

THE KINETICS OF THE EXTRACTION OF Al(III) AND In(III) INTO ISOBUTYRYLACETONE ADSORBED ON A SUPPORT

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The equilibration rate has been studied for the extraction of aluminium(III) and indium(III) into 5-methyl-2,4-hexanedione (isobutyrylacetone) adsorbed on a support, hydrophobized silica or hydrophobized expanded perlite (natural volcanic glass of the rhyolite group). Equilibrium is established at times longer than 80 minutes. The effect of the amount of adsorbed reagent, the temperature, the composition of the adsorbed organic phase and the presence of some anions in the aqueous phase on the extraction rate has been monitored. The results obtained permit explanation of the behaviour of the two ions encountered earlier during their extraction chromatography.

During column extraction chromatography of aluminium, gallium and indium using a stationary solution of 5-methyl-2,4-hexanedione (isobutyrylacetone, HL), disagreement was found between the values of the elution volumes for these metal ions, calculated from the results of their distribution in liquid-liquid extraction, and the values obtained during their distribution on a column¹. It was proposed that this disagreement is caused by the low rate of the process in which a species capable of passing from the mobile polar phase across the interface into the stationary less polar phase is formed from the inorganic ion. Therefore, during the flow of the mobile phase through each theoretical plate of the column, part of the metal ions would be converted into an extractable chelate that would be distributed between the two phases according to the conditions and the rest of the ions would remain free and would thus pass through the column more rapidly than expected from the distribution ratio values, D , determined for batch extraction.

The kinetics of the distribution of inorganic ions during transfer of chelates between an aqueous phase and an organic phase adsorbed on a support have not yet been studied. The kinetics of liquid-liquid extraction of chelates have been treated in two reviews^{2,3}. The kinetics of the extraction of β -diketonates have also been studied⁴⁻⁶. It has been found⁶ that enolization of the β -diketone is the rate-determining step in the chelate distribution between two liquid phases.

This paper has been aimed at determining the effect of the thickness of the organic phase layer, the temperature, the kind of solvent and the HL concentration and of the presence of the anions of some weak acids on the establishment of the distribution equilibrium during transfer of a metal ion in the form of the HL chelate from the aqueous phase into the organic phase adsorbed on a support. Al(III) and In(III) ions were selected for the study of these dependences; their separation by extraction chromatography with a stationary HL solution has already been studied¹. The same

supports were used as those employed as column packings in ref.¹, *i.e.* hydrophobized silica and hydrophobized expanded perlite.

EXPERIMENTAL

Solutions and Chemicals Used

An aluminium stock solution was prepared by dissolving the weighed chemically pure metal (Soyuzkhimeksport) in hydrochloric acid, evaporating to dryness and dissolving the residue in 0.1M-HCl. The aluminium content (0.8190 mg/l) was checked gravimetrically using 8-hydroxyquinoline⁷. An indium stock solution, labelled with ^{114m}In with an activity of $1.11 \cdot 10^8 \text{ s}^{-1} \text{ ml}^{-1}$ (3 mCi/ml) (Institute of Nuclear Research, Swierk, Poland), was obtained by dissolving pure indium (min 99.99%) in hydrochloric acid, evaporating to dryness and dissolving the residue in 0.1M-HCl. Before the solution was diluted to the required volume, 0.1 ml of an InCl₃ solution containing ^{114m}In with the given activity was added. Isobutyrylacetone and its solutions were obtained by procedures described elsewhere¹.

Instruments

The pH values were measured on a Radelkis OP 201/P instrument (Hungary) with an OP 8071—A combined electrode from the same manufacturer and photometric measurements were performed using a VSU-2 spectrophotometer (Zeiss, Jena, GDR). The radioactivity of the samples was measured using a NZQ 715 automatic instrument (Tesla, Liberec) with a NaI(Tl) well scintillation detector; the measuring conditions were 1.1 kV with a sensitivity of 0.03. A constant temperature was maintained during equilibration using a UTU ultrathermostat (Poland) connected with a flow-through heater made in the laboratory and attached to a shaker (a frequency of 160 min⁻¹ and an axial deviation of approx. 3 cm).

