DISTRIBUTION OF DIBENZYL SULFOXIDE BETWEEN THE AQUEOUS AND ORGANIC PHASES

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The distribution of dibenzyl sulfoxide (DBSO) between toluene or tetrachloromethane and aqueous solution of nitric, hydrochloric, or perchloric acid was investigated for different acid concentrations. The solubility of DBSO in the two solvents was established (0.0555 mol l^{-1} in toluene, 0.0121 mol l^{-1} in tetrachloromethane at 20°C) and its distribution constants K_D were determined for the systems toluene–water and CCl$_4$–water (133.7 and 27.4, respectively, at 20°C). Employing the dependence of the distribution ratio of DBSO on the Hammett function for nitric and perchloric acids solutions ($1-6$M) and taking into account the extraction of the solvates of these acids as described previously, the value of the DBSO protonation constant was calculated to be K_{H1} (B + H$^+$ $\rightleftharpoons$ BH$^+$) = $1.00 \cdot 10^{-2}$, and more accurate values of the extraction constants of the nitric acid solvates were obtained, K_{ex1} (HNO$_3$. B) $1.1 \cdot 10^{-3}$ and K_{ex2} ((HNO$_3$)$_2$. B) $4.3 \cdot 10^{-5}$. Owing to the lower solubility of DBSO in water as well as in acid solutions as compared with aliphatic or cyclic sulfoxides and also with tri-n-butylphosphate, solution of DBSO in toluene suits better as the stationary phase for extraction chromatography of metal salts.

For the application of dibenzyl sulfoxide (DBSO) as an extracting agent for liquid–liquid extraction or as a stationary phase for extraction chromatography (RPPC), it is prerequisite to know the distribution of the sulfoxide between the aqueous and the organic phases in different conditions. Since sulfoxides are proton acceptors, their distribution between the two phases will be appreciably affected by the kind and concentration of the acid in the aqueous phase. A part of DBSO originally dissolved in the organic solvent and brought in contact with the aqueous phase is transferred into the latter, which affects the degree of extration of the component forming an extractable solvate with the sulfoxide and can bring about a change of the capacity ratios of these solvates during the extraction chromatographic process and cause "bleeding" of the column.

The aim of this work was to establish the dependence of the distribution ratio of DBSO on its initial concentration in the organic phase and on the concentration of a strong monobasic acid (nitric, hydrochloric, or perchloric) in the aqueous phase. Toluene and tetrachloromethane were chosen as the solvents, since during the dissolution in the former a considerably high inductive interaction can operate, whereas in the latter only weak dispersion forces occur during the dissolution.

EXPERIMENTAL

Dibenzyl sulfoxide was purified as described previously[1], its purity was checked by acidimetric titration in nonaqueous medium[2] (content 99·7%). The concentrations of the mineral acid solutions were determined volumetrically using $KHCO_3$ as the standard substance. The extractions were accomplished in ground-in test tubes at $20 \pm 1°C$ on a rotary shaking machine (60 rpm) using the ratio $V_{org} : V_{aq} = 1$. In case that the separation of the organic and the aqueous phases was not sharp enough, the mixture was centrifuged after the extraction. An aliquot of the aqueous phase was pipetted for the photometric determination of the DBSO concentration. The reasons for the analysis of the aqueous phase and the photometric determination procedure have been explained previously[3].

RESULTS AND DISCUSSION

The concentration of DBSO in the equilibrium aqueous phase after the extraction was followed in dependence on the extraction duration, and the extraction equilibrium was found to establish within 15 min. All the extractions of DBSO were therefore performed for this time.

The effect of the DBSO concentration in the initial organic solution on the degree of its extraction was investigated. In the concentration region $2 . 10^{-3}$ to $5 . 10^{-2}$M- -DBSO in toluene and $1 . 10^{-3}$ to $1 . 10^{-2}$M-DBSO in tetrachloromethane the distribution ratio of DBSO (D_B) was found constant (Table I) and hence identical with the distribution constant (K_D) value, amounting to 133·7 for the toluene–water system and 27·4 for the tetrachloromethane–water system. The upper limit of the DBSO concentrations applied is given by its solubility in the respective solvent. A saturated solution of DBSO (at 20°C) in toluene contains $0·0555 \ mol \ l^{-1}$ DBSO, in tetrachloromethane $0·0121 \ mol \ l^{-1}$ DBSO. The K_D values as well as the solubilities in the two solvents are in accordance with the forces operating during the dissolution in the two solvents, as mentioned above.
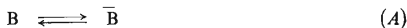
TABLE I
Dependence of the Distribution Ratio (D_B) of Dibenzyl Sulfoxide on Its Initial Concentration in the Organic Phase

c_{org} $10^{-3} \ mol \ l^{-1}$	D_B	
	toluene	tetrachloromethane
1·00	—	26·8
2·00	132	26·8
5·00	138	27·7
10·00	131	28·8
50·00	134	—

