

Isotope effects of gallium and indium in cation exchange chromatography

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Abstract The isotope effects of gallium ($^{69/71}\text{Ga}$) and indium ($^{113/115}\text{In}$) have been determined in the system: strong cation exchanger (Dowex 50-X8)/HCl. The signs of gallium and indium effects were opposite, i.e., the heavier isotope of gallium was fractionated into the resin phase, while the heavy isotope of indium was fractionated into the liquid phase. The values of unit separation gains were found to be $+3.0 \times 10^{-5}$ for gallium and -2.0×10^{-4} for indium. A possible explanation of the effects is proposed.

Key words isotope separation • chemical isotope effects • ion-exchange chromatography

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Introduction

The role of isotopically pure materials in micro-electronic industry is recently growing up because of their higher thermal conductivity and lower crystal lattice noise in comparison with the materials of natural isotope composition. These phenomena are best recognized for silicon, however, the isotopically-engineered materials of gallium and indium can also effectively increase the performance and reliability of the devices used in wireless communication, optoelectronics, semiconductor lasers, high frequency integrated circuits, etc. [3, 8, 11].

The career of isotopically engineered materials depends mostly on the isotope separation cost, i.e. on the effectiveness of isotope enrichment methods. The enrichment by chemical methods, like liquid-liquid extraction or ion-exchange chromatography, is worth taking into consideration.

These circumstances motivated us to undertake these studies in order to select the systems characterized by high isotope separation factor. Till now, no fractionation data of gallium and indium isotopes in the chemical systems have been published. We started our work with chromatographic systems as they enabled multiplying the unit enrichment factor.

Naturally occurring gallium and indium consist of two isotopes of the abundance: ^{69}Ga (60.16%), ^{71}Ga (39.84%) and ^{113}In (4.28%), ^{115}In (95.72%). All the isotopes have the odd mass number and different spin numbers: $I_{69} = 1+$, $I_{71} = 3/2-$ and $I_{113} = 1+$, $I_{115} = 9/2+$. Both elements belong to group 13 of periodic table with the general configuration of free atoms: Ga – [Ar] $3d^{10}4s^24p^1$, In – [Kr] $4d^{10}5s^25p^1$.

In aqueous hydrochloric solution Ga^{3+} is weakly coordinated, whereas In^{3+} forms a series of fairly stable

chloride complexes. The values of their stability constants are $\beta_1 = 0.01$ for gallium and: $\beta_1 = 2.32$, $\beta_2 = 3.6$ and $\beta_3 = 4.0$ for indium [12]. It was reasonable to assume that this difference in stability would influence the process of isotope fractionation in the studied systems.

Experimental

Reagents

Ga_2O_3 and In_2O_3 (reagent grade, 99.999%) was purchased from Sigma Aldrich. The feed solutions were prepared by dissolving the oxides in hydrochloric acid.

The strong acidic cation-exchanger, Dowex 50-X8, was used. The resin was purified from the fraction below 400 mesh by repeated sedimentation in order to reduce the pressure drop in the column. All other reagents were analytical grade.

Determination of distribution coefficient (K_d)

The batch method was employed. 1 g of the resin was equilibrated in the vials with 10 ml of the acid containing 0.1 mmol of the given metal. The distribution coefficient was calculated using the equation:

$$(1) \quad K_d = (V/m) * [(C_{\text{feed}} - C_{\text{eq}})/C_{\text{eq}}]$$

where: V is the volume of the solution in the system, in ml; m is the mass of the dry resin, in grams; C_{feed} is the initial concentration of the metal; C_{eq} is the concentration of the metal in the solution after equilibration.

Column experiments

The slurred resin was packed into the column, 100 cm high and 0.5 cm in inner diameter. The HCl solution of proper concentration was flowed through the column for at least 24 h with a flow rate of 0.3 ml/min controlled by a peristaltic pump, Masterflex Easy Load II. Then, the metal band was created at the top of the column by injecting a sample solution containing 2.7 mg of Ga or 4.1 mg of In. The band was eluted by hydrochloric acid with a flow rate of 0.11 ml/min. The so-called merry-go-round method was applied, i.e. the band was repeatedly cycled over the column in order to increase the number of theoretical plates, N_p . After a certain number of cycles, N_c , the band was eluted to a fraction collector (Pharmacia LKB, Redi-Frac) in 2 ml portions.