Supports

Silica and perlite were pretreated in the same manner as previously¹; however, another procedure was employed for hydrophobization. A sieved fraction (0.100—0.125 mm) was dried at 200°C first in a drying oven and then in an evacuated flask connected with a tube containing P₂O₅ (7 h, 2—2.7 kPa). 1 ml of dichlorodimethylsilane per 10 g of support was then injected into the closed evacuated flask using a syringe through a stop-cock. After 12 h standing, the support was again heated for 5 h to 200°C with continuous evacuation. The last traces of hydrogen chloride were then expelled by heating the support, spread over a large area, in the air. The hydrophobized support was dried at 120°C before impregnation.

An HL extract in light petroleum, obtained by decomposition of its cupric salt, was used for support impregnation with pure HL. The hydrophobized support was stirred with the extract and the solvent was evaporated with continuous stirring. The amount of HL deposited was checked by weighing. During impregnation with HL solutions, the support was stirred for 15 to 20 min in an HL solution in the required solvent. In all cases the support remained granular after the impregnation.

Analytical Methods

The aluminium concentration in the aqueous phase was determined photometrically with Eriochromcyanine R (ref.⁸). During monitoring of the sorption on impregnated perlite a surfactant

had to be added to the mixture to be able to stir the impregnated support grains in the aqueous phase. The surfactant (detergent) added affected the aluminium absorbance in the determination using the above method. Therefore, in this case a calibration curve was constructed in the presence of an identical amount of the detergent as in the distribution.

The indium concentration was determined radiometrically by measuring the γ -radiation of the ^{114m}In nuclide (0.192 MeV, half-time 48.5 d). An aliquot of the aqueous phase was evaporated in an aluminium dish (2 cm in diameter) containing filter paper and the number of impulses was measured.

Procedure

20 ml vessels, containing 0.2 g of impregnated support and 10 ml of the aqueous phase, were used for equilibration. The aqueous phase contained the same volumes of the aluminium salt solution (20 to 80 $\mu\text{g Al/ml}$) and of a buffer solution of pH 4 (4.896 g $\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O} + 10 \text{ml } 100\% \text{CH}_3\text{COOH}$ per litre) during sorption on impregnated silica and 2.5 ml of the metal salt solution, 2.5 ml of the buffer solution and 5 ml of a dilute detergent solution ($6 \cdot 10^{-2}\%$) during sorption on impregnated perlite. The mixture was shaken in the flow-through heater. Samples were taken from the vessels at selected time intervals. An aliquot part of the aqueous phase was then separated by a pipette with a filter inset and analyzed. During monitoring of the back-extraction rate, the aqueous phase was separated under vacuum and the support with the sorbed element was shaken at the same temperature with 0.2M- HClO_4 ; portions of the aqueous phase were again taken at given intervals and analyzed.

RESULTS AND DISCUSSION

The Effect of the Amount of HL Used for Impregnation on the Rate of the Aluminium Salt Sorption

Both hydrophobized supports were impregnated with amounts of HL such that, with respect to the amount of Al(III) in the system, the HL : Al molar ratio equalled 1.5, 3 or 7.5, i.e. substoichiometric, stoichiometric and overstoichiometric amount. The amount of aluminium present in the system was varied, so that the amount of HL in the system did not increase proportionately to the HL : Al ratio. The amounts of HL (per 0.2 g of the support) present in the system at the individual HL : Al ratios were: ratio of 1.5—44 $\mu\text{mol HL}$; 3—21 $\mu\text{mol HL}$, 7.5—89 $\mu\text{mol HL}$. The distributions were followed at temperatures of 20, 40, 60 and 80°C. The curves for the time dependence of the amount of aluminium sorbed (in %) on silica were analogous to the curve in Fig. 1 at all the temperatures. The line segments on curve 3 express the confidence limits of the measurement, calculated from the results of parallel determinations. It is evident from the shape of the curves that equilibrium is not completely attained even after 80 minutes. The sorbed portion of the aluminium at a certain time is smallest at an HL : Al molar ratio of 1.5 and largest at a ratio of 3. If the sorption rate is evaluated according to the increase in the sorbed fraction per time unit, then the effect of the amount of HL deposited on the sorption rate is manifest only in the beginning (up to 5 or 10 min) and later the sorption proceeds at vir-