Furthermore, the distribution of DBSO was measured in dependence on the concentration of the acid in the original aqueous phase in the range $1-6$ mol l^{-1}. Although the solvation of the metal salts and thereby the degree of their extraction usually rises with the increasing acid concentration in the aqueous phase, concentrations of the acids exceeding 6 mol l^{-1} were not applied, since — as has been observed — contact of sulfoxide with, *e.g.*, concentrated hydrochloric acid is accompanied by a deep chemical conversion of the sulfoxide resulting in a drop of its extractability[4]; from DBSO a precipitate is formed on the action of concentrated hydrochloric acid solutions[1]. The dependence of the distribution ratio on the monobasic acid concentration is apparent from Table II.

For toluene as the solvent, the effect of the acids on the decrease of the DBSO distribution ratio in dependence on their concentration was found in the order $HNO_3 < HCl < HClO_4$; for tetrachloromethane as the solvent, the order is $HCl \approx \approx HNO_3 < HClO_4$.

In the system studied, the following equilibria with the corresponding equilibrium constants occur (B is dibenzyl sulfoxide, HX the monobasic acid, bar over the formula denotes the component present in the organic phase):

$$B \; \rightleftharpoons \; \overline{B} \tag{A}$$

$$K_D = [B]_{org}/[B]_{aq} \tag{1}$$

$$B + H^+ \; \rightleftharpoons \; BH^+ \tag{B}$$

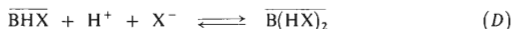$$K_{H1} = [BH^+]_{aq}/[B]_{aq}[H^+]_{aq} \tag{2}$$

TABLE II

Dependence of the Distribution Ratio of Dibenzyl Sulfoxide (*D*) on the Acid (HX) Concentration for the Extraction with Toluene or Tetrachloromethane

Concentration of dibenzyl sulfoxide in toluene $5 \cdot 10^{-2}$ mol l^{-1}, in tetrachloromethane $1 \cdot 10^{-2}$ mol l^{-1}.

| c_{HX} mol l^{-1} | D | | | | | |
| | HCl | | HNO_3 | | $HClO_4$ | |
	toluene	CCl_4	toluene	CCl_4	toluene	CCl_4
1·00	112·1	23·7	115·0	21·3	75·1	6·5
2·00	97·0	18·1	103·2	16·7	52·7	5·1
3·00	82·1	13·9	89·2	12·9	40·0	4·4
4·00	76·0	10·6	84·9	10·3	33·0	2·5
5·00	66·0	7·2	78·7	8·8	28·9	1·3
6·00	65·0	4·4	79·8	9·6	26·9	0·7

$$B + H^+ + X^- \rightleftarrows \overline{BHX} \qquad (C)$$

$$K_{ex1} = [BHX]_{org}/[B]_{org} [H^+]_{aq} [X^-]_{aq} \qquad (3)$$

$$\overline{BHX} + H^+ + X^- \rightleftarrows \overline{B(HX)_2} \qquad (D)$$

$$K_{ex2} = [B(HX)_2]_{org}/[BHX]_{org} [H^+]_{aq} [X^-]_{aq} . \qquad (4)$$

In the preceding work[1] the K_{ex1} and K_{ex2} values were determined from the dependence of the acid distribution ratio (D_H) on the concentration of DBSO for a constant acid concentration. Taking into account the equilibria $(A)-(D)$, a relation can be derived for the distribution ratio of DBSO (D_B), and from the latter it is possible to calculate the protonation constant of DBSO (K_{H1}) knowing the K_{ex1} and K_{ex2} values. As expected, the K_{H1} value so calculated was dependent upon the acid concentration and did not comply with the basicity of sulfoxides. The requisite K_{ex1} and K_{ex2} values were therefore recalculated by employing the activity of hydrogen ions; the values obtained for the distribution between the nitric acid aqueous solution and DBSO solution in toluene ($3.82 . 10^{-2}$ and $7.2 . 10^{-4}$) did not differ considerably from those found previously ((4.6 ± 1.8) $. 10^{-2}$ and $3 . 10^{-3} \pm 1 . 10^{-2}$) owing to the fact that the activity coefficient for 4M-HNO$_3$ (the concentration at which the $D_H = f(c_B)$ dependence was measured) approaches unity.

