# EXTRACTION OF POLYETHYLENE GLYCOLS WITH DICARBOLIDE SOLUTIONS IN NITROBENZENE

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The extraction of polyethylene glycol of average molecular mass 400 (PEG 400) with dicarbolide solution in nitrobenzene and of longer-chain polyethylene glycol, of average molecular mass 1 500 (PEG 1 500), with chlorinated dicarbolide solution in nitrobenzene was studied. During the extraction of PEG 400, the polyethylene glycol solvates the $H_{org}^+$ ion in the organic phase giving rise to the $HL_{org}^+$ species (L is polyethylene glycol). The obtained value of the extraction constant $K_{ex}(HL_{org}^+) = 933$ is consistent with published data of metal extraction. Extraction of PEG 1 500 was treated applying the simplified assumption that the thermodynamic behaviour of PEG 1 500 is the same as that of $n$ molecules of polyethylene glycol with relative molecular mass $1\,500/n$, each solvating one cation. For this model, the value of $n = 3\cdot2 \pm 1\cdot1$ and the values of the extraction constants of the $HL_{1/n,org}^+$ and $HL_{2/n,org}^+$ species were obtained by using the adapted program LETAGROP. This value of $n$ is consistent with published extraction data in the presence of polyethylene glycol with a relative molecular mass from 200 to 1 000.

Previously[1-4] we investigated the extraction of divalent and trivalent cations with solutions of bis-1,2-dicarbollylcobaltate(III) (dicarbolide) in nitrobenzene in the presence of polyethylene glycols with relative molecular mass 200, 300 or 400 (PEG 200, PEG 300, PEG 400). We demonstrated that the equilibrium data for the extraction of divalent cations can be interpreted assuming that in the organic phase, only two species compete in the compensation of the negative charge of the dicarbollylcobaltate(III) anion $B^-$, viz. protonated polyethylene glycol $\left(HL_{org}^+\right)$ and the complex of the metal ion with polyethylene glycol $\left(ML_{org}^{2+}\right)$. In the extraction of $Eu^{3+}$ and $Ce^{3+}$ ions, the cation can bind more than one molecule of polyethylene glycol, e.g. to form the $ML_{org}^{3+}$, $ML_{2,org}^{3+}$ and $ML_{3,org}^{3+}$ species (in addition, the deprotonated form of the complex, which may be hydrated, also occurs in the organic phase).

The situation is different if the extraction is conducted in the presence of long-chain polyethylene glycols, viz. PEG 600 to PEG 20 000. Apparently, these molecules with large numbers of oxyethylene units can solvate more than one cation, as proved experimentally for the $Pb^{2+}$ and $Ba^{2+}$ ions[5].

If the occurrence of species of the $H_mL^{m+}$ type $\left(m = 1, 2, 3, \ldots\right)$ in the organic

phase is assumed, however, the mathematical description of the extraction of poly-
ethylene glycol with relative molecular mass in excess of 400 leads to dependences
of the distribution ratio $D$ on the concentrations of the components which disagree
with reality. Actually, the distribution ratio of polyethylene glycol increases linearly
with the concentration of dicarbolide in the organic phase $c_B$ (theoretically, the slope
of the dependence of log $D$ on log $c_B$ should be $m$); on the other hand, the assumption
of the occurrence of a single species, $HL_{org}^+$, disagrees with the experimental dependence
of the distribution ratio on the concentration of polyethylene glycol.

   In the present work it is demonstrated that the extraction of long-chain polyethylene
glycols with solutions of dicarbolide in nitrobenzene can be described satisfactorily in
terms of a simplified model in which it is assumed that a long polyethylene glycol
molecule behaves in a manner similar to that of several shorter molecules whose
length (or, more precisely, number of oxyethylene units) meets the requirement of
(nearly) complete solvation of the cation concerned, $H_{org}^+$ ion our case. Furthermore,
the model of extraction of PEG 400 suggested previously is verified by independent
measurement of distribution of this polyethylene glycol in the water–nitric acid–
–nitrobenzene–dicarbolide system.