Analysis

The metal content in consecutive fractions was followed qualitatively by spot tests [5] and then determined quantitatively by atomic absorption analysis with flame atomization.

The isotope ratios, R ($^{69/71}\text{Ga}$, $^{113/115}\text{In}$) in selected fractions was determined by an inductively-coupled-

plasma mass spectrometer, ICP-MS Elan 9000, Perkin Elmer Sciex. Prior to the analysis, the chlorides were removed from the samples containing more than 10 μg of metal by evaporation with 4 M HNO_3 to dryness in teflon vials and dissolving the residue in 0.1 M HNO_3 . For single measurements, the samples of 6 ml containing 25 ppb of gallium were taken. The relative standard deviation of the measurement was usually less than 0.05%.

The local separation factor, defined as $q_i = R_i/R_{\text{feed}}$, or the local enrichment gain, defined as $\epsilon_i = \ln(q_i)$, were calculated from the data.

Results and discussion

Preliminary experiments revealed that it is possible to elute gallium and indium in the form of symmetric bands, suitable for the band elution methods. The parameters of the bands (elution volume, height and width) depend on the distribution ratio, K_d , which itself is related to the concentration of the acid as shown in Fig. 1. The values of K_d decrease when the concentration of acid increases. For gallium, this phenomenon is observed in the range of stronger acid than for indium, thus reflecting the differences in values of the mentioned above stability constants of complexes of Ga^{3+} and In^{3+} with counter ion in the solution. It is to be noted that the same value of the distribution ratio of metal ions, i.e. $K_d \approx 4$, was maintained by the acid concentrations: 0.5 M HCl for indium and 2.5 M for gallium.

The results of the column experiments are summarized in Table 1 and presented in Figs. 2a and 2b, as the relation between the observed local enrichment gain (ϵ_i) vs. eluted fraction of metal ($\Delta n/n$). The S-shape relation was typical of all the experiments presented. The opposite slopes of the S-shape curves demonstrate an opposite sign of indium and gallium isotope effects. In fact, the heavy isotope of indium, ^{115}In , was fractionated into the solution phase whereas the heavy isotope of gallium, ^{71}Ga , into the resin phase.

This finding revealed that the equilibrium of the isotope exchange reactions (Eqs. (2) and (3)) is shifted

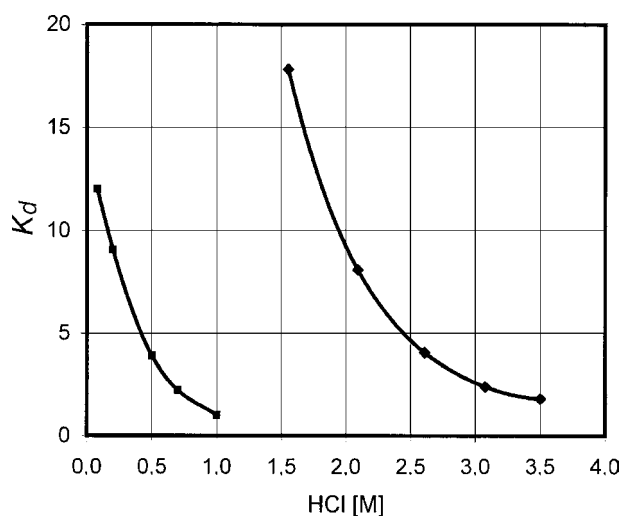


Fig. 1. K_d of Ga and In vs. acid concentration in the Dowex 50-X8/HCl system.

Table 1. Results of the column experiments

	HCl [M]	N_c	$N_{tp}^{(1)}$	$Q_{max}^{(2)}$	$\epsilon_u \cdot 10^{-5}^{(3)}$
Gallium	2.25	7	3100	1.08	+2.8
	2.5	9	3700	1.01	+3.3
	3.0	8	4100	1.008	+3.1
Indium	0.5	1	1100	1.032	-19.0
	0.5	9	10,000	1.075	-19.0

⁽¹⁾ N_{tp} is the number of theoretical plates, calculated from the formula $N = 8 \cdot (V_{el}/\beta)$, where V_{el} is the elution volume and β is the band width at the concentration C_{max}/e .

⁽²⁾ Q_{max} is the process separation factor equal to the ratio $R_{(front\ end)}/R_{(rear\ end)}$, where both R values are extreme observed.

