EQUILIBRIUM AND KINETICS OF THE EXTRACTION OF GALLIUM(III) FROM SODIUM HYDROXIDE SOLUTIONS WITH 7-DODECENYL-8-QUINOLINOL (KELEX 100)*

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The influence of hydroxide ions concentration of the aqueous sodium hydroxide solution, at constant sodium concentrations, on the gallium extraction with Kelex 100 was examined in the hydroxide concentration range from 0.02 to 0.5 mol dm^{-3}. The percentage of extracted gallium increased from 51% to 98% within the investigated hydroxide concentration range. The influence of sodium concentration (from 1 to 6 mol dm^{-3}) on the gallium extraction was also studied at constant pH values. The decrease of extracted gallium is slight for the sodium concentration up to 3 mol dm^{-3}, while for the higher ones it is pronounced. The extraction kinetics was studied using a mixer-type apparatus. The rate expression of the extraction reaction of gallium with Kelex 100, for both lower and higher hydroxide concentrations are ascertained.

In recent years there has been an increased interest in the metal extraction from alkaline solutions. The recovery of gallium has been extensively investigated due to its excellent electronic properties. A summary covering almost 20 years research work has recently been published by Reznik et al.[1,2]. Several extractants have been proposed[1 – 7], but Kelex 100 was found to be particularly efficient for liquid–liquid extraction of gallium from high alkaline media[1,2,7 – 12]. Leveque and Helgorsky[7,9], using originally Kelex 100 (substituted hydroxyquinolinol) for solvent extraction of gallium from Bayer process aluminate solutions, discovered that the extraction rate was very slow. To enhance the extraction rate Helgorsky and Leveque[13] and Fourre and Bauer[14,15] experimented with various surfactants to speed up the recovery. Subsequently, Fourre and Bauer[15] attributed faster extraction to the mechanism involving reaction at the interface between gallium ions in the aqueous and the organic phase.

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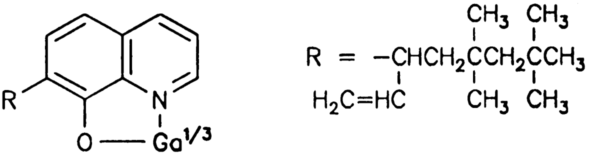
Other approaches, to increase the slow recovery rate, include modification of Kelex 100 molecule itself. Bauer and Pescher–Cluzeau[16] synthesized 5-substituted 8-quinolinol, but the extractant did not show any improvement. Although various types of 8-quinolinol were synthesized by a number of Japanese companies[17,18], no commercial applications have been reported.

In the previous paper[19] we investigated the influence of temperature, nature of diluents and modifiers, and Kelex 100 concentration on both the equilibrium distribution and the extraction rate of gallium(III) from aqueous NaOH solutions. In this paper, results of the investigations of equilibrium and kinetics of the gallium(III) extraction from sodium hydroxide solution with Kelex 100 are summed up. The effect of hydroxide and sodium concentrations on the gallium extraction was investigated.

THEORETICAL

With a reagent such as Kelex 100, gallium can be extracted in the organic phase as a complex[7]:



and in alkali solutions according to the reaction[1,2,7]:

$$Ga(OH)^-_{4(aq)} + 3\,HL_{(org)} \rightleftharpoons GaL_{3(org)} + OH^-_{(aq)} + 3\,H_2O_{(aq)}\,,$$

where HL denotes Kelex 100.

Kelex 100 exhibits a very low solubility in neutral and alkaline aqueous solutions and a high interfacial activity[20,21]. Therefore, the heterogeneous interfacial reaction must be considered in analysis of the rate mechanism of this extraction system.

The factors which can influence the gallium(III) extraction are following: gallium concentration, extractant concentration, and acidity or alkalinity of aqueous solution. Acidity or alkalinity can affect the existence of various gallium(III) species in the aqueous phase and Kelex 100 species as well. Unfortunately, there are no available literature data, detailed and exact, on existence of certain ion species of gallium in aqueous solutions dependent on pH, i.e. hydroxide concentration. Hydrolysis of Ga in alkaline solutions is especially insufficiently investigated. Reznik et al.[1] have reported that Ga can exist not only in the form of mononuclear complexes (ranging from simple Ga^{3+} ion to $Ga(OH)_6^{3-}$ ion species) but in the form of polynuclear complexes (of different compositions: $[Ga_n(OH)_{mn}]^{(3-m)n}$; $[Ga_{n+1}(OH)_{3n+4}]^{-1}$; $Na_nGa(OH)_{3+n}$) especially in concentrated alkaline solutions as well.