### EXPERIMENTAL

Polyethylene glycols PEG 400 and PEG 1 500 (Koch–Light, pure) were used as received. Solutions
of dicarbolide and heptachlorodicarbolide were prepared as described in ref.[3] The other chemicals
used were of reagent grade purity.
   Distribution of the polyethylene glycols between the aqueous and organic phases (the con-
centrations) was determined by applying the method of concentration-dependent distribution[6],
using [133]Ba of standard radiochemical purity (U.S.S.R.). The activities were measured with a well-
-type NaI(Tl) scintillation crystal interfaced to an NK 350 gamma analyzer (Gamma, Budapest).
   Extractions were performed so that 2 ml volumes of each phase were agitated for 30 min at
$25 \pm 1°C$ in 10 ml glass test tubes fitted with polyethylene stoppers. A time of 2 min was sufficient
for the equilibrium to establish.

### RESULTS AND DISCUSSION

Extraction of polyethylene glycol (henceforth L) of relative molecular mass 1 500 with
a solution of the acid form of heptachloro bis-1,2-dicarbollylcolbatate(III) (hence-
forth $H^+B^-$) in nitrobenzene was examined at four different concentrations of
the extracting agent in the organic phase within the concentration region of $c_B = 0.3$
to 10 mmol $l^{-1}$. The starting concentration of PEG 1 500 in the aqueous phase $(c_L)$ was
0.02, 0.06, 0.2, 0.6 and 2 times the concentration of $H^+B^-$ in the organic phase.
The aqueous phase contained invariably nitric acid in a concentration of 0.5 mol $l^{-1}$.
The results, in the form of the dependence of $Z = c_{L,org}/c_{B,org}$ on $[L]_{aq}$ (where the
subscripts org and aq refer to the organic and aqueous phases, respectively), are given
in Table I and shown in Fig. 1.

The extraction of polyethylene glycol of relative molecular mass 400 with the acid form of bis-1,2-dicarbollylcobaltate(III) in nitrobenzene was examined at four concentrations of the extracting agent within the concentration region of 1 to 10 mmol. $. l^{-1}$; the starting concentration of polyethylene glycol in the aqueous phase was 0·1 to $2·8c_B$. The results are given in Table II and shown in Fig. 2.

The distribution constant of PEG 400 in the water–nitrobenzene system, $K_D = = 1·1 . 10^{-3}$, was taken from our earlier paper[1]. For PEG 1 500, the value of $K_D \approx \approx 2 . 10^{-4}$ was obtained by the concentration-dependent distribution method. The distribution coefficient of PEG 1 500 in the water–nitrobenzene system could be determined approximately only, because this polyethylene glycol is low extracted by nitrobenzene itself. This did not affect the accuracy of the determination of the extraction constants, the stability constants of the extractable species in the organic phase, however, could not be determined with a sufficient accuracy.

In the first stage, the experimental dependence of $Z$ on log $[L]_{aq}$ was interpreted by means of the program MESAK (ref.[7]). This program, which is based on the differential relations derived by Sillén[8], provides the average composition of the organic phase in the form of the dependence of $\bar{p}$ on $\bar{q}$ where $\bar{p}$ and $\bar{q}$ are the average values of

TABLE I

Equilibrium values of log $[L]_{aq}$ and $Z$ for the extraction of PEG 1 500 with a solution of chlorinated dicarbolide in nitrobenzene; $c(HNO_3) = 0·5$ mol $l^{-1}$, $t = 25°C$

| log $[L]_{aq}$ | $Z$ | log $[L]_{aq}$ | $Z$ |
|---|---|---|---|
| $c_B = 0·3$ mmol $l^{-1}$ | | $c_B = 3·0$ mmol $l^{-1}$ | |
| −6·398 | 0·019 | −5·774 | 0·019 |
| −6·014 | 0·057 | −5·504 | 0·066 |
| −4·880 | 0·156 | −5·108 | 0·197 |
| −3·907 | 0·253 | −3·105 | 0·338 |
| −3·310 | 0·366 | −2·305 | 0·350 |
| $c_B = 1·0$ mmol $l^{-1}$ | | $c_B = 10$ mmol $l^{-1}$ | |
| −6·330 | 0·019 | −6·047 | 0·020 |
| −5·966 | 0·059 | −5·801 | 0·060 |
| −5·120 | 0·192 | −4·848 | 0·199 |
| −3·534 | 0·307 | −2·598 | 0·348 |
| −2·799 | 0·411 | −1·815 | 0·470 |