⁽³⁾ ϵ_u is the unit separation gain calculated by the Glueckauf theory.

to the right hand side for gallium, but to the left hand side for indium:

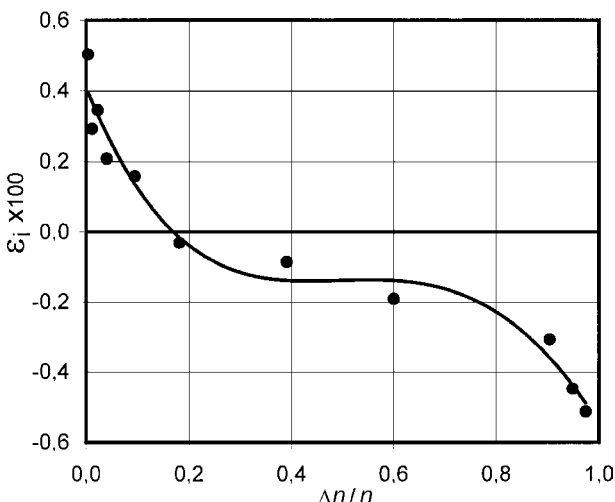
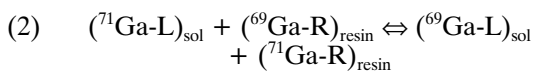


Fig. 2a. Local separation gain vs. eluted fraction of gallium; 2.5 M HCl.

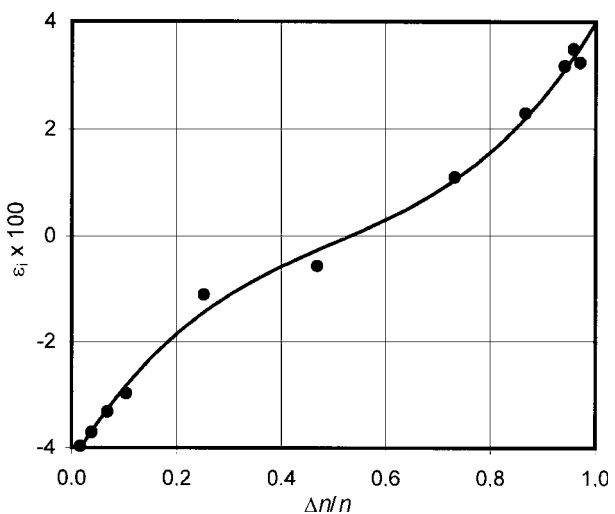


Fig. 2b. Local separation gain vs. eluted fraction of indium; 0.25 M HCl.

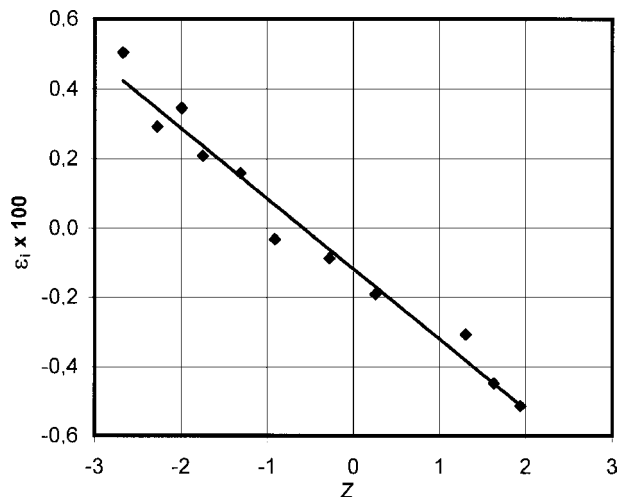


Fig. 3a. Gallium local separation gain vs. eluted fraction in Z units; 2.5 M HCl.

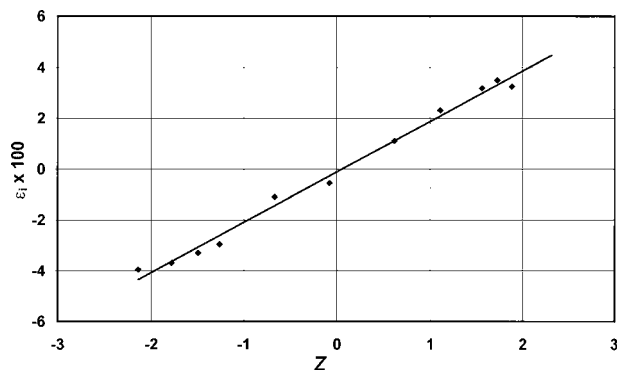
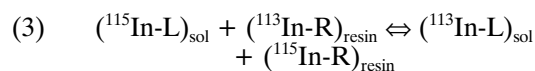


Fig. 3b. Indium local separation gain vs. eluted fraction in Z units; 0.25 M HCl.



where: L and R represent a ligand and the resin.

