EXTRACTION OF IRON WITH DIBENZYL SULFOXIDE SOLUTION SORBED ON SILICA GEL

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The amount of dibenzyl sulfoxide (DBSO) sorbed on silica gel from toluene solutions was measured for different silica gel hydrophobization procedures and in dependence on the initial DBSO concentration in the solution. From silica gel impregnated with DBSO solution, the sulfoxide is washed out by hydrochloric acid even if the acid has been saturated by shaking with 0·05M solution of DBSO in toluene. The effect of HCl and DBSO concentrations on the recovery of iron was investigated both for liquid–liquid extraction and for extraction with the extractant solution sorbed on silica gel. The recoveries for the two cases are equal, which implies that the ratios of the activity coefficients of the reagent and of the extracted complex for the liquid–liquid extraction and for the extraction with the extractant sorbed on hydrophobized silica gel are the same.

In our previous works, we have studied the distribution of dibenzyl sulfoxide (DBSO) between aqueous phase containing a strong mineral acid and organic phase constituted by DBSO solution in an organic solvent[1] and distribution of iron, cobalt, nickel, and copper between aqueous phase containing hydrochloric or nitric acid and organic phase represented by solution of DBSO in toluene[2]. The aim of those works was to obtain quantitative data on the distribution of the components, requisite for suggesting a suitable extraction–chromatographic system.

In extraction chromatography, the nature of the distribution of the component separated is the same as in liquid–liquid extraction, and thus, *e.g.*, the values of the distribution ratios D of metals, found from extraction, should be applicable, for instance, to the calculation of their retention volumes in extraction chromatography, provided that only the distribution equilibrium takes place and that the dynamic conditions in the column allow the same equilibrium to establish as during the static distribution. In fact, the value of the activity coefficient of the extracting agent changes on the sorption of its solution on the support, the value of the activity coefficient of the metal-containing species, however, changes likewise; it can be thus shown[3] that the D value found from liquid–liquid extraction should be equal to that found *via* the distribution between the aqueous phase and the organic phase bound to a support, which affects the activity coefficient of the extractant. However, some cases exist[4], where mutually different D values were obtained from the two types of distribution.

The aim of the present work was to compare the distribution ratio values of iron obtained during liquid–liquid extraction with those obtained for sorption of iron on silica gel binding stationary DBSO solution. Of the elements studied previously,

iron was selected because its distribution ratio D is high enough and can be thus determined with the necessary accuracy, and also with regard to the convenient properties of its ^{59}Fe isotope.

EXPERIMENTAL

Chemicals

The purification of dibenzyl sulfoxide and the determination of its purity have been described[1]. The preparation of the iron stock solution and its ^{59}Fe-labelling have also been reported[2]. The other chemicals used were reagent grade purity, the solvents were distilled; silica gel Silpearl (Kavalier, Votice), d_p 35—58 μm, served as the support.

Support Treatment and Hydrophobization

The silica gel was purified by decantation and washing with dilute HCl (1 : 3) until negative reaction for iron, washing with water to pH 5 of the filtrate, and final washing with ethanol. The silica gel was then dried on air, the above grain size was picked out by screening, dried at 200°C for 3 h, and hydrophobized in two steps. In the first step, the treated and dried silica gel was dried in vacuum (1—1·5 kPa) at 200°C for 7 h in a flask connected to a drying trap containing P_2O_5. After cooling, dimethyldichlorosilane was added cautiously to the silica gel in the evacuated flask (5 ml per 1 g of silica gel), the system was allowed to stand at room temperature for two days, the gaseous components were removed from the flask, and the silica gel was washed with anhydrous methanol and dried at 120°C.

A portion of the hydrophobized silica gel was shaken for 2 h with 1% solution of hexamethyldisilazane in toluene (2·5 ml per 1 g of silica gel), filtered out, washed with toluene, and dried at 120°C for 12 h.

The degree of hydrophobization was examined in two ways: thermogravimetrically[5] (TGA) and by employing sorption of methyl red[6].

In the former case (TGA), thin layer portions of the silica gel were allowed to come in contact with atmospheric humidity and then subjected to TGA; the results are shown in Fig. 1.