the coefficients in the equation

$$pL_{aq} + qH^+_{org} \rightleftharpoons L_p H^{q+}_{q,org} \,. \qquad (A)$$
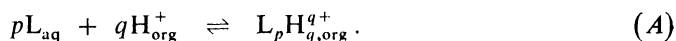
In agreement with published data, the $\bar{p}$ and $\bar{q}$ values for the extraction of PEG 400 were $1{\cdot}0 \pm 0{\cdot}2$; for the water–$HNO_3$–PEG 1 500–nitrobenzene–heptachlorodicarbolide system the $\bar{p}$ value decreased with increasing polyethylene glycol concentration in the aqueous phase from the starting value of approximately 1 down to less than $0{\cdot}5$ (the $\bar{p}$ and $\bar{q}$ values are not very accurate in this case because of the inaccuracy of the experimental data).

In both cases the final experimental data handling involved the use of the minimization program LETAGROP (refs[9−11]). Minimized was the relative value of the generating function $Z$ in the organic phase, i.e.

$$U = \sum [(Z_{calc} - Z_{exp})/Z_{calc}]^2 \,, \qquad (1)$$

where the subscripts calc and exp refer to the values calculated based on the equilibrium constants and the experimental data, respectively.
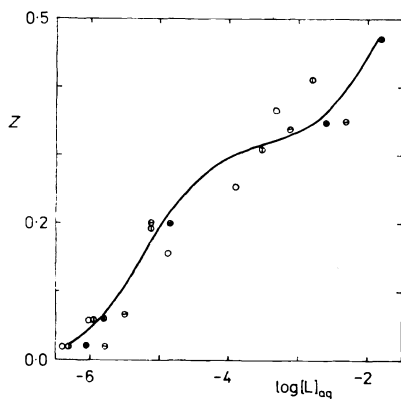


FIG. 1

Extraction of PEG 1 500 with a solution of chlorinated dicarbolide in nitrobenzene, concentration of nitric acid in the aqueous phase $0{\cdot}5$ mol $l^{-1}$; $c_B$ (mmol $l^{-1}$): ○ $0{\cdot}3$, ◉ $1{\cdot}0$, ◔ $3{\cdot}0$, ◎ $10$. Full line calculated for $n = 3{\cdot}2$, log $K_{ex}(HL_{1/n}) = 4{\cdot}71$ and log $K_{ex}(HL_{2/n}) = 6{\cdot}07$
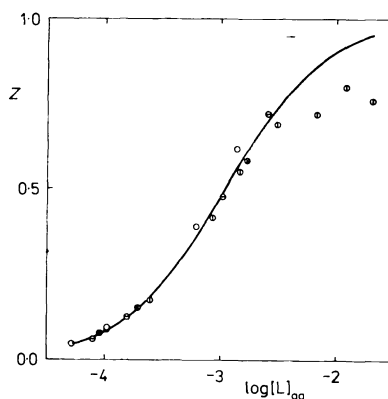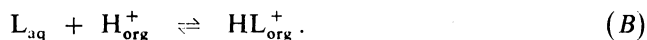
FIG. 2

Extraction of PEG 400 with a solution of dicarbolide in nitrobenzene, concentration of nitric acid in the aqueous phase $0{\cdot}5$ mol . $l^{-1}$; $c_B$ (mmol $l^{-1}$): ○ $1{\cdot}0$, ⊖ $2{\cdot}0$, ◉ $4{\cdot}0$, ◉ $10$. Full line calculated for $K_D = 1{\cdot}1 \cdot 10^{-3}$ and log $K_{ex}(HL^+) = 2{\cdot}97$

The extraction of polyethylene glycol PEG 400 was interpreted satisfactorily assuming that $p = q = 1$, hence, that the reaction is

$$L_{aq} + H_{org}^+ \rightleftharpoons HL_{org}^+ . \tag{B}$$

The assumption that the $HL_{2,org}^+$ species is extracted was ruled out, the minimum of the $U$ function being found for the zero value of the extraction constant. Some differences were observed between the calculated and experimental values at $Z \rightarrow 1$, apparently due to the nonideal behaviour of the polyethylene glycol at higher concentrations. The equilibrium constant of reaction $(B)$, $K_{ex} = [HL_{org}^+]/[L][H_{org}^+]$, whose logarithm is $\log K_{ex} = 2.97 \pm 0.04$ $(U = 0.136)$, and the corresponding stability constant of the $HL^+$ species in nitrobenzene, $\log K(HL_{org}^+) = 5.97$, are in a good agreement with published values calculated from extraction data for systems involving $Sr^{2+}$, $Ba^{2+}$, $Ce^{3+}$ and $Eu^{3+}$ ions.