tually identical rates with various amounts of HL in the system. The comparison of curves 1 and 2 in Fig. 1 is interesting. An increase in the amount of HL per support weight unit, *i.e.* an increase in the thickness of the organic phase layer deposited on the support, leads to a decrease in the sorbed aluminium fraction at a certain time. This assumption is verified by the results of the aluminium sorption on perlite with deposited HL (Fig. 2), obtained under identical conditions (except for the temperature) as the curves in Fig. 1 for silica. However, as the specific surface area of perlite is approximately 100 times less than that of silica⁹, the same amount of HL per weight unit of perlite forms a thicker layer than on silica. In agreement with this fact, the sorbed fraction of the aluminium at a certain time is smaller for all the HL : Al ratios than on silica under equivalent conditions. The differences in the sorbed Al fractions at various HL : Al molar ratios are also smaller and the three curves have almost the same shape, in view of the confidence limits for the determination of aluminium, shown in Fig. 2. Therefore, an increase in the thickness of the organic phase layer leads to a decrease in the differences in the sorption rate due to the presence of a substoichiometric or overstoichiometric amount of HL. The curves for the sorption on perlite exhibit a maximum at all temperatures; the maximum increases with increasing temperature. The reversibility of the sorption was verified for both HL-impregnated supports by monitoring the desorption rate. The curves for the time

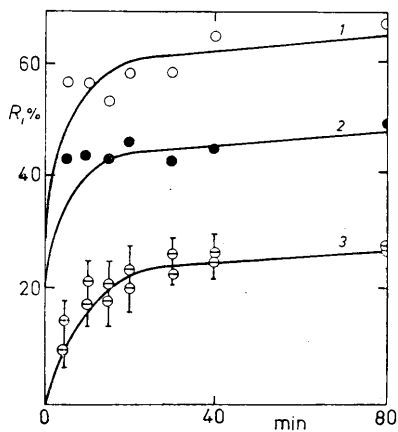


FIG. 1

The Effect of the Amount of Isobutyrylacetone Deposited on Silica on the Aluminium(III) Salt Sorption Rate

Hydrophobized silica, 100–125 μm , pH 4.0, t 40°C, the HL : Al molar ratio: 1 3.0; 2 7.5; 3 1.5.

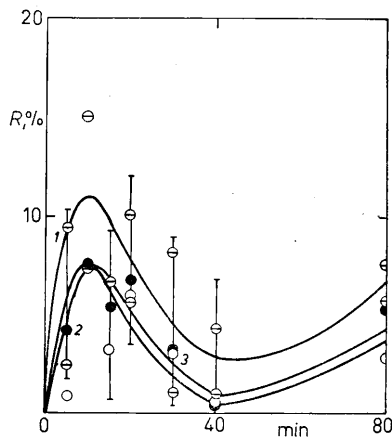


FIG. 2

The Effect of the Amount of Isobutyrylacetone Deposited on Perlite on the Aluminium(III) Salt Sorption Rate

Hydrophobized perlite, 100–125 μm , pH 4.0, t 20°C, the HL : Al molar ratio: 1 1.5; 2 7.5; 3 3.0.

dependence of the fraction desorbed from silica and perlite at 80°C have the inverse shape to that of the sorption curves, *i.e.* a minimum appears after 10 min desorption from perlite. On an increase in the temperature the sorption rate on the impregnated supports increases similarly for silica and perlite.