In the latter case, a portion (~30 mg) of the dry support was shaken for 5 h with 10 ml of methyl red solution in anhydrous benzene (6 mg/l), the solid phase was removed by centrifugation, and the absorbance of the solution was measured in a 1 cm or 3 cm cell at 490 nm (*i.e.*, λ_{max}). The amount of the dye sorbed was calculated by employing the absorption coefficient obtained by measuring the absorbance of the dye solution before adsorption. The doubly hydrophobized silica gel sorbed 0·05 mg of methyl red per 1 mg of the gel, the singly hydrophobized silica gel sorbed 0·89 mg/g. For a comparison: sorption of methyl red on Ftoroplast (PTFE, USSR), 0·04 mg/g; on commercially modified silica gel C_{18} (reversed phase), 0·21 mg/g.

Support Impregnation

Two impregnation procedures were applied: In the one, hydrophobized silica gel portions were shaken with DBSO solutions in toluene of different concentrations (always 5 g of silica gel with 2·3 ml of the solution) in a tightly sealed flask, and the (loose) mixture was allowed to stand for 24 h. In the other procedure, the hydrophobized silica gel was shaken for 3 h with 0·05M-DBSO in toluene, which is a nearly saturated solution at room temperature (5 g of silica gel with 50 ml of the solution). The support was then filtered out and dried on air.

Determination Methods and Apparatus

The amount of DBSO sorbed on the silica gel was determined from the weight increment after the sorption and drying at 120°C. The volume of the sorbed toluene solution of DBSO was determined as follows: A known quantity of the support was placed in a column and the DBSO solution was added in an amount such that its level was in the height of the top of the support column. The column was washed with water which had been saturated with the extractant by shaking with a solution of DBSO in toluene of the appropriate concentration, and the effluent was collected in a graduated cylinder until the organic phase no longer washed out; the volume of the latter was then read off (V_m). In another graduated cylinder containing the same quantity of the support, V ml of the DBSO solution in toluene was pipetted, and after mixing, the system was allowed to stand for 24 h. The volume of the liquid above the support column was read off (V'), and the sorbed volume of the solution (V_s) was calculated by means of the relation $V_s = V - V' - V_m$.

The sulfoxide content in the aqueous phase was determined according to[7]. The distribution of iron was monitored by detection of gamma radiation using a scintillation probe equipped with an NaI(Tl) well-type crystal, interfaced to an NZQ 715 automatic unit for measuring radioactive samples (Tesla, Liberec). A VSU 2P spectrophotometer (Zeiss, Jena) was used for the absorbance measurements.

RESULTS AND DISCUSSION

Sorption of Dibenzyl Sulfoxide on Hydrophobized Silica Gel and its Desorption

The sorption equilibrium was found to be attained after 2 hours' shaking. The sorbed amount of DBSO depended on the degree of hydrophobization: during the sorption from 0·05M-DBSO in toluene, 0·0108 g DBSO/g sorbed on the doubly hydrophobized silica gel, 0·163 g DBSO/g on the singly hydrophobized sample, and 0·181 g DBSO/g on the unhydrophobized sample. The results of TGA and of the methyl red sorption indicate that after the one-step hydrophobization (with dimethyldichlorosilane), a number of sorption centres remain on the silica gel surface, so that silica gel hydrophobized in this manner cannot be regarded as inert support for extraction chromatography. The doubly hydrophobized silica gel exhibited the following dependence of the sorbed amount of DBSO on its initial concentration in the toluene solution:

c_{DBSO}, mol l^{-1}:	0·03	0·04	0·05
Sorbed, g DBSO/g silica gel:	0·0105	0·0110	0·0108

Hence, the sorbed amount of DBSO is independent of its concentration for $c > 0{\cdot}03$ mol l^{-1}. Lower concentrations were not tested, with regard to the fact that the sorbed amount of DBSO must not be low in relation to the required column capacity, determined by the sensitivity of detection of metal ions in the eluate; concentrations higher than 0·05 mol l^{-1} were not tested because solution of that concentration is nearly saturated at room temperature.

Dried, twice hydrophobized silica gel was found to sorb 0·450 ml of toluene, or 0·455 ml of 0·05M solution of DBSO in toluene, per 1 g, hence practically equal volumes of the solvent and the solution. The concentration of DBSO, calculated from the weight of DBSO sorbed on 1 g of the support from 0·05M-DBSO in toluene (0·0108 g) and from the volume of the retained organic phase, is 0·103 mol l^{-1}, which is 1·8 times higher than the previously found[1] concentration of saturated solution in this solvent at room temperature. Obviously, DBSO is retained by the support through soaking of the solution into the pores as well as through preferred adsorption on the remaining sorption centres on the hydrophobized silica gel (hence, also the —Si—O—Si-groups – see, *e.g.*[8]).

