Solvent Extraction of Microamounts of Cesium from Water into Nitrobenzene by Using Hydrogen Dicarbollylcobaltate in the Presence of Dicyclohexyl-18-crown-6

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Extraction distribution of microamounts of cesium in the water—HNO$_3$—nitrobenzene—hydrogen dicarbollylcobaltate—dicyclohexyl-18-crown-6 (L) system has been investigated. The equilibrium data have been explained assuming that the complexes HL$^+$, CsL$^+$, and CsL$_2^+$ are extracted into the organic phase. The values of extraction and stability constants of the species in nitrobenzene saturated with water have been determined.

The observation that macrocyclic polyethers form stable complexes with alkali and alkaline earth metal cations has stimulated a great deal of interest in these crown compounds for their possible applications in various fields of chemistry and biology [1, 2]. Extensive thermodynamic data suggest that the stability of macrocyclic complexes depends on the relative cation and ligand cavity size, the number of ligands and spatial arrangements of their bonding sizes, the substitution on the macrocyclic ring, and the solvent effects [3, 4].

The dicarbollylcobaltate anion and some of its halogen derivatives are very useful reagents for the extraction of alkali metal cations (especially Cs$^+$), and also – in the presence of polyoxyethylene compounds – for the extraction of Sr^{2+} and Ba^{2+} from aqueous solutions into an organic polar phase, both under laboratory conditions for purely theoretical or analytical purposes [5—7], and on the technological scale for the separation of some high-activity isotopes in the reprocessing of irradiated nuclear fuel [8—10].

In the present communication, the solvent extraction of microamounts of cesium using a nitrobenzene solution of hydrogen dicarbollylcobaltate (H$^+$B$^-$) in the presence of dicyclohexyl-18-crown-6 (L) was studied. We intended to find the composition of the species present in the nitrobenzene phase and to determine the corresponding equilibrium constants.

EXPERIMENTAL

Dicyclohexyl-18-crown-6 (a mixture of isomers) was supplied by Ventron, Karlsruhe, Germany. Cesium dicarbollylcobaltate, Cs$^+$B$^-$, was synthesized in the Institute of Inorganic Chemistry, Řež, Czech Republic, using the method published by *Hawthorne et al.* [11].

The nitrobenzene solution of hydrogen dicarbollylcobaltate (H$^+$B$^-$) was prepared from Cs$^+$B$^-$ by the procedure described in Ref. [12]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide ^{137}Cs (Techsnaveksport, Russia) was of standard radiochemical purity.

The extraction experiments in the two-phase water—HNO$_3$—Cs$^+$ (microamounts)—nitrobenzene—H$^+$B$^-$—dicyclohexyl-18-crown-6 (DCH18C6) system were performed in 10 cm^3 glass test tubes with polyethylene stoppers using 2 cm^3 of each phase. The test tubes filled with the solutions were shaken for 2 h at (25 ± 1) °C using a laboratory shaker. Under these conditions, an equilibrium in the system under study has established after approximately 30 min of shaking. Then the phases were separated by centrifugation (5 min, 2500 min^{-1}). Afterwards, 1 cm^3 of samples was taken from each phase and their γ-activities were measured using a well-type NaI(Tl) scintillation detector connected to a single-channel γ-analyzer RFT Strahlungsmessgerät 20 026 (RFT, Dresden, Germany).

The equilibrium distribution ratio of cesium, D, was determined as a ratio of the measured radioactivities of ^{137}Cs in the nitrobenzene and aqueous samples.

RESULTS AND DISCUSSION

The dependences of the logarithm of the cesium distribution ratios (log D) on the logarithm of the nu-

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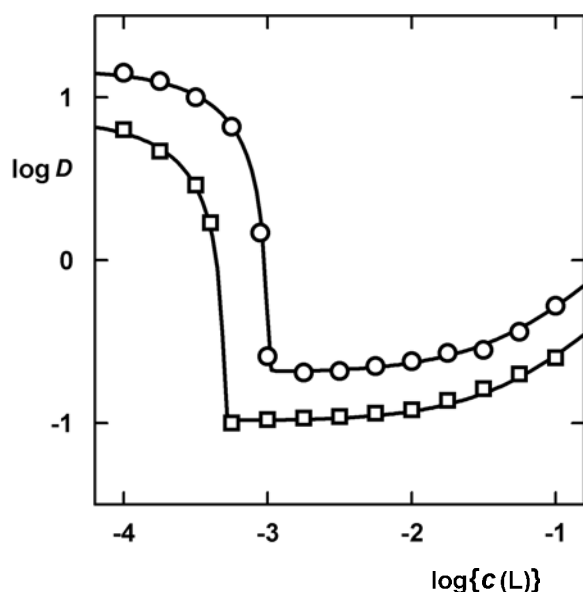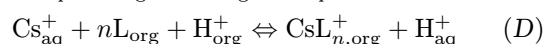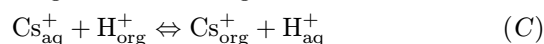
Fig. 1. Log D as a function of $\log\{c(L)\}$ for the system water—HNO$_3$—Cs$^+$ (microamounts)—nitrobenzene—H$^+$B$^-$—DCH18C6. ○ $c(\text{HNO}_3) = 0.10$ mol dm^{-3}, $c_B = 0.001$ mol dm^{-3}; □ $c(\text{HNO}_3) = 0.10$ mol dm^{-3}, $c_B = 0.0005$ mol dm^{-3}. The curves were calculated using the constants given in Table 2.