The extraction rate of gallium(III)$_{(aq)}$ ion with HL from alkaline solutions of constant Na concentrations may generally be represented, in a similar way as it has been done by other researchers[12,22 – 25], by the following equation:

$$-\frac{\mathrm{d}[\mathrm{Ga}]_{(aq)}}{\mathrm{d}t} = k\,[\mathrm{Ga}]^{a}_{(aq)}\,[\mathrm{HL}]^{b}_{(org)}\,[\mathrm{OH}^-]^{c}_{(aq)}\,, \qquad (1)$$

where t is the time, k is the rate constant, and a, b and c are the constants.

If both the extractant and hydroxyl ions concentrations are constant and present in large excess relative to gallium, Eq. (*1*) can be rewritten:

$$-\frac{\mathrm{d}[\mathrm{Ga}]_{(aq)}}{\mathrm{d}t} = q\,[\mathrm{Ga}]^{a}_{(aq)}\,, \qquad (2)$$

where q is equal to $k\,[\mathrm{HL}]^{b}_{(org)}\,[\mathrm{OH}^-]^{c}_{(aq)}$. The concentrations of $[\mathrm{HL}]_{(org)}$ and $[\mathrm{OH}^-]_{(aq)}$ are kept constant in a series of experiments. If the hydroxyl-ions concentration is kept constant, then the pseudo rate constant q_{HL} can be defined as:

$$q_{\mathrm{HL}} = k\,[\mathrm{OH}^-]^{c}_{(org)}\,[\mathrm{HL}]^{b}_{(org)}\,. \qquad (3)$$

On the other hand, when the extractant concentration is kept at a constant $[\mathrm{HL}]_{(org)}$ value, the pseudo rate constant q_{OH} can be defined as follows:

$$q_{\mathrm{OH}} = k\,[\mathrm{HL}]^{b}_{(org)}\,[\mathrm{OH}^-]^{c}_{(aq)}\,. \qquad (4)$$

The reaction orders b and c can be calculated as the slopes of the straight lines: $\log(q_{\mathrm{HL}}) = f(\log[\mathrm{HL}]_{\mathrm{org}})$ or $\log(q_{\mathrm{OH}}) = f(\log[\mathrm{OH}^-]_{\mathrm{aq}})$.

EXPERIMENTAL

The stock solution of gallium was prepared by dissolving 0.613 g of pure Ga in 15 ml concentrated nitric acid and diluted to 500 ml with distilled water. The working solutions of 70 mg Ga dm^{-3} were prepared by adding appropriate quantities of sodium nitrate and sodium hydroxide to the stock solution. The influence of $[\mathrm{OH}^-]$ concentration on the extraction was examined in the sodium hydroxide concentration range from 0.02 to 0.5 mol dm^{-3} In these experiments the sodium concentration was kept constant by adding $\mathrm{NaNO_3}$, $c_{\mathrm{Na}} = 0.5$ mol dm^{-3}. Variations in the sodium hydroxide concentrations from 1 to 6 mol dm^{-3} were made by adding appropriate quantities of sodium hydroxide to the gallium solution.

Kelex 100 was kindly supplied by SCHERING Industrial Chemical Co. The reagent was purified by acid and water washing cycles[26] before dilution. Other reagents (dodecanol and heptane) of p.a. purity grade were used "as received". The effect of extractant concentration was examined for Kelex 100 concentrations between 0.3 and 8.5 vol.% (0.0075 – 0.212 mol dm^{-3}) in the organic phase.

The experiments were carried out in a stirred-glass cell (inner diameter 50 mm and height 100 mm), jacketed for temperature control. A glass baffle arrangement was added to improve mixing and minimize vortex formation. Equal volumes (50 ml each) of the aqueous and the organic phase were mixed by twoblades propeller type impeller at 1 600 r.p.m. This agitation speed is in the "plateau region" were further increase of the stirring speed has no effect on the extraction rate. The temperature was kept at 25 ± 0.5 °C in all experiments. Samples of 2 ml were taken after short time intervals followed by a fast phase separation. The gallium concentration was analyzed in the aqueous phase using a Perkin–Elmer 5000 atomic absorption spectrophotometer. The pH was measured at a BECKMAN Φ 71 pH-meter. The concentrations of gallium in the organic phase were calculated by means of material balance.

