

EXTRACTION OF CESIUM WITH BIS[UNDECAHYDRO-7,8-DICARBAUNDECA-BORATO(2-)]COBALTATE(1-) IN THE PRESENCE OF 18-CROWN-6Petr VANURA^a and Emanuel MAKRLIK^b^a Department of Analytical Chemistry, Prague Institute of Chemical Technology, 166 28 Prague, Czech Republic; e-mail: petr.vanura@vscht.cz^b Department of Chemistry, Faculty of Education, Charles University, 116 39 Prague, Czech Republic

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Extraction of cesium with a nitrobenzene solution of bis[undecahydro-7,8-dicarbaundecaborato(2-)]cobaltate(1-) in the presence of 18-crown-6 (18C6, L) has been investigated. The equilibrium data and typical dependences of the Cs distribution ratios on the analytical concentration of 18C6 in the system under study can be 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.

Key words: Water-nitrobenzene extraction system; Cesium; 18-Crown-6; Bis[undecahydro-7,8-dicarbaundecaborato(2-)]cobaltate(1-).

In our previous works¹⁻⁴, we dealt with the extraction of Sr^{2+} and Ba^{2+} ions using a nitrobenzene solution of H^+ bis[undecahydro-7,8-dicarbaundecaborato(2-)]cobaltate(1-) (H^+ bis-1,2-dicarbollylcobaltate, H^+B^-) in the presence of polyethylene glycols, polyethers and crown ethers. These ions (M^{2+}) have been found to be extracted in the form of the $ML_{n,org}^{2+}$ complexes. The occurrence of maxima on the plot of metal ion distribution ratio (D) vs the total polyoxonium compound concentration, $c(L)$, has been explained in terms of competition between the charged $ML_{n,org}^{2+}$ complexes and protonated PEG (HL_{org}^+) upon the balancing of the dicarbollylcobaltate electrostatic charge in the organic phase.

During the extraction of perchloric acid with a nitrobenzene solution of dibenzo-18-crown-6 (DB18C6), the complexes HL^+ and $H_2L_2^{2+}$ have been proved in the organic phase⁵. Extraction of cesium using a nitrobenzene solution of H^+B^- in the presence of DB18C6 has been investigated; the complexes CsL^+ and CsL_2^+ have been found in the organic phase⁶.

On the other hand, the extraction of strontium with a nitrobenzene solution of H^+ bis-1,2-dicarbollylcobaltate in the presence of 15-crown-5 (15C5) can be explained by a simple model involving the presence of the species HL^+ , HL_2^+ and SrL_2^{2+} in the organic

phase. The complex SrL^{2+} , which exists in aqueous solution, has not been found in the nitrobenzene phase⁷.

The aim of this paper is to study the extraction of microamounts of cesium with the nitrobenzene solution of H^+B^- in the presence of 18-crown-6 (18C6, L). We intended to find the composition of species present in the organic phase and to determine the respective equilibrium constants.

EXPERIMENTAL

18-Crown-6 (Merck, Darmstadt, Germany) was used without any purification. Cesium salt of bis-1,2-dicarbollylcobaltate, Cs^+B^- , was synthesized in the Institute of Inorganic Chemistry, Rez near Prague, Czech Republic. The hydrogen form of bis-1,2-dicarbollylcobaltate (H^+B^-) was prepared from the corresponding cesium salt (Cs^+B^-) by the procedure described in ref.³. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide ^{137}Cs (Techsnav-eksport, Russia) was of standard radiochemical purity.