Interpretation of the extraction in the water–nitric acid–PEG 1 500–chlorinated dicarbolide–nitrobenzene system in terms of such a simple model failed; the calculated dependences of $Z$ on $\log [L]_{aq}$ did not fit the experimental data. Taking into acount findings concerning the behaviour of long-chain polyethylene glycols[5,12], the following

TABLE II

Equilibrium values of $\log [L]_{aq}$ and $Z$ for the extraction of PEG 400 with a solution of dicarbolide in nitrobenzene; $c(HNO_3) = 0.5$ mol l$^{-1}$, $t = 25°C$

| $\log [L]_{aq}$ | $Z$ | $\log [L]_{aq}$ | $Z$ |
|---|---|---|---|
| $c_B = 1.0$ mmol l$^{-1}$ | | $c_B = 4.0$ mmol l$^{-1}$ | |
| $-4.290$ | $0.049$ | $-4.039$ | $0.077$ |
| $-3.979$ | $0.095$ | $-3.710$ | $0.151$ |
| $-3.215$ | $0.390$ | $-2.776$ | $0.582$ |
| $-2.859$ | $0.616$ | | |
| | | $c_B = 10$ mmol l$^{-1}$ | |
| $c_B = 2.0$ mmol l$^{-1}$ | | $-3.988$ | $0.090$ |
| $-4.109$ | $0.061$ | $-3.612$ | $0.176$ |
| $-3.813$ | $0.123$ | $-3.070$ | $0.415$ |
| $-2.980$ | $0.476$ | $-2.829$ | $0.552$ |
| $-2.592$ | $0.720$ | $-2.512$ | $0.692$ |
| | | $-2.168$ | $0.720$ |
| | | $-1.921$ | $0.800$ |
| | | $-1.691$ | $0.761$ |

assumptions were adopted: *1*) A molecule of a long-chain polyethylene glycol can solvate several $(n)$ $H_{org}^+$ ions in the organic phase, and *2*) from the thermodynamic point of view, this molecule behaves like $n$ molecules of polyethylene glycol with a shorter chain whose length (i.e., number of ethylene oxide units) corresponds to the solvation of one $H_{org}^+$ ion.

The extraction of PEG 1 500 then can be expressed by the equation

$$mL_{1/n,aq} + H_{org}^+ \rightleftharpoons HL_{m/n,org}^+ . \qquad (C)$$
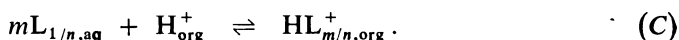
For this equation, a block named UBBE was set up for the program LETAGROP; this made it possible to determine the value of $n$ and to calculate the equilibrium constant(s) of Eq. $(C)$, defined as

$$K_{ex,m} = [HL_{m/n}^+]_{org}/[H^+]_{org}[L_{1/n}]_{aq}^m , \qquad (2)$$

where

$$[L_{1/n}]_{aq} = nc_{L,aq} \qquad (3)$$

and

$$c_{L,org} = (1/n)\left([L_{1/n}]_{org} + \sum_{m=1}^{M} m[HL_{m/n}]_{org}\right). \qquad (4)$$

The distribution constant of the model molecule $L_{1/n}$,

$$K_D = [L_{1/n}]_{org}/[L_{1/n}]_{aq} , \qquad (5)$$

then is identified with the distribution constant of PEG 1 500 in the water–nitrobenzene system. The results are given in Table III.