The Effect of the HL Concentration in the Stationary Phase and the Effect of the Diluent Type on the Indium(III) Salt Sorption Rate

An indium(III) salt was employed for the study of this dependence, assuming that indium(III) ions would affect the equilibration rate in the same manner as aluminium(III) ions. 25% and 50% HL solutions in toluene and chloroform were used for the impregnation. The amount of indium used corresponded to a HL : In molar ratio of 3 (for the 50% solution) and 1.5 (for the 25% solution). The effect of temperature was monitored only up to 60°C, because of the volatility of the solvents. According to the $K_{ex}(\text{In})$ value for the water-HL benzene solution¹⁰, indium should be completely transferred into the organic phase during batch extraction at pH 4, at both HL concentrations used. Considering the high D value (10^{32} or 10^{12} for $c(\text{HL})_{\text{org}} = 3.90$ or 1.95M , respectively), it can be assumed that the recovery in the indium extraction would be 100% even if toluene is used as the solvent instead of benzene.

It can be assumed that the HL solubility in toluene will differ only a little from that in benzene, so that the difference between K_D (HL, toluene-water) and K_D (HL, chloroform-water) will be similar to that between K_D (HL, benzene-water) ≈ 95 and K_D (HL, chloroform-water) ≈ 460 (ref.¹¹). If it is assumed that the extractable species (*i.e.* the InL_3 chelate) is formed in the aqueous phase, then the extraction using toluene as the diluent should proceed more rapidly than with chloroform. The results obtained are given in Table I. In the table, the letter c denotes combinations of the support, temperature, the HL concentration and the time of the contact of the two phases, for which the indium fraction sorbed was larger with chloroform as the diluent and the letter t those for which the fraction sorbed was larger with toluene. The letter 0 denotes a difference of less than 5% in the sorption. The number of cases of faster sorption with toluene as the solvent is considerably larger for silica (15 : 5) than for perlite (10 : 12), where there is virtually no difference. This is apparently again connected with the greater thickness of the organic phase layer on perlite, so that the time required for mass transport through this layer determines the equilibration time, as it is substantially longer than the time required for completion of the other processes.

The Effect of Weak Acid Anions on the Indium Salt Sorption Rate

The formation of a β -diketonate from an aquo-complex can be considered as a displacement reaction. The octahedral In(III) complexes are outer-orbital complexes and

should be kinetically labile. Since some outer-orbital complexes are of a transitional type between labile and inert complexes², it was decided to discover whether the extraction rate is increased using so-called ligand catalysis². The catalytically-active ligand should rapidly form a complex with an aquo-indium(III) cation, with a stability lower than that of the complex with the β -diketone. As HL is a weak acid, the rate of the chelate distribution depends on the pH of the aqueous phase. Therefore the effect of complexing anions was monitored at the same pH as in the previous experiments (4.0).

Since it followed from the previous experiments that the sorption proceeded fastest using silica impregnated with a 25% HL solution in toluene at 20°C, these conditions were also selected for the study of the effect of anions on the indium sorption rate. By potentiometric titration of $5 \cdot 10^{-2}$ M-solutions of sodium propionate, citrate, benzoate and potassium phthalate with 1M-HCl to pH 4.0, buffer solutions were obtained which were then used in the procedure described above. The results are depicted in Fig. 3. For the sake of comparison, the curve obtained using an acetate buffer is also given. The anions used did not markedly affect the indium sorption rate on the impregnated support. The higher rate in the presence of acetate (curve 1) is probably caused by a higher buffering capacity and hence by a certain difference in the resultant pH. Therefore it cannot be assumed that the aquo-indium(III) ion is of a transitional type from the point of view of kinetic stability.