merical value of the total (analytical) concentration of the ligand DCH18C6 in the initial aqueous phase, $\log\{c(L)\}$, were measured for two initial concentrations of hydrogen dicarbollylcobaltate in the nitrobenzene phase ($c_B = 0.0005$ mol dm^{-3} and 0.001 mol dm^{-3}) in the presence of DCH18C6 ($c(L) = 0.0001$—0.10 mol dm^{-3}); the initial concentration of nitric acid in the aqueous phase, $c(\text{HNO}_3)$, was 0.10 mol dm^{-3}. The mentioned initial concentrations c_B, $c(\text{HNO}_3)$, and $c(L)$ are always related to the volume of one phase. The results are given in Fig. 1.

With respect to the previous results [13—18], the considered water—HNO$_3$—Cs$^+$ (microamounts)—nitrobenzene—H$^+$B$^-$—DCH18C6 extraction system can be described by the set of reactions

$$\text{L}_{\text{aq}} \Leftrightarrow \text{L}_{\text{org}} \tag{A}$$

$$\text{H}_{\text{org}}^+ + \text{L}_{\text{org}} \Leftrightarrow \text{HL}_{\text{org}}^+ \tag{B}$$

$$\text{Cs}_{\text{aq}}^+ + \text{H}_{\text{org}}^+ \Leftrightarrow \text{Cs}_{\text{org}}^+ + \text{H}_{\text{aq}}^+ \tag{C}$$

$$\text{Cs}_{\text{aq}}^+ + n\text{L}_{\text{org}} + \text{H}_{\text{org}}^+ \Leftrightarrow \text{CsL}_{n,\text{org}}^+ + \text{H}_{\text{aq}}^+ \tag{D}$$

$$\text{H}_{\text{aq}}^+ + \text{L}_{\text{aq}} \Leftrightarrow \text{HL}_{\text{aq}}^+ \tag{E}$$

$$\text{Cs}_{\text{aq}}^+ + \text{L}_{\text{aq}} \Leftrightarrow \text{CsL}_{\text{aq}}^+ \tag{F}$$

to which the following equilibrium constants

$$K_{\text{D}} = \frac{[\text{L}_{\text{org}}]}{[\text{L}_{\text{aq}}]} \tag{1}$$

$$\beta(\text{HL}_{\text{org}}^+) = \frac{[\text{HL}_{\text{org}}^+]}{[\text{H}_{\text{org}}^+][\text{L}_{\text{org}}]} \tag{2}$$

Table 1. Comparison of Three Different Models of Cesium Extraction from the Aqueous Solution of Nitric Acid Using the Nitrobenzene Solutions of H$^+$B$^-$ in the Presence of Dicyclohexyl-18-crown-6

Cesium complexes in the organic phase	$\log\{K_{\text{ex}}\}^a$	U^b
CsL$^+$	9.13 ± 0.08	0.33
CsL$_2^+$	11.18 (11.48)	8.35
CsL$^+$, CsL$_2^+$	9.01 ± 0.02, 10.21 ± 0.07	0.02

a) The values of the extraction constants are given for each complex. The reliability interval of the constants is given – in agreement with Ref. [21] – as $3\sigma(K)$, where $\sigma(K)$ is the standard deviation of the constant K. These values are expressed in the logarithmic scale using the approximate relation $\log\{K\} \pm (\log\{[K + 1.5\sigma(K)]\} - \log\{[K - 1.5\sigma(K)]\})$. For $\sigma(K) > 0.2K$, the previous relation is not valid and then only the upper limit is given in the parentheses in the form $\log\{K\}(\log\{[K + 3\sigma(K)]\})$ [21].
b) The error square sum $U = \Sigma(\log D_{\text{calc}} - \log D_{\text{exp}})^2$.