The corresponding values of unit separation gains, ${}^{\text{Ga}}\epsilon_u$ and ${}^{\text{In}}\epsilon_u$, related to the equilibrium constant of isotope exchange reaction as $\epsilon_u = \ln K$, are shown in the last column of Table 1. They have been calculated by the Glueckauf theory [6, 7] as ${}^{\text{Mc}}\epsilon_u = S/N^{0.5}$, where S is the slope of linear function of ϵ_i against the $\Delta n/n$ value at x-axis scaled in standardize differences (Z) of normal distribution (Figs. 3a and 3b). The same results could be obtained by plotting ϵ_i against $\Delta n/n$ on a probability graph paper.

It is to be noted that the absolute value of the unit separation gain for indium, ${}^{\text{In}}\epsilon_u$, was found to be about one order higher than that for gallium, ${}^{\text{Ga}}\epsilon_u$, but of the opposite sign. It was also observed that the fractionation of gallium isotope is not sensitive to the concentration of hydrochloric acid in the range 2.0–3.0 M.

The classic theory of isotope effects [2], based on analysis of vibration energy, yields the following expression of ϵ_u in terms of the reduced partition function ratio (RPFR) and molar fractions of gallium or indium species involved in the system, $x_i y_i$:

$$(4) \ln K = \epsilon_u = \ln(x_1 f_{\text{Me}^{+3}} + x_2 f_{\text{MeCl}^{+2}} + \blacklozenge\blacklozenge\blacklozenge\blacklozenge)_{\text{resin}} - \ln(y_1 f_{\text{Me}^{+3}} + y_2 f_{\text{MeCl}^{+2}} + \blacklozenge\blacklozenge\blacklozenge\blacklozenge)_{\text{sol}}$$

where: f denotes RPFR. Difference in respect to the hydration spheres around metal ions is omitted for simplicity.

From this theory, the generalization follows that the heavy isotope should concentrate in the chemical species with stronger bonds to the element involved in the isotope exchange reaction.

As for indium we have $\ln \epsilon_u < 1$, the summing up in brackets (if possible) should result in higher absolute value of the sum for the solution phase than for the resin phase. This means that rather strong complexes of indium in solution create stronger bonds to the element involved in the isotope exchange reaction than the resin phase does. Thus, the heavy isotope of indium is fractionated to the solution phase.

The small absolute value of the unit separation factor of gallium revealed little difference between the state of the complexes in the solution and the resin phases, reflecting the low value of stability constants of gallium complexes in respect of those of indium.

Additionally, the opposite sign of the gallium effect, ${}^{\text{Ga}}\epsilon_u > 1$, suggests that also other factors, not only the effect of complexation, contribute significantly to the small overall effect.

The differences in the structure of hydration spheres of the metal ion in solution and resin phase and field shift effect should be taken into consideration.

The influence of hydration on isotope effect was revealed and discussed in course of the studies of the fractionation of the isotopes of uranium [9] and strontium [10]. The mass independent field shift effect is known to have the opposite sign in respect to the effect that originates from inter- and intramolecular vibration and, in some cases, can change the sign of the total effect [1, 4].

Summary

The isotopes of gallium and indium fractionate in cation exchanger/hydrochloride acid system. The separation factor can be multiplied by the band elution “merry-go round” method. The signs of gallium and indium isotope effect were found to be opposite, i.e., the heavier isotope of gallium was fractionated into the resin phase,

while the heavy isotope of indium was fractionated into the liquid phase. The values of unit separation gains were found to be $+3.0 \times 10^{-5}$ for gallium and -2.0×10^{-4} for indium. It is proposed that the complex species in the liquid phase are mainly responsible for fractionation of indium isotopes, whereas the difference in hydration or other factors may play a significant role in the fractionation of gallium isotopes.

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