The percentage of extracted gallium was calculated as:

$$E = \frac{c_{\mathrm{org}}}{c^0} 100 , \tag{5}$$

where subscript org and superscript 0 denote the gallium concentrations in the organic phase and total gallium concentration, respectively.

Our preliminary experiments showed that the percentage of extracted gallium depends on the presence of oxygen in the system. This is in accordance with literature[2] and our previous study[19]. Therefore, N_2 gas was bubbled through the solution during the extraction, preventing the extractant oxidation.

RESULTS AND DISCUSSION

The effects of hydroxide (constant sodium concentration, c_{Na} = 0.5 mol dm^{-3}) and sodium hydroxide concentrations on the rate of solvent extraction of gallium are shown in Figs 1 and 2, respectively. Further increase of the sodium hydroxide concentration (above 1 mol dm^{-3}) in the aqueous prolongs the time for reaching equilibrium. In the investigated hydroxide concentration range the time for reaching equilibrium is getting shorter with increase of alkalinity from 20 h to 50 min. Dependence of equilibrium distribution coefficients of gallium (K_d) vs sodium hydroxide concentrations is plotted in Fig. 3. The figure reveals that the extraction of gallium is not uniform within the

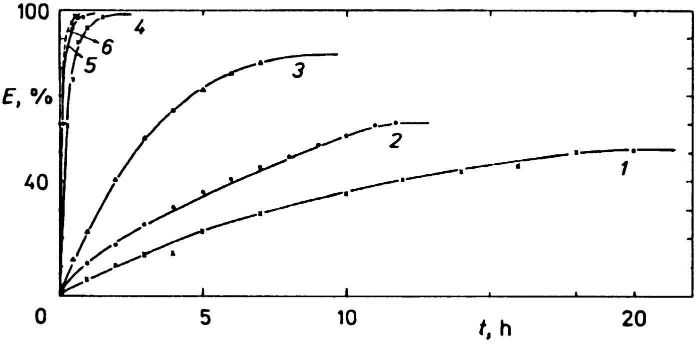


FIG. 1

Influence of hydroxide ions concentration at constant sodium concentration (c_{Na} = 0.5 mol dm^{-3}) on the rate of reaching equilibrium. $c_{\mathrm{Ga(aq)}}$ = 70 mg dm^{-3}; organic phase: 8.5 vol.% Kelex 100, 10 vol.% dodecanol in heptane. Sodium hydroxide concentrations: *1* 0.02, *2* 0.03, *3* 0.05, *4* 0.10, *5* 0.20, *6* 0.50 (mol dm^{-3})

investigated sodium concentration range. It is also evident that the mechanism of extraction of Ga from alkaline solutions by Kelex 100 (in the presence of dodecanol as a modifier) is a very complex one. There are three different mechanisms in the investigated NaOH concentration range. In the NaOH concentration range from 0.02 to 0.1 mol dm^{-3} the equilibrium distribution coefficient increases with increasing concentration of hydroxides, while further increase of hydroxide concentrations leads to decrease of K_d. In the NaOH concentration region from 0.02 to 0.1 mol dm^{-3} the slope of the straight line $\log K_d$ vs $\log c_{NaOH}$ is equal to ≈ 2, in the NaOH concentration range from 0.1 to 2 mol dm^{-3} the slope is ≈ –0.25, while in the range from 2 to 6 mol dm^{-3} the slope is ≈ –2. Sato and Oishi[12] have also investigated the influence of Na-hydroxide concentrations (from 0.1 to 6 mol dm^{-3}) on extraction of Ga by Kelex 100 in kerosene, but without adding alcohol, i.e., a modifier. Slopes of the straight lines $\log K_d$ vs $\log c_{NaOH}$ for different Kelex concentrations (from 0.025 to 0.1 mol dm^{-3}) were from –0.43 to –0.76. Sato et al.[11] have proved that addition of 2-ethylhexyl alcohol (as a modifier) into the organic phase changes considerably the $\log K_d$ vs $\log c_{NaOH}$ dependence. For the investigated NaOH concentration range (from 0.4 to 6.0 mol dm^{-3}) they obtained a nonlinear dependence for $\log K_d$ vs $\log c_{NaOH}$. On the basis of the experimental results given in paper[11] (Fig. 1b) one can conclude that the $\log K_d$ vs $\log c_{NaOH}$ dependence (for different Kelex 100 concentrations) in the NaOH concentration range from 0.4 to 1.0 mol dm^{-3} can be approximated by straight lines which slopes are in the region from –0.35 to –0.45. Unfortunately, due to insufficient number of experimental points (only two) it is not possible to determine a slope of the mentioned dependence in the NaOH concentration region from 3 to 6 mol dm^{-3}. It is evident, however, that the slope in the part of the stated dependence is much greater than –1. Accordingly, bearing in mind that similar results are not available in literature, we can conclude that our results are