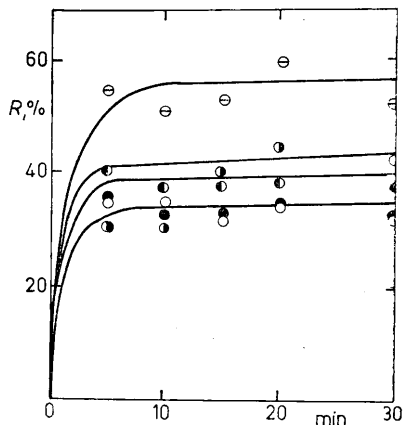
For the sorption of aluminium(III) or indium(III) ions on an inert support impregnated with the liquid HL reagent or with its solution, an identical reaction scheme to that for the distribution of these ions in the liquid-liquid system can be assumed:

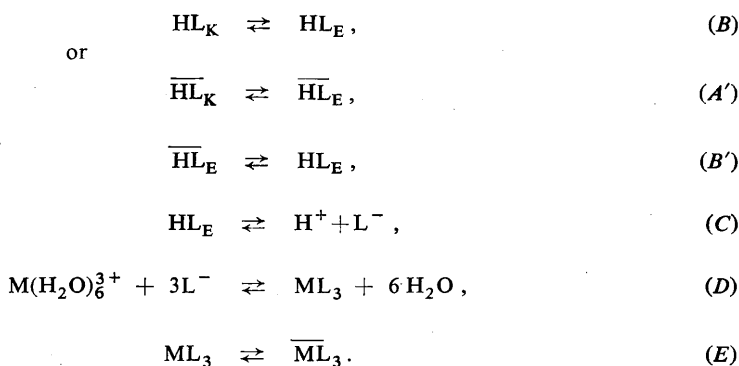


FIG. 3

The Effect of Weak Acid Anions on the Sorption Rate of an Indium(III) Salt on Silica Coated with a 25% Isobutyrylacetone Solution in Toluene

Hydrophobized silica, 100–125 μm , pH 4.0, t 20°C, the HL : In molar ratio equal to 1.5, the sum of the acid and the salt concentrations in the buffer solution, $5 \cdot 10^{-2}$ M. \ominus acetate; \bullet propionate; \circ phthalate; \circ benzoate; \bullet citrate.





The dash above the formula of a compound indicates its presence in the organic phase. Subscripts E and K denote the enol and keto forms of HL, respectively. Reactions (A), (B') and (E) express the mass transport and reaction (C) is very rapid. The effect of the individual processes on the equilibration rate in the studied system, which is given by the slowest process of reactions (A)–(E), can be best evaluated considering the effect of the composition of the stationary organic phase. During the sorption on silica, the process takes place in the so-called kinetic region², where the rate of processes (B) or (A') and (D), *i.e.* of the chemical reactions, is smaller than that of processes (A) or (B') and (E), *i.e.* of mass transport. Here the effect of the solvent type on the distribution rate becomes manifest (Table I). During the sorption on perlite, whose specific surface area is substantially smaller than that of silica and on which the

TABLE I
The Effect of the Diluent Type on the Equilibration Rate

Contact min	Silica				Perlite			
	20°C		60°C		20°C		60°C	
	25%	50%	25%	50%	25%	50%	25%	50%
5	0 ^a	t ^b	t	0	t	c ^c	t	0
10	c	t	t	0	t	c	0	c
15	0	0	t	t	t	c	0	c
20	c	0	t	t	t	c	0	c
30	c	0	t	t	t	c	t	c
40	c	0	t	t	t	c	0	c
80	c	t	t	t	t	0	t	c

^a The difference in the sorbed fraction when toluene or chloroform are used is smaller than 5%.

^b The rate is higher with toluene as the solvent. ^c The rate is higher with chloroform as the solvent.

process takes place in the region of diffusion control², the differences in the diluent employed have no effect on the equilibration rate. The thick organic phase layer on the support has the same effect in this distribution procedure as slow stirring of the two liquid phases during extraction. The slowest, and consequently rate-determining, processes are then (A) or (B') and (E).

If reaction (D) is not retarded by the kinetic inertness of the aquo-ion, then the slowest process, determining the ion sorption rate on an impregnated support in the kinetic region, is the β -diketone enolization (reaction (B) or (A') (refs^{2,6,12}).

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