The extraction experiments on the system water– HNO_3 – Cs^+ (microamounts)–18C6–nitrobenzene– H^+B^- were performed in 10 ml glass test-tubes with polyethylene stoppers using 2 ml of each phase. The test-tubes were shaken for 2 h at 25 ± 2 °C using a laboratory shaker. Under these conditions the equilibrium in the system under study has established after approximately 20 min of shaking. Then the phases were separated by centrifugation (5 min, 2 500 r.p.m.). After centrifugation, 1 ml samples were taken from each phase and their γ -activities were measured using a well-type $\text{NaI}(\text{Tl})$ scintillation detector connected with a single channel γ -analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratio of cesium, D , was determined as a ratio of the measured radioactivities of 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 total (analytical) concentration of the ligand 18C6 in the initial aqueous phase ($\log c(L)$) were measured for two concentrations of nitric acid in the aqueous phase ($c(\text{HNO}_3) = 0.098$ and 0.30 mol/l) and for two concentrations of bis-1,2-dicarbollylcobaltate in the nitrobenzene phase ($c_B = 0.002$ and 0.003 mol/l) in the presence of 18C6 ($c(L) = 1.8 \cdot 10^{-4}$ – 0.1 mol/l). All concentrations are always related to the volume of the respective phase. The results are given in Table I and Fig. 1.

With regard to the results of previous papers^{1–10}, the system water– HNO_3 – Cs^+ (microamounts)–18C6–nitrobenzene– H^+B^- can be described by the set of reactions



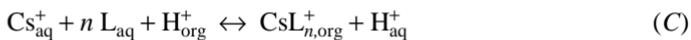


TABLE I

$\log D$ as a function of $\log c(\text{L})$ (L is 18C6) for cesium extraction from aqueous solutions of nitric acid with nitrobenzene solutions of H^+B^-

$\log D$	$\log c(\text{L})$	$\log D$	$\log c(\text{L})$
$c(\text{HNO}_3) = 0.30 \text{ mol/l}, c_{\text{B}} = 0.003 \text{ mol/l}$			
-3.745	1.104	-2.252	0.183
-3.495	1.117	-2.000	0.204
-3.252	1.131	-1.699	0.182
-3.000	1.005	-1.495	0.215
-2.699	0.779	-1.252	0.201
-2.505	0.194	-1.000	0.243
$c(\text{HNO}_3) = 0.098 \text{ mol/l}, c_{\text{B}} = 0.002 \text{ mol/l}$			
-3.745	1.391	-2.252	0.472
-3.495	1.405	-2.000	0.477
-3.252	1.378	-1.699	0.501
-3.000	1.232	-1.495	0.475
-2.699	0.536	-1.252	0.530
-2.495	0.488	-1.000	0.542

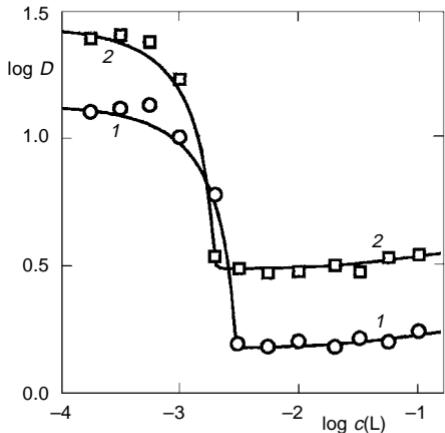


FIG. 1
 $\log D$ as a function of $\log c(\text{L})$ in the system water- HNO_3 - Cs^+ (microamounts)-18C6-nitrobenzene- H^+B^- . 1 $c(\text{HNO}_3) = 0.3 \text{ mol/l}, c_{\text{B}} = 0.003 \text{ mol/l}$; 2 $c(\text{HNO}_3) = 0.098 \text{ mol/l}, c_{\text{B}} = 0.002 \text{ mol/l}$. The curves were calculated for the constants given in Table III



to which the following equilibrium constants

$$K_D = \frac{[\text{L}_{\text{org}}]}{[\text{L}_{\text{aq}}]} \quad (I)$$

$$K_{\text{ex}}(\text{HL}_{\text{org}}^+) = \frac{[\text{HL}_{\text{org}}^+]}{[\text{H}_{\text{org}}][\text{L}_{\text{aq}}]} \quad (2)$$