Thus it is possible to prepare silica gel impregnated with the extractant of some desired concentration, by shaking with 0·455 ml of DBSO solution of the concentration in question per 1 g, or to prepare support whose surface is saturated with DBSO by shaking with excess DBSO solution (0·05M).

The desorption equilibrium establishes within 60 minutes' shaking of the impregnated support with hydrochloric acid. The dependence of the degree of DBSO desorption on the acid concentration is demonstrated by the dependence of the sulfoxide equilibrium concentration in the aqueous phase on the initial acid concentration:

c_{HCl}, mol l^{-1}:	0	1·0	2·0	3·0	4·0	5·0	6·0	7·0
c_{DBSO}, 10^{-4} mol l^{-1}:	3·3	6·3	7·6	8·3	8·5	8·8	9·1	9·6

Hence, the fraction of DBSO that is washed off the impregnated support grows with increasing concentration of the acid. Hydrochloric acid (4M) washes out 45% DBSO in the static arrangement (using the ratio of 25 ml of the acid per 1 g of the support). If, however, 4M-HCl saturated by shaking with 0·05M-DBSO in toluene is used, only 3% DBSO is washed off the support in identical conditions. The desorption of DBSO by hydrochloric acid is due predominantly to its dissolution in this acid[1]; at higher acid concentrations (> 6M), decomposition of the sulfoxide may play a part too. The fact that DBSO is washed off the impregnated support even by acid saturated with the extractant can be explained taking into account that the equilibrium concentration of DBSO in aqueous solution obtained by shaking with 0·05M-DBSO in toluene is not the same as that occurring on the support impregnated with excess 0·05M-DBSO in toluene, because the concentration of DBSO in the latter case exceeds 0·05 mol l^{-1}.

Sorption of Fe(III) *on Silica Gel Impregnated with Dibenzyl Sulfoxide Solution in Toluene*

The time course of sorption of Fe(III) on the support impregnated in different ways is apparent from Fig. 2. The time necessary for the distribution equilibrium to establish

is practically the same for the liquid–liquid extraction and for the extraction with the bound extractant of the same concentration (*e.g.*, 0·05M). If, however, the support whose surface has been saturated with DBSO and toluene is used, the distribution equilibrium establishes more slowly. In the former case the support binds 0·0053 g DBSO/g, in the latter case 0·0108 g/g; the enhanced concentration of DBSO on the support is responsible for the slower sorption of the metal. For the study of sorption on the support with stationary 0·05M-DBSO, the system was shaken for 5 minutes, which – according to Fig. 2 – corresponds to the establishing equilibrium.

The conditions of the Fe(III) sorption on the impregnated silica gel are to be chosen so as to approach closely the conditions of sorption, or extraction, on the column. In the extraction chromatography column used[9], the volume of the mobile (aqueous) phase was 1·0 ml, that of the stationary (organic) phase 0·96 ml (column 15 × 0·49 cm containing 2·10 g of the impregnated silica gel, d_p 35–58 μm). Since, however, it was not practicable to shake 2·10 g of the support with 1 ml of the solution and to sample an aliquot of the liquid phase for the iron determination, the volume of the aqueous phase was increased to 5 ml per 2·10 g of the support.

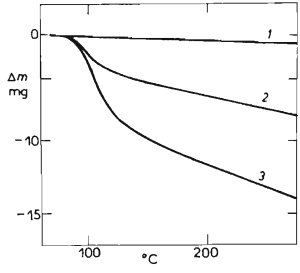

FIG. 1

Thermograms of Differently Hydrophobized Silica Gel

1 Doubly hydrophobized (with dimethyldichlorosilane and hexamethyldisilazane), *2* singly hydrophobized (with dimethyldichlorosilane), *3* unhydrophobized.