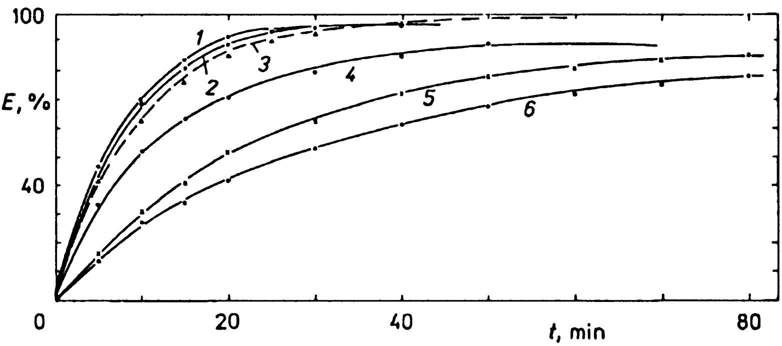


FIG. 2

Influence of sodium hydroxide concentrations on the solvent extraction of gallium. $c_{Ga(aq)} = 70$ mg dm^{-3}; organic phase: 8.5 vol.% Kelex 100, 10 vol.% dodecanol in heptane. Sodium hydroxide concentrations: *1* 1.0, *2* 2.0, *3* 3.0, *4* 4.0, *5* 5.0, *6* 6.0 (mol dm^{-3})

qualitatively in good agreement with the results of Sato et. al.[11,12]. It should be mentioned here that are no experimental results in literature on extraction for the NaOH concentration range from 0.02 to 0.1 mol dm^{-3}.

It might be concluded, from the obtained results, that the solvent extraction of gallium depends very much on the composition of the aqueous phase, i.e. on the concentration of $[OH^-]$ ions.

The influence of sodium hydroxide concentration in the aqueous phase on the gallium extraction has been also studied by some other authors[7,8,11,12,27]. Sato et. al.[12,27] have found that the distribution coefficients of gallium decrease with increasing aqueous concentration of sodium hydroxide in the concentration range from 0.1 to 6 mol dm^{-3}. The distribution coefficient (K_d) of gallium was determined for various Kelex 100 concentrations. The plot log K_d vs log Kelex 100 concentration, at constant sodium hydroxide concentration (4 mol dm^{-3}), gives a straight line slope ≈ 2 (Fig. 4). Accordingly, it can be assumed the 1 : 2 chelate, GaL_2, was extracted into the organic phase at this sodium hydroxide concentration. It should be pointed out here that a similar linear dependence was obtained[19] for lower NaOH concentration (0.5 mol dm^{-3}) as well, but with slope of ≈ 3. Therefore, on the basis of the experimental results obtained for gallium extraction from solutions of 2 – 6 mol dm^{-3} NaOH concentrations and assuming that Ga exist in aqueous solution of the stated NaOH concentration range as $Na[Ga(OH)_4]$ well dissociated as Na^+ and $[Ga(OH)_4^-]$, the equilibrium equation can be written as

$$2\,[Ga(OH)_4]^-_{(aq)} + 4\,HL_{(org)} \rightleftharpoons [GaL_{2_{(org)}}]_2 + 4\,OH^-_{(aq)} + 4\,H_2O_{(aq)}\,.$$