$$K_{\text{ex}}(\text{Cs}_{\text{org}}^+) = \frac{[\text{Cs}_{\text{org}}^+][\text{H}_{\text{aq}}^+]}{[\text{Cs}_{\text{aq}}^+][\text{H}_{\text{org}}^+]} \tag{3}$$

$$K_{\text{ex}}(\text{CsL}_{n,\text{org}}^+) = \frac{[\text{CsL}_{n,\text{org}}^+][\text{H}_{\text{aq}}^+]}{[\text{Cs}_{\text{aq}}^+][\text{L}_{\text{org}}]^n[\text{H}_{\text{org}}^+]} \tag{4}$$

$$\beta(\text{HL}_{\text{aq}}^+) = \frac{[\text{HL}_{\text{aq}}^+]}{[\text{H}_{\text{aq}}^+][\text{L}_{\text{aq}}]} \tag{5}$$

$$\beta(\text{CsL}_{\text{aq}}^+) = \frac{[\text{CsL}_{\text{aq}}^+]}{[\text{Cs}_{\text{aq}}^+][\text{L}_{\text{aq}}]} \tag{6}$$

correspond; subscripts aq and org denote the aqueous and organic phases, respectively.

A subroutine UBBE, based on the relations given above, mass balance of the crown ligand, and the electroneutrality conditions in both phases, was formulated [19, 20] and introduced into a more general least-squares minimizing program LETAGROP [21] used for determination of the "best" values of the extraction constants $K_{\text{ex}}(\text{CsL}_{n,\text{org}}^+)$. The minimum of the sum of errors in log D, *i.e.* the minimum of the expression

$$U = \Sigma(\log D_{\text{calc}} - \log D_{\text{exp}})^2 \tag{7}$$

was sought.

The values log $K_{\text{D}} = 2.15$ [16], $\log\{\beta(\text{HL}_{\text{org}}^+)\} = 7.7$ [17], $\log K_{\text{ex}}(\text{Cs}_{\text{org}}^+) = 3.15$ [16], $\log\{\beta(\text{HL}_{\text{aq}}^+)\} = -0.29$ [18], and $\log\{\beta(\text{CsL}_{\text{aq}}^+)\} = 0.98$ [18] were used for the respective calculations. The results are listed in Table 1, from which it is evident that the extraction data can be best explained assuming the cesium complex species CsL$^+$ and CsL$_2^+$ to be extracted into the nitrobenzene phase.

Fig. 2 presents the contributions of the species Cs$_{\text{org}}^+$, CsL$_{\text{org}}^+$, and CsL$_{2,\text{org}}^+$ to the total cesium concentration in the equilibrium nitrobenzene phase. From
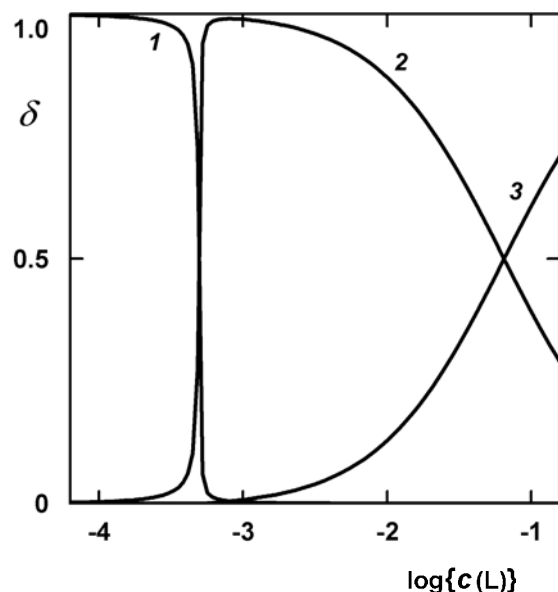
Fig. 2. Distribution diagram of cesium in the equilibrium nitrobenzene phase of the system water—HNO₃—Cs⁺ (microamounts)—nitrobenzene—H⁺B⁻—DCH18C6 in the forms of Cs^+, CsL^+, and CsL_2^+. $c(HNO_3) = 0.10$ mol dm⁻³, $c_B = 0.001$ mol dm⁻³. 1. $\delta(Cs^+) = [Cs_{org}^+]/c(Cs^+)_{org}$, 2. $\delta(CsL^+) = [CsL_{org}^+]/c(Cs^+)_{org}$, 3. $\delta(CsL_2^+) = [CsL_{2,org}^+]/c(Cs^+)_{org}$, where $c(Cs^+)_{org} = [Cs_{org}^+] + [CsL_{org}^+] + [CsL_{2,org}^+]$. The distribution curves were calculated using the constants given in Table 2.