$$K_{\text{ex}}(\text{CsL}_{n,\text{org}}^+) = \frac{[\text{CsL}_{n,\text{org}}^+][\text{H}_{\text{aq}}^+]}{[\text{Cs}_{\text{aq}}^+][\text{L}_{\text{aq}}]^n [\text{H}_{\text{org}}^+]} \quad (3)$$

$$\beta(\text{HL}_{\text{aq}}^+) = \frac{[\text{HL}_{\text{aq}}^+]}{[\text{H}_{\text{aq}}^+][\text{L}_{\text{aq}}]} \quad (4)$$

$$\beta(\text{CsL}_{\text{aq}}^+) = \frac{[\text{CsL}_{\text{aq}}^+]}{[\text{Cs}_{\text{aq}}^+][\text{L}_{\text{aq}}]} \quad (5)$$

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 of both phases, was formulated^{1,4} and introduced into a more general least-squares minimizing program LETAGROP (ref.¹¹) used for the evaluation of the "best" values of the 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

$$U = \sum (\log D_{\text{calc}} - \log D_{\text{exp}})^2 \quad (6)$$

was sought.

The values $\log K_{\text{ex}}(\text{Cs}_{\text{org}}^+) = 3.20$ (ref.⁶), $K_D = 0.10$ (ref.⁸), $\log \beta(\text{HL}_{\text{aq}}^+) = 0.77$ (ref.⁹), $\log K_{\text{ex}}(\text{HL}_{\text{org}}^+) = 6.56$ (ref.⁹) and $\log \beta(\text{CsL}_{\text{aq}}^+) = 0.99$ (ref.¹⁰) were used for the calculations. The results are listed in Table II. From here it is evident that the extraction data can be explained assuming the cesium species CsL^+ and CsL_2^+ to be extracted into the nitrobenzene phase.

Figure 2 presents the contribution of the species H_{org}^+ and HL_{org}^+ to the total acidity of the organic phase while Fig. 3 depicts the contribution of the species Cs_{org}^+ , $\text{CsL}_{\text{org}}^+$ and

$\text{CsL}_{2,\text{org}}^+$ to the total cesium concentration in the organic phase. From Fig. 3 it follows that the "sandwich" type complex $\text{CsL}_{2,\text{org}}^+$ in the nitrobenzene phase is present in significant concentrations only at relatively high concentrations of the 18C6 ligand in the system under study.

Knowing the values already given above and the extraction constants $\log K_{\text{ex}}(\text{CsL}_{\text{org}}^+) = 8.74$ and $\log K_{\text{ex}}(\text{CsL}_{2,\text{org}}^+) = 9.84$ determined here, then the stability constants of the complexes HL^+ , CsL^+ and CsL_2^+ in the nitrobenzene phase defined as

$$\beta(\text{HL}_{\text{org}}^+) = \frac{[\text{HL}_{\text{org}}^+]}{[\text{H}_{\text{org}}^+][\text{L}_{\text{org}}]} \quad (7)$$

TABLE II

Comparison of three different models of cesium extraction from aqueous solutions of nitric acid with nitrobenzene solutions of H^+B^- in the presence of 18-crown-6

Cesium complexes in the organic phase	$\log K_{\text{ex}}^a$	U^b
CsL^+	8.84 ± 0.07	0.20
CsL_2^+	10.73 (11.04)	6.14
$\text{CsL}^+, \text{CsL}_2^+$	$8.74 \pm 0.03, 9.84 \pm 0.11$	0.02

^a The reliability interval of the constants are given as $3s(K)$, where $s(K)$ is the standard deviation of the constant K (ref.¹¹). These values are expressed in the logarithmic scale using the approximate relation $\log K \pm \{\log [K + 1.5s(K)] - \log [K - 1.5s(K)]\}$. For $s(K) > 0.2 K$, the previous relation is not valid and then only the upper limit is given in the parenthesis in the form $\log K (\log (K + 3s(K))$. ^b The error-square sum $U = \Sigma(\log D_{\text{calc}} - \log D_{\text{exp}})^2$.

