Mixed Solvent Effect with Dibutyl Phosphate

Modification of a Method[1] for the Preparation of Carrier-free Yttrium-90

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Dialkyl phosphoric acids have been used[1,2] for the separation of ^{90}Y from its parent ^{90}Sr. Dibutyl phosphate ($=$ HA) is preferred by us since the equilibrium constant,

$$K = [YA_3(HA)_3]_{org}\ [Y^{3+}]^{-1}[H^+]^3[H_2A_2]_{org}^{-3}.$$

is larger for the dibutyl phosphate (DBP) — chloroform system[1] (log $K = 3.22 \pm 0.13$) than for the dioctyl phosphate-toluene system[3] (log $K \sim 1.3$), and since the equilibria for DBP have been more fully investigated[4,5]. Dioctyl phosphate (DOP) has a lower solubility in water[3] than DBP due to the fact that it contains larger hydrocarbon groups. Consequently, DOP will have a larger distribution ratio than DBP. However, with chloroform the distribution ratio of DBP is 74 for a 0.1 M solution, and the loss of DBP into 0.1 M HNO$_3$ is not a serious problem.

This suggested modification of the method previously given by Dyrssen[1] allows ^{90}Y to be back-extracted into HNO$_3$ with better recovery at lower acidity and less contamination of DBP. This is accomplished by the addition of methyl *isobutyl* carbinol (hexol) to the chloroform phase containing 0.1 M DBP and the ^{90}Y extracted from ^{90}Sr + ^{90}Y in 0.1 M HNO$_3$.

This mixed solvent effect may be explained by the formation of a 1 : 1 complex between DBP (HA) and hexol (B) which reduces the concentration of HA and H$_2$A$_2$, and thus the extraction of Y^{3+} according to equations given below. There is no reason to believe that a trialkyl phosphate is formed, i.e. (BuO)$_2$((CH$_3$)$_2$CHCH$_2$CH(CH$_3$)O)PO, in the presence of an aqueous phase. These conclusions were drawn from a study[5] of the extraction of Eu^{3+} and Am^{3+} by DBP in different solvents carried out at this institute, as well as a study[5] of DBP itself in the same set of solvents.

The effect of addition of hexol on the distribution of ^{90}Y (org/aq) is shown in

Table 1. Distribution of ^{90}Y at 25°C between 15 ml 0.1 M DBP in chloroform (alcohol-free) and 15 ml 0.1 M HNO$_3$, for various amounts of hexol added. The two phases were shaken for one minute by hand and then separated by centrifugation.

ml hexol		0	0.05	0.1
0.2	0.5	1	2	5
log q		$(+2.13)^a$	$+2.055$	$+2.012$
$+1.897$	$+1.523$	$+1.040$	$+0.154$	-1.655

^{a} extrapolated value, measured value in Ref.[5] : 2.17.

Table 1. It is possible from these data to calculate $[H_2A_2]_{org}$ from

$$[H_2A_2]_{org}^3 = qK^{-1}[H^+]^3 \text{ ; } \log K = 3.03$$

and C_B from the known volume of hexol added:

$$C_B = v(v + 15)^{-1}\ 7.95$$

Using the following relations

$$C_B = [HAB]_{org} + [B]_{org}$$

$$0.1 \cdot 15(v + 15)^{-1} = 2\ [H_2A_2]_{org} + [HAB]_{org}$$

$$10^{4.61} = [H_2A_2]_{org}[HA]_{org}^{-2} \quad (Ref.[5])$$

we could calculate the value of

$$K_B = [HAB]_{org}[HA]_{org}^{-1}[B]_{org}^{-1}$$

as log $K_B = 2.21$ for hexol and DBP in chloroform. This value is larger than for TBP in chloroform[1], probably because TBP and CHCl$_3$ form a complex.

With these constants and equations it is possible to calculate the distribution of ^{90}Y and DBP for the following two pairs of organic—aqueous solvents (cf. Fig 1):

0.1 M DBP in CHCl$_3$/0.1 M HNO$_3$:

$$\log q_Y = +\ 2.13$$
$$\log q_A = +\ 1.87$$

hexol $+$ 0.1 M DBP in CHCl$_3$ $(1 + 5)/1$ M HNO$_3$:

$$\log q_Y = -\ 3.43$$
$$\log q_A = +\ 2.58$$

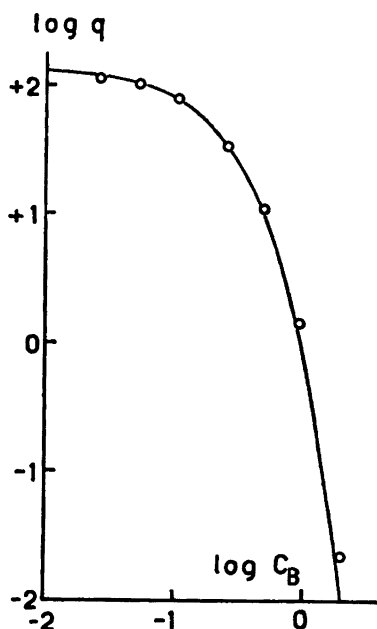*Recommended procedure:* 5 ml of a 0.1 M HNO$_3$ solution containing ^{90}Sr is shaken

Fig. 1. Distribution of ^{90}Y between a solution of 0.1 M DBP in chloroform and 0.1 M HNO₃ as a function of the conc. of hexol in the chloroform phase. The curve is calculated with equations in the text assuming that the lowering of q is due to formation of a complex between DBP and hexol.

with 5 ml of 0.1 M DBP in alcohol-free chloroform. The amount of ^{90}Sr extracted is less than 10^{-2} %. This amount may be reduced by a factor of 10^4 by washing the organic layer with 5 ml of 0.1 M HNO₃; 1 % of ^{90}Y is lost for each wash. The ^{90}Y is quantitatively back-extracted into 5 ml of 1 M HNO₃ after the addition of 1 ml of methyl isobutyl carbinol (hexol). The aqueous phase then contains about 0.0003 M DBP. The DBP conc. can, however, be lowered by a factor of 400 by washing the 1 M HNO₃ phase with 1 ml of hexol + 5 ml of chloroform. In this way the conc. of DBP can be reduced to a very low level and the final solution will only contain volatile substances (HNO₃), water, chloroform and hexol) in addition to the [90]Y.

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The Composition of Rat Milk Fat

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Rats are extensively used in experiments on nutrition, e.g. for the study of the role of fats. It is therefore of interest to know the composition of the fat in the milk consumed by the suckling young rat.

Investigations on this problem have been carried out by Hallanger and Schultze [1], who found it possible to increase the content of polyenoic acids (mainly dienoic) by increasing the content of such fatty acids in the diet.

The aim of the present study was to determine not only the polyenoic fatty acids but also the chain length of the fatty acids in milk fat of rats receiving the stock diet commonly used in our laboratory.

To study this problem the fat fraction of rat milk was isolated and converted into methyl esters which were analyzed by means of gas-liquid chromatography [2]. The column consisted of 0.9 m Celite 545 with silicone elastomer E 301. The carrier gas used was nitrogen at a rate of 1 l per hour, and the temperatures applied ranged from 160°C to 225°C. Assuming the areas lying under the recorded curves to be proportional to the molar percentages of the individual components, the following composition (Table 1) was found (in per cent w/w of the fatty acid mixture).