Assuming $[H^+]_{aq} = [X^-]_{aq}$ and $y_B = y_{HXB} = y_{(HX)_2B} = 1$ (the fact that the nitric acid HXB and $(HX)_2$B solvates in toluene do not dissociate has been confirmed[1]), the dependence of the distribution ratio of DBSO

$$D_B = c_{B,org}/c_{B,aq} = ([B]_{org} + [HXB]_{org} + [(HX)_2B]_{org})/([B]_{aq} + [HB^+]_{aq}) \qquad (5)$$

on the activity of hydrogen ions can be described by the relation

$$D_B = \frac{K_D\{1 + K_{ex1}[H^+]_{aq}^2 y_\pm^2(1 + K_{ex2}[H^+]_{aq}^2 y_\pm^2)\}}{1 + K_{H1}[H^+]_{aq} y_\pm}, \qquad (6)$$

from which K_{H1} can be calculated.

When the above K_{ex1} and K_{ex2} values and the activity coefficients[5] were employed, the K_{H1} values obtained were of the order of 10^0, which again did not conform to the basicity of DBSO and to its place among other weak bases. For this reason, the Hammett function[6] was used instead of the activity of hydrogen ions, and the protonation constant of the weak base was determined from the extraction data by the procedure suggested by Arnett and coworkers[7]. This procedure has been applied to the determination of protonation constants of weak bases also by Klofutar and coworkers[8], who, however, did not take into account the extraction of the acid in

the solvate form into the organic phase. For the dissociation constant of the acid conjugate to DBSO (not the protonation constant, as referred to in[8]), they found the value $pK_a = -2.03$.

Arnett as well as Klofutar only took into account the equilibria (A) and (B), so that

$$D_B = [B]_{org}/([B]_{aq} + [HB^+]_{aq}) = K'_D/(1 + K_{H1} h_0), \qquad (7)$$

where K'_D is the distribution constant of the base influenced by the salting-out effect of the strong mineral acid, and $h_0 = 10^{-H_0}$.

The assumption that only the two above equilibria occur should be confirmed by the linearity of the plot of D_B vs $D_B h_0$, since from Eq. (7),

$$D_B = K'_D - K_{H1} D_B h_0. \qquad (8)$$

For the system HNO_3–solution of DBSO in toluene, however, the plot is only linear up to $c_{HX} < 3$ mol l^{-1}.

Allowance was therefore made also for the extraction of the acid into the organic phase, hence, the equilibria (C) and (D) were considered. A relation analogous to Eq. (6) was obtained, viz.

$$D_B = K_D[1 + K_{ex1} h_0^2(1 + K_{ex2} h_0^2)]/(1 + K_{H1} h_0), \qquad (9)$$

from which $pK_{H1} = 2.00$ was calculated by nonlinear regression for the distribution of DBSO in the presence of nitric as well as perchloric acid.

This value was confirmed also by measurements of the $D_H = f(c_{HX})$ dependence employing the Hammett function. The H_0 values for nitric and perchloric acids were taken from ref.[9].

Using the above equilibria (A) and (D) with the corresponding equilibrium constants and the mass balance of DBSO,

$$c_B = [B]_{org} + [HXB]_{org} + [(HX)_2B]_{org} + [B]_{aq} + [HB^+]_{aq} =$$
$$= [B]_{org}\{1 + K_{ex1} h_0^2(1 + K_{ex2} h_0^2) + K_D^{-1}(1 + K_{H1} h_0)\}, \qquad (10)$$

the following relation can be derived for D_H:

$$D_H = \frac{K_{ex1} h_0^2 c_B(1 + 2K_{ex2} h_0^2)}{[H^+]_{aq}\{1 + K_{ex1} h_0^2(1 + K_{ex2} h_0^2) + K_D^{-1}(1 + K_{H1}h_0)\}}. \qquad (11)$$

After conversion to the function $D_H[H^+]_{aq} = f(h_0)$, the K_{H1} value was again calculated by nonlinear regression ($0.94 . 10^{-2}$ for HNO_3 and $1.0 . 10^{-2}$ for $HClO_4$).