This table demonstrates that a molecule of PEG 1 500 is theoretically capable of solvating as many as 3 molecules of $H^+$ $(n \approx 3)$. Within the concentration range examined, the presence of species whose composition corresponds to the hypothetic formulas $HL_{1/3,org}$ and $HL_{2/3,org}^+$ was proved, whereas the presence of the species $HL_{org}^+$ was not, its inclusion in the model which comprised the two former species resulting in no marked decrease in the $U$ function value. The use of the nearest integer, $n = 3$, instead of the calculated value of $n = 3\cdot20$ also little affected the $U$ value. The calculated relative molecular mass of the hypothetic species solvating the $H_{org}^+$ ion $M_r = 467$ (i.e. 10 ethylene oxide units), is consistent with our previous finding that unlike PEG 600 and PEG 1 000, the polyethylene glycols PEG 200 to PEG 400 solvate a single proton in the organic phase.

The dependence of the concentration fractions of the $H_{org}^+$, $HL_{1/n,org}^+$ and $HL_{2/n,org}^+$ species $(n = 3\cdot20)$ from the total analytical concentration of $H^+B^-$ in the organic phase $(\delta)$ on $[L]_{aq}$ is shown in Fig. 3, demonstrating that the $HL_{1/3,org}^+$ species is

TABLE III

Comparison of the various models of extraction of PEG 1 500 from $0.5M$-$HNO_3$ with a solution of chlorinated dicarbolide in nitrobenzene; $c_B = 0.3 - 10$ mmol $l^{-1}$, $c_L = (0.02 - 2) c_B$

| $n$ | $\log K_{ex}{}^a$ | $U^b$ | $s^c$ |
|---|---|---|---|
| | $HL_{1/n,org}^+$ | | |
| $2.78 \pm 0.8$ | $4.69 \pm 0.15$ | $1.4529$ | $0.2842$ |
| $(3)^d$ | $4.70 \pm 0.15$ | $1.5063$ | $0.2816$ |
| | $HL_{1/n,org}^+$, $HL_{2/n,org}^+$ | | |
| $3.20 \pm 1.13$ | $4.71 \pm 0.16, 6.07$ (max. $6.73$) | $1.3072$ | $0.2772$ |
| $(3)^d$ | $4.70 \pm 0.15, 5.84$ (max. $6.46$) | $1.3193$ | $0.2707$ |
| | $HL_{1/n,org}^+$, $HL_{2/n,org}^+$, $HL_{3/n,org}^+$ | | |
| $3.35 \pm 0.7$ | $4.71 \pm 0.16, 6.28$ (max. $6.70$) , $5.28 \pm 0.001$ | $1.3099$ | $0.2863$ |
| $(3)^d$ | $4.70 \pm 0.15, 5.82$ (max $6.61$), $5.28 \pm 0.04$ | $1.3187$ | $0.2836$ |

[a] The confidence interval of the $K_{ex}$ constants[8] is $\pm 3 s(K)$, where $s(K)$ is the standard deviation of constant $K$. The approximate formula $\log K = \log K \pm \{\log [K + 1.5s(K)] - \log [K - 1.5s(K)]\}$. This relation does not hold at $s(K) > 0.2K$, and therefore only the maximum limit is given in the form $\log K = \log K$ (max. $\log [K + 3s(K)]$); [b] for 20 experimental points; [c] standard deviation estimate, calculated as $s = [U/(n_p - n_c)]^{1/2}$, where $n_p$ is the number of experimental points and $n_c$ is the number of constants determined (including $n$ if this is determined by calculation); [d] calculated for the preselected value of $n = 3$.



