ = 6 mol/L, $c_{Ga}$ = 0.00425 mol/L, and $c_S$ = 0.008 mol/L, $r$ = 1.

$f(1/T)$ in accordance with the integral form of the Vant Hoff equation

$$\log K_{ex} = -\Delta H/(2.303RT) + \text{const} \quad (4)$$

The thermodynamic parameters $\Delta G$ and $\Delta S$ at 25°C were calculated from the equations

$$\Delta G = -RT\ln K_{ex}, \quad (5)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (6)$$

They were –24.4 kJ/mol and 105 J mol$^{-1}$ K$^{-1}$, respectively. The positive value of $\Delta S$ suggests that extraction is determined by the entropy factor.

Thus, the extraction of Ga(III) by the test reagent from hydrochloric acid solutions occurs in accordance with the anion-exchange mechanism. The reagent is more efficient than the commercial extractant Primene 81-R and the well-known extractant HMP, and it can be recommended for the selective separation of Ga(III) from In(III) and Al(III) by extraction from hydrochloric acid solutions.

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