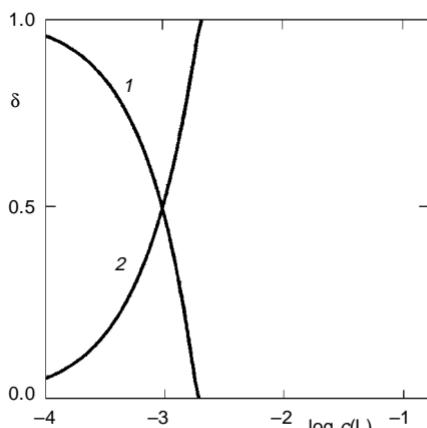


FIG. 2
Fractions of the species containing H^+ (δ) present in the organic phase of the system water- HNO_3 - Cs^+ (microamounts)-18C6-nitrobenzene- H^+B^- as functions of $\log c(L)$. $c(\text{HNO}_3) = 0.098 \text{ mol/l}$, $c_{\text{B}} = 0.002 \text{ mol/l}$. 1 $\delta(\text{H}^+)$, 2 $\delta(\text{HL}^+)$. The curves were calculated for constants $\log K_D = -1.00$ and $\log K_{\text{ex}}(\text{HL}^+) = 6.56$

$$\beta(\text{CsL}_{\text{org}}^+) = \frac{[\text{CsL}_{\text{org}}^+]}{[\text{Cs}_{\text{org}}^+][\text{L}_{\text{org}}]} \quad (8)$$

$$\beta(\text{CsL}_{2,\text{org}}^+) = \frac{[\text{CsL}_{2,\text{org}}^+]}{[\text{Cs}_{\text{org}}^+][\text{L}_{\text{org}}]^2} \quad (9)$$

TABLE III

The equilibrium constants for the water-HNO₃-Cs⁺-(microamounts)-18C6-nitrobenzene-H⁺B⁻ system

Equilibrium	$\log K$
$\text{L}_{\text{aq}} \leftrightarrow \text{L}_{\text{org}} (A)$	-1.0 ^a
$\text{H}_{\text{aq}}^+ + \text{L}_{\text{aq}} \leftrightarrow \text{HL}_{\text{aq}}^+ (D)$	0.77 ^b
$\text{Cs}_{\text{aq}}^+ + \text{L}_{\text{aq}} \leftrightarrow \text{CsL}_{\text{aq}}^+ (E)$	0.99 ^c
$\text{Cs}_{\text{aq}}^+ + \text{H}_{\text{org}}^+ \leftrightarrow \text{Cs}_{\text{org}}^+ + \text{H}_{\text{aq}}^+$	3.20 ^d
$\text{H}_{\text{org}}^+ + \text{L}_{\text{aq}} \leftrightarrow \text{HL}_{\text{org}}^+ (B)$	6.56 ^b
$\text{Cs}_{\text{aq}}^+ + \text{L}_{\text{aq}} + \text{H}_{\text{org}}^+ \leftrightarrow \text{CsL}_{\text{org}}^+ + \text{H}_{\text{aq}}^+$	8.74
$\text{Cs}_{\text{aq}}^+ + 2 \text{L}_{\text{aq}} + \text{H}_{\text{org}}^+ \leftrightarrow \text{CsL}_{2,\text{org}}^+ + \text{H}_{\text{aq}}^+$	9.84
$\text{H}_{\text{org}}^+ + \text{L}_{\text{org}} \leftrightarrow \text{HL}_{\text{org}}^+$	7.56
$\text{Cs}_{\text{org}}^+ + \text{L}_{\text{org}} \leftrightarrow \text{CsL}_{\text{org}}^+$	6.54
$\text{Cs}_{\text{org}}^+ + 2 \text{L}_{\text{org}} \leftrightarrow \text{CsL}_{2,\text{org}}^+$	8.64
$\text{HL}_{\text{aq}}^+ \leftrightarrow \text{HL}_{\text{org}}^+ (F)$	0.1
$\text{CsL}_{\text{aq}}^+ \leftrightarrow \text{CsL}_{\text{org}}^+ (G)$	2.1

^a Ref. ⁸; ^b ref. ⁹; ^c ref. ¹⁰; ^d ref. ⁶.