FIG. 3

Dependence of the fraction of the $H_{org}^+$ (1), $HL_{1/n,org}^+$ (2), and $HL_{2/n,org}^+$ (3) species from the total concentration of the acid form of chlorinated dicarbolide ($\delta$) on $\log [L]_{aq}$ for the extraction of PEG 1 500 with a solution of chlorinated dicarbolide in nitrobenzene; concentration of nitric acid in the aqueous phase $0.5$ mol $l^{-1}$. The values of $n = 3.2$, $\log K_{ex}(HL_{1/n}) = 4.71$ and $\log K_{ex}(HL_{2/n}) = 6.07$ were used for the calculation
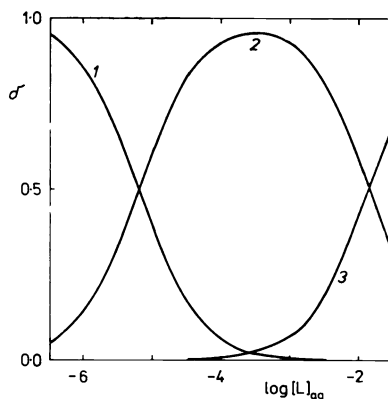
predominantly formed over the examined concentration region of L; this species is only converted to $HL^+_{2/3,org}$ at higher polyethylene glycol concentrations in the system. The fact that a molecule of PEG thus solvates in average three $H^+_{org}$ ions in the nitrobenzene phase is apparently responsible for the extraction constant of the hypothetic $HL^+_{1/3}$ species being about two orders of magnitude higher than the corresponding extraction constant of PEG 400, although the distribution constant of PEG 1 500 is lower than that of PEG 400. This is due to the exceedingly high protonation constant of this species in the nitrobenzene phase, where $\log K(HL^+_{1/3,org}) \approx 8\cdot4$. The next type of extraction of PEG 1 500, where there are less than three $H^+$ ions per polyethylene glycol molecule, proceeds considerably less readily; the corresponding equilibrium constant of the reaction

$$HL^+_{1/3,org} + L_{1/3} \;\rightleftharpoons\; HL^+_{2/3,org}, \tag{D}$$
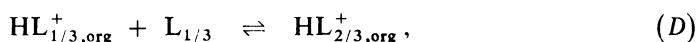
$\log K = 1\cdot4$ $(K = K_{ex1}/K_{ex2})$, is nearly two orders of magnitude lower than the $K_{ex}$ value for PEG 400. The second consecutive constant, corresponding to the reaction of the hypothetic species $HL^+_{1/3,org}$ and $L_{1/3,org}$ in the organic phase, has the value of $\log K(HL^+_{2/3,org}) = 5\cdot1$; it must be borne in mind, however, that the protonation constants in nitrobenzene involve a high error due to the low accuracy of determination of $K_D$ for PEG 1 500.

It is noteworthy that equations alternative to Eqs $(B)$ and $(C)$ can be used to describe the extraction of polyethylene glycol with dicarbolide, e.g. the formation of the $HL^+$ or $HL^+_{m/n}$ species in the aqueous phase and their extraction exchange for the $H^+$ ion in the organic phase, or the extraction of polyethylene glycol molecules or the $L_{1/n}$ species into the organic phase and their protonation in this phase. These two mechanisms are thermodynamically equivalent to the reactions $(B)$ and $(C)$, respectively. The description in terms of equations $(B)$ and $(C)$ was chosen with regard to the facts that the formation of the $HL^+$ species in the aqueous phase has not been proved (in analogy with the behaviour of cyclic polyethers, the protonation constant of polyethylene glycol in water can be expected to be low), and that the distribution constant of PEG 1 500 in the water–nitrobenzene system is not known with sufficient accuracy. In the approach used, only those concentrations that are known accurately enough are included in the equilibrium constants; the accuracy of the constants in equations $(B)$ and $(C)$ then is unaffected by the values of the protonation constants of polyethylene glycol in water and of the distribution constants of polyethylene glycol in the water–nitrobenzene system, which are unknown or known with a lower accuracy.

It should be noted that while the extraction of polyethylene glycol with nitrobenzene increases in order PEG 1 500 < PEG 1 000 < PEG 600 < PEG 400 < PEG 300 < < PEG 200, the extraction of low concentrations of polyethylene glycols with dicarbolide solutions in nitrobenzene increases in the reverse order, hence PEG 200 <

< PEG 300 < PEG 400 < PEG 600 < PEG 1 500. However, the extraction is decreasing with saturation of the organic phase more rapidly for PEG 1 500 and PEG 600 than for PEG 200 − PEG 400, the $c_L/c_B$ concentration ratio in the oranic phase (i.e., the Z value) never attaining the value of unity. At high concentrations of PEG 200 and PEG 300, on the other hand, the Z value can exceed unity and the $HL^+_{q,org}$ species can be formed[13]. These facts are consistent with the suggested mechanism of extraction of PEG 1 500 and can be looked upon as an indirect evidence for it.

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