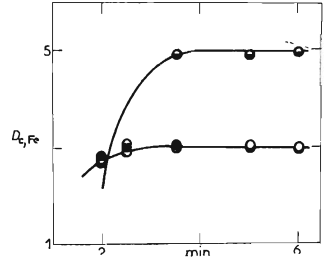

FIG. 2

Effect of the Shaking Duration on the Extraction of Fe(III) from 6·0M-HCl Saturated with the Extractant

○ Extraction with 0·05-DBSO in toluene, ● extraction with 0·05M-DBSO in toluene sorbed on doubly hydrophobized silica gel, ◒ sorption of Fe(III) on silica gel whose surface has been saturated with DBSO and toluene.

The liquid–liquid extraction was also performed using the ratio $r = V_{org} : V_{aq} = 0{\cdot}96 : 5$. The concentration distribution ratios ($D_c = c_{org}/c_{aq}$) were calculated for both distribution procedures.

The effect of the hydrochloric acid concentration on the iron distribution ratio (D_{Fe}) was examined for the liquid–liquid extraction applying the above r value and for the extraction with the extractant bound to the support in the two different ways. The results are apparent from Fig. 3. The D_c values calculated from the iron retention volume (V_R) in LLC using the system hydrophobized silica gel–aqueous solution of HCl ($D_c = (V_R - V_S)/V_m$) (see[9]) are shown as well. Obviously, the iron recovery obtained during the liquid–liquid extraction is the same as that obtained using a support impregnated with equally concentrated DBSO solution, not only in static arrangement, but also in dynamic arrangement (on the column). With the support saturated with DBSO and toluene, the recovery in otherwise identical conditions is higher, again both in static and in dynamic arrangements. Thus in the case of distribution of iron, the iron D value remains unaltered if the extractant is bound to the support, which is consistent with the theoretical treatment[3]. The disagreement between the two D values found in[4] may be due to an interaction of the silica gel surface with the sorbed element (chromium), or – which is more likely – to the fact that in the work[4] a support was used whose surface was saturated with the extractant and which thus contained, as we have proved in the present work, a higher concentration of DBSO than the extractant in the liquid–liquid extraction with 0·05M-DBSO solution.

The effect of the initial concentration of the sorbed DBSO solution on the distribution of iron was also investigated using a constant concentration of hydrochloric acid. The following data were obtained; the D_{Fe} values for liquid–liquid extraction

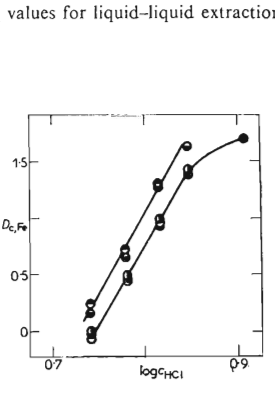

FIG. 3

Dependence of log D_{Fe} on log c_{HCl}

○ Extraction of Fe(III) with 0·05M-DBSO in toluene, ● extraction with 0·05M-DBSO in toluene sorbed on silica gel, ◒ sorption of Fe(III) on silica gel whose surface has been saturated with DBSO and toluene, ◑ D_c values calculated from V_R for chromatography on silica gel with sorbed 0·05M-DBSO in toluene, ◓ D_c values calculated from V_R for chromatography on silica gel whose surface has been saturated with DBSO and toluene.

in identical conditions (c_{HCl} = 6·5M, acid saturated with the extractant, V_{org} = = 0·96 ml, V_{aq} = 5·0 ml, c_{Fe} = 8 . 10^{-4}M) are also given for a comparison:

c_{DBSO}, mol l^{-1}:	0·01	0·02	0·03	0·05
$D_{c,Fe}$ (support):	0·35	1·32	2·49	7·65
$D_{c,Fe}$ (liquid):	0·33	1·24	2·30	7·90

In this case, too, the results of the two procedures are practically the same.

It can be thus deduced that the mechanism of distribution of the reagent as well as of iron is the same for liquid–liquid extraction and for sorption (extraction) on a support with bound extractant, which takes place during extraction chromatography. The identical shapes of the $D = f(c_{HCl})$ and $D_{Fe} = f(c_{DBSO})$ dependences for the two distribution methods indicate that the extractable species formed in the two cases have the same composition (see[2]). This also bears out the conclusion arrived at by Siekierski[3,10], that the ratios of the activity coefficients of the extracting agent and of the extracted complex in the free organic phase (extractant) and in the organic phase adsorbed on silica gel are the same.

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