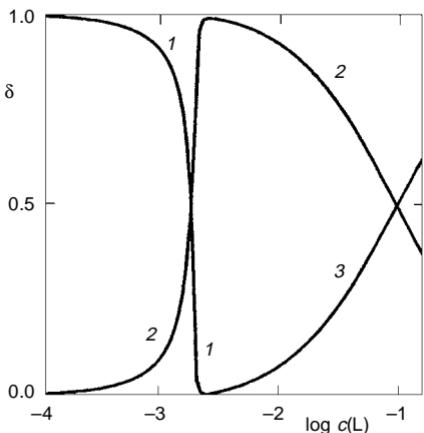


FIG. 3

Fractions of the species containing Cs⁺ (δ) present in the organic phase of the system water-HNO₃-Cs⁺ (microamounts)-18C6-nitrobenzene-H⁺B⁻ as functions of log c(L). $c(\text{HNO}_3) = 0.098 \text{ mol/l}$, $c_B = 0.002 \text{ mol/l}$. 1 $\delta(\text{Cs}^+)$, 2 $\delta(\text{CsL}^+)$, 3 $\delta(\text{CsL}_{2,\text{org}}^+)$. The curves were calculated for the constants given in Table III

can be evaluated using the simple relations:

$$\log \beta(\text{HL}_{\text{org}}^+) = \log K_{\text{ex}}(\text{HL}_{\text{org}}^+) - \log K_D \quad (10)$$

$$\log \beta(\text{CsL}_{\text{org}}^+) = \log K_{\text{ex}}(\text{CsL}_{\text{org}}^+) - \log K_{\text{ex}}(\text{Cs}_{\text{org}}^+) - \log K_D \quad (11)$$

$$\log \beta(\text{CsL}_{2,\text{org}}^+) = \log K_{\text{ex}}(\text{CsL}_{2,\text{org}}^+) - \log K_{\text{ex}}(\text{Cs}_{\text{org}}^+) - 2 \log K_D \quad (12)$$

Finally, the individual extraction constants of the cations HL^+ and CsL^+ , denoted $K_i(\text{HL}^+)$ and $K_i(\text{CsL}^+)$, respectively, in the water–nitrobenzene system, corresponding to the transfer of these complex cations from the aqueous into the nitrobenzene phase¹²



were evaluated using the following relationships

$$\log K_i(\text{HL}^+) = \log K_{\text{ex}}(\text{HL}_{\text{org}}^+) - \log \beta(\text{HL}_{\text{aq}}^+) + \log K_i(\text{H}^+) \quad (13)$$

$$\log K_i(\text{CsL}^+) = \log K_{\text{ex}}(\text{CsL}_{\text{org}}^+) - \log \beta(\text{CsL}_{\text{aq}}^+) + \log K_i(\text{H}^+) \quad (14)$$

where $\log \beta(\text{HL}_{\text{aq}}^+) = 0.77$ (ref.⁹), $\log \beta(\text{CsL}_{\text{aq}}^+) = 0.99$ (ref.¹⁰) and $\log K_i(\text{H}^+) = -5.7$ (ref.¹²). The respective equilibrium constants are summarized in Table III.

In conclusion it should be noted that the higher stability of the species HL^+ , CsL^+ and $\text{CsL}_{2,\text{org}}^+$, where L is 18-crown-6, in nitrobenzene saturated with water (Table III) in comparison with the stability of the analogous complexes of H^+ and Cs^+ with dibenzo-18-crown-6 in this medium ($\log \beta(\text{HL}_{\text{org}}^+) = 3.56$, $\log \beta(\text{CsL}_{\text{org}}^+) = 4.30$ and $\log \beta(\text{CsL}_{2,\text{org}}^+) = 6.35$; see ref.⁶) can be obviously explained on the basis of the higher flexibility of the 18-crown-6 ligand compared with the relatively rigid structure of dibenzo-18-crown-6.

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