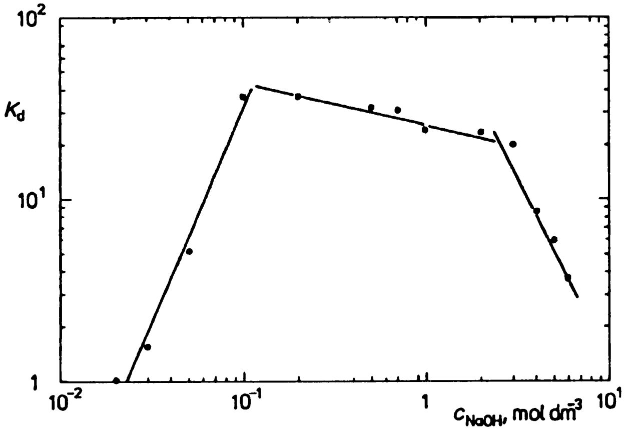


FIG. 3

Dependence of the distribution coefficient of gallium on the aqueous sodium hydroxide concentrations. $c_{Ga(aq)}$ = 70 mg dm^{-3}; organic phase: 8.5 vol.% Kelex 100, 10 vol.% dodecanol in heptane

As in similar studies on the extraction kinetics using mixer-type apparatus, the kinetic data were rearranged as a plot based on the irreversible first order reaction rate with respect to the gallium ion in the aqueous phase, according to Eq. (*2*). The concentration dependencies $\log (c^0_{\mathrm{Ga}}/c_{\mathrm{Ga}})$ vs mixing time, *t*, where c^0_{Ga} and c_{Ga} denote gallium concentrations at $t = 0$ and time, *t*, for different hydroxide (at constant sodium) concentrations are presented in Fig. 5. The slopes of the obtained straight lines representing a relationship between $\log (c^0_{\mathrm{Ga}}/c_{\mathrm{Ga}})$ vs *t* were calculated applying the least square method. Dependencies of the pseudo rate constants, q_{OH} (defined by Eq. (*4*) in the logarithmic form), on the hydroxide concentrations are given in Table I.

From the obtained values for q_{OH} the reaction order c was calculated as a slope of the straight line which represents the dependencies of $\log q_{\mathrm{OH}}$ on log (OH) (see Fig. 6). From Fig. 6, two distinct slopes are evident. In the hydroxide concentration range from 0.03 to 0.20 mol dm^{-3} the slope of the straight line obtained by the least square method is 2, which means that the reaction order c is equal to 2. Over the hydroxide concentra-

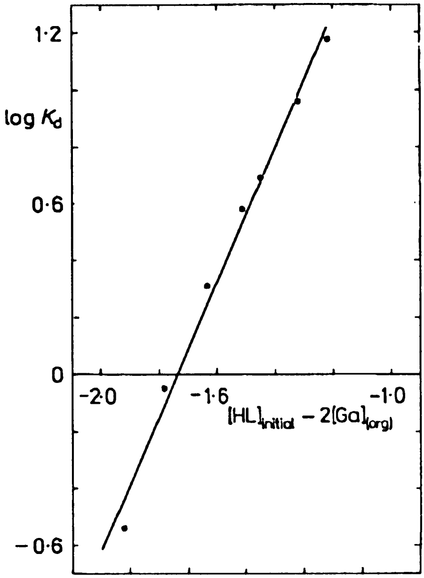


FIG. 4

Dependence of the distribution coefficient on the Kelex 100 concentration at a constant sodium hydroxide concentration of 4 mol dm^{-3}. Slope = 2.38, $r = 0.995$

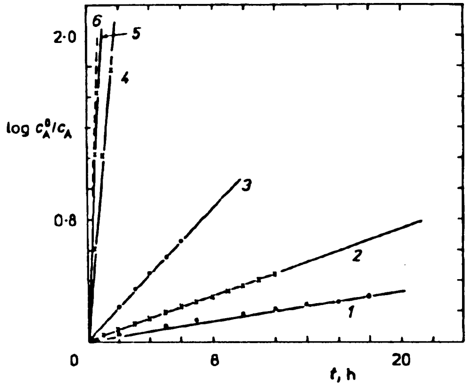


FIG. 5

Concentration dependencies vs mixing time for different hydroxide concentration values. $c_{\mathrm{Ga(aq)}}$ = 70 mg dm^{-3}, c_{Na} = 0.5 mol dm^{-3}; organic phase: 8.5 vol.% Kelex 100, 10 vol.% dodecanol in heptane. Hydroxide concentrations: *1* 0.02, *2* 0.03, *3* 0.05, *4* 0.10, *5* 0.20, *6* 0.50 (mol dm^{-3})

tion of 0.20 up to 0.5 mol dm^{-3}, the q_{OH} values are independent on the log [OH$^-$] values, so that in this region of alkalinity the reaction order c is zero.