The extraction constant values published previously[1] were also recalculated by using the Hammett function. The dependence $D_H = f(c_B)$ with $c_{HX} = $ const was employed, and the nitric acid extraction constants $K_{ex1} = 1.1 \cdot 10^{-3}$ and $K_{ex2} = 4.3 \cdot 10^{-5}$ were obtained by nonlinear regression from Eq. (11); these values are to be regarded as more correct than those calculated *via* the hydrogen ion concentration.

An analogous calculation for the system $HClO_4$–DBSO–toluene led to unlikely values of the two constants $(K_{ex2} > K_{ex1})$, which is probably due to a higher error of determination of the low acid concentration in the organic phase and to the H_0 value rapidly increasing with the perchloric acid concentration.

From the dependence of D_B on c_{HX} (Figs 1 and 2), nitric acid and hydrochloric acid are seen to suit better as the mobile phase than perchloric acid from the point of view of the stationary phase washing during the extraction chromatography; also, solvates of sulfoxides with chlorides or nitrates are better extracted than the analogous solvates with perchlorates. Owing to the lower solubility of DBSO in the aqueous phase, toluene is a more suitable solvent than tetrachloromethane.

In comparison with other aliphatic or cyclic sulfoxides, DBSO appears to be more advantageous for extraction chromatography. Its solubility in water $(0.092$ g/l at $20°C)$ is lower than that of cyclic $(>4$ g/l$)$ or aliphatic $(0.1-4$ g/l$)$ sulfoxides[10,11] and also lower than that of tri-n-butylphosphate $(0.25$ g/l$)$. With $V_{org} = V_{aq}$ and in
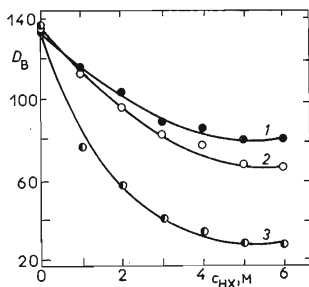

Fig. 1

Dependence of the Distribution Ratio of Dibenzyl Sulfoxide in the System Toluene––Acid Solution on the Concentration of the Acid in the Aqueous Phase
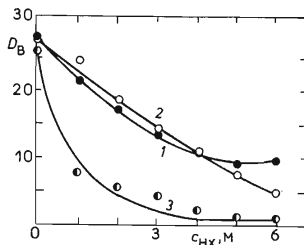
1 HNO$_3$; *2* HCl; *3* HClO$_4$.

Fig. 2

Dependence of the Distribution Ratio of Dibenzyl Sulfoxide in the System Tetrachloromethane–Acid Solution on the Concentration of the Acid in the Aqueous Phase

1 HNO$_3$; *2* HCl; *3* HClO$_4$.

the concentration region $1-6M$-HCl, only $1\cdot3-1\cdot5\%$ of the DBSO originally present in the organic phase is transferred into the aqueous phase, as against, *e.g.*, the 20% of methyl-4,8-dimethylnonyl sulfoxide passing from *p*-xylene into the aqueous phase of $8M$-HCl (ref.[12]). A shortcoming of DBSO for extraction or for extraction chromatography is its lower solubility in the organic solvent applied.

LIST OF SYMBOLS

c	total concentration (mol l^{-1})
D	distribution ratio (concentration)
H_0	Hammett function ($H_0 = pK_a - \log [BH^+]/[B]$)
h_0	10^{-H_0}
K_a	dissociation constant (*e.g.*, $K (BH^+ \rightleftarrows B + H^+)$)
K_D	distribution constant
K_{ex}	extraction constant (*e.g.*, $K (\overline{B} + H^+ + X^- \rightleftarrows \overline{BHX})$)
K_{H1}	protonation constant (*e.g.*, $K (B + H^+ \rightleftarrows BH^+)$)
y	activity coefficient (molar)

Square brackets denote equilibrium concentrations (mol l^{-1}), subscripts org and aq refer to the organic and aqueous phases, respectively.

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