Table 2. Equilibrium Constants in the Water—HNO₃—Cs⁺ (Microamounts)—Nitrobenzene—H⁺B⁻—DCH18C6 Extraction System

Equilibrium	$\log\{K\}$
$L_{aq} \Leftrightarrow L_{org}$	2.15^a
$H_{aq}^+ + L_{aq} \Leftrightarrow HL_{aq}^+$	-0.29^b
$Cs_{aq}^+ + L_{aq} \Leftrightarrow CsL_{aq}^+$	0.98^b
$Cs_{aq}^+ + H_{org}^+ \Leftrightarrow Cs_{org}^+ + H_{aq}^+$	3.15^a
$Cs_{aq}^+ + L_{org} + H_{org}^+ \Leftrightarrow CsL_{org}^+ + H_{aq}^+$	9.01
$Cs_{aq}^+ + 2L_{org} + H_{org}^+ \Leftrightarrow CsL_{2,org}^+ + H_{aq}^+$	10.21
$H_{org}^+ + L_{org} \Leftrightarrow HL_{org}^+$	7.7^c
$Cs_{org}^+ + L_{org} \Leftrightarrow CsL_{org}^+$	5.86
$Cs_{org}^+ + 2L_{org} \Leftrightarrow CsL_{2,org}^+$	7.06
$HL_{aq}^+ \Leftrightarrow HL_{org}^+$	4.4
$CsL_{aq}^+ \Leftrightarrow CsL_{org}^+$	4.5

a) Ref. [16], *b*) Ref. [18], *c*) Ref. [17].

this figure it follows that the "sandwich" type complex $CsL_{2,org}^+$ is present in significant concentrations only at relatively high amounts of the DCH18C6 ligand in the system under study.

Knowing the value $\log K_{ex}(Cs_{org}^+) = 3.15$ [16] as well as the extraction constants $\log\{K_{ex}(CsL_{org}^+)\} = 9.01$ and $\log\{K_{ex}(CsL_{2,org}^+)\} = 10.21$ determined here (Table 1), the stability constants of the complexes CsL_{org}^+ and $CsL_{2,org}^+$ in the nitrobenzene phase defined as

$$\beta(CsL_{org}^+) = \frac{[CsL_{org}^+]}{[Cs_{org}^+][L_{org}]} \qquad (8)$$

$$\beta(CsL_{2,org}^+) = \frac{[CsL_{2,org}^+]}{[Cs_{org}^+][L_{org}]^2} \qquad (9)$$

can be evaluated applying the simple relations

$$\log\{\beta(CsL_{org}^+)\} =$$
$$= \log\{K_{ex}(CsL_{org}^+)\} - \log K_{ex}(Cs_{org}^+) \qquad (10)$$

$$\log\{\beta(CsL_{2,org}^+)\} =$$
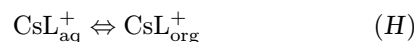$$= \log\{K_{ex}(CsL_{2,org}^+)\} - \log K_{ex}(Cs_{org}^+) \qquad (11)$$

Furthermore, the individual extraction constants of the cations HL^+ and CsL^+ in the water—nitrobenzene system, denoted by $K_i(HL^+)$ and $K_i(CsL^+)$,

respectively, corresponding to the following equilibria

$$HL_{aq}^+ \Leftrightarrow HL_{org}^+ \qquad (G)$$

$$CsL_{aq}^+ \Leftrightarrow CsL_{org}^+ \qquad (H)$$

were calculated employing the relationships

$$\log K_i(HL^+) = \log\{\beta(HL_{org}^+)\} - \log\{\beta(HL_{aq}^+)\} +$$
$$+ \log K_D + \log K_i(H^+) \qquad (12)$$
$$\log K_i(CsL^+) = \log\{K_{ex}(CsL_{org}^+)\} - \log\{\beta(CsL_{aq}^+)\} +$$
$$+ \log K_D + \log K_i(Cs^+) \qquad (13)$$

where $\log K_i(H^+) = -5.7$ [22]. The respective equilibrium constants are summarized in Table 2.

In conclusion, it should be noted that somewhat higher stability of the species CsL^+ and CsL_2^+, where L = 18-crown-6, in nitrobenzene saturated with water ($\log\{\beta(CsL_{org}^+)\} = 6.54$ and $\log\{\beta(CsL_{2,org}^+)\} = 8.64$) [14] in comparison with the stability of the analogous complexes of Cs^+ with dicyclohexyl-18-crown-6 in this medium determined here ($\log\{\beta(CsL_{org}^+)\} = 5.86$ and $\log\{\beta(CsL_{2,org}^+)\} = 7.06$ – see Table 2) can be obviously explained on the basis of the higher flexibility of the 18-crown-6 ligand than in the case of the more rigid structure of dicyclohexyl-18-crown-6.

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