The influence of sodium hydroxide at concentration above 0.5 mol dm^{-3} on the pseudo rate constant, q (denoted as q_{NaOH}), is shown in Table I. The values for the pseudo rate constant q_{NaOH} are obtained as slopes of the straight lines which represent a relationship between log (c^0_{Ga}/c_{Ga}) vs mixing time, t, for different NaOH concentrations. The reaction order b can be calculated in the same way as for the reaction order c. The

TABLE I

Dependencies of q_{OH} on hydroxide concentration for constant sodium concentration (c_{Na} = 0.5 mol dm^{-3}) and q_{NaOH} on sodium hydroxide concentration. Organic phase: 8.5 vol.% Kelex 100; 10 vol.% dodecanol in heptane

[OH$^-$] mol dm^{-3}	q_{OH} min^{-1}	c_{NaOH} mol dm^{-3}	$q_{NaOH} \cdot 10^3$ min^{-1}
0.02	0.27	0.50	49.0
0.03	0.57	1	39.8
0.05	1.8	2	35.0
0.10	19.7	3	34.9
0.20	41.2	4	21.0
0.50	48.9	5	10.4
		6	7.9

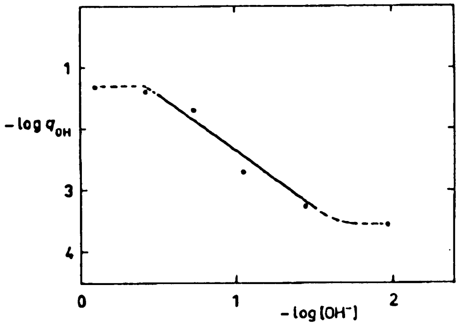


FIG. 6

Dependence of log q_{OH} on log [OH$^-$]. $c_{Ga(aq)}$ = 70 mg dm^{-3}; organic phase: 8.5 vol.% Kelex 100, 10 vol.% dodecanol in heptane

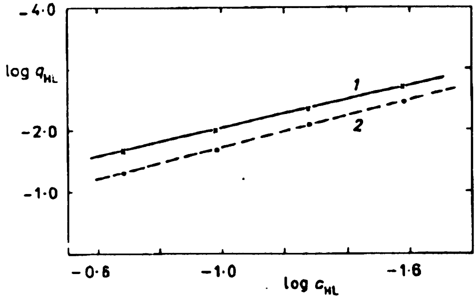


FIG. 7

The rate constants q_{HL} dependence on the extractant concentration for two hydroxide concentration values. c_{Na} = 0.5 mol dm^{-3}. Hydroxide concentrations: *1* 0.10, *2* 0.50 (mol dm^{-3})

increase in extractant concentration leads to enhanced extraction rates. The pseudo rate constant q_{HL} (defined by Eq. (*3*)) was calculated according to Eq. (*2*) for four different extractant concentrations and each of the two chosen hydroxide concentration values in the aqueous phase. The plot log q_{HL} vs log c_{HL}, is given in Fig. 7. For the two hydroxide concentration values, the slopes of obtained straight lines are equal to 1, so it can be deduced that the reaction order b is 1 as well.

The rate expression of the extraction reaction of gallium with Kelex 100, given by Eq. (*1*), can be described by Eq. (*6*) for the hydroxide concentration from 0.03 to 0.20 mol dm^{-3} and for the Kelex 100 concentrations in the range 1 – 8.5 vol.% in the organic phase:

$$-\frac{\mathrm{d}[\mathrm{Ga}]_{(\mathrm{aq})}}{\mathrm{d}t} = k\,[\mathrm{Ga}]_{(\mathrm{aq})}\,[\mathrm{HL}]_{(\mathrm{org})}\,[\mathrm{OH}^-]^2_{(\mathrm{aq})}\,. \qquad (6)$$

For the hydroxide concentrations higher than 0.20 mol dm^{-3} and the same concentration range of the extractant, the rate expression is:

$$-\frac{\mathrm{d}[\mathrm{Ga}]_{(\mathrm{aq})}}{\mathrm{d}t} = k\,[\mathrm{Ga}]_{(\mathrm{aq})}\,[\mathrm{HL}]_{(\mathrm{org})} \qquad (7)$$

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