Extraction of Lead with Nitrobenzene Solution of Strontium Dicarbollylcobaltate in the Presence of 18-crown-6

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Abstract. From extraction experiments with ^{85}Sr as a tracer, the extraction constant corresponding to the equilibrium $Pb^{2+}(aq) + SrL^{2+}(nb) \rightleftharpoons PbL^{2+}(nb) + Sr^{2+}(aq)$ taking place in the two - phase water – nitrobenzene system (L = 18-crown-6; aq = aqueous phase, nb = nitrobenzene phase) was evaluated as $\log K_{ex}(Pb^{2+}, SrL^{2+}) = 1.5$. Further, the stability constant of the PbL^{2+} complex in nitrobenzene saturated with water was calculated: $\log \beta_{nb}(PbL^{2+}) = 12.9$.

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 branches of chemistry and biology [1, 2]. Extensive thermodynamic data [3, 4] suggest that the stability of macrocyclic complexes depends on the relative cation and ligand cavity size, the number and spacial arrangements of the ligand bonding sites, the substitution on the macrocyclic ring and the solvent effects.

The cyclic polyether 18-crown-6 has six oxygen atoms in the polyether ring, that are bond places of this ionophore [1, 5].

The aim of the present communication was to determine especially the stability constant of the complex species PbL^{2+}, where L is 18-crown-6, in nitrobenzene saturated with water.

Experimental

18-crown-6 was supplied by Merck, Darmstadt, Germany. Cesium dicarbollylcobaltate (CsDCC) was synthesized in the Institute of Inorganic Chemistry, Řež, Czech Republic. The radionuclide ^{85}Sr (DuPont, Belgium) was of standard radiochemical purity. Nitrobenzene and all other chemicals (analytical grade, Lachema, Brno, Czech Republic) were used without further purification.

In order to obtain the solution of HDCC in nitrobenzene, the solution of CsDCC in this medium (0.2 mol dm^{-3}) was twice equilibrated with equal volumes of 15% (v/v) *n*-propanol in diluted H_2SO_4 of the concentration of about 1 mol dm^{-3}. H_2SO_4 and *n*-propanol were removed from the organic phase by a ten-fold equilibration with the solution of H_2SO_4 in distilled water (about 1 mol dm^{-3}) of an equal volume, followed by two equilibrations with distilled water. The concentration of HDCC in the nitrobenzene solution was determined by neutralization titration (NaOH, bromocresol green) after a ten-fold dilution with ethanol or acetone. The equilibration of the nitrobenzene solution of HDCC with stoichiometric $Sr(OH)_2$, which was dissolved in the aqueous solution of $Sr(NO_3)_2$ (0.2 mol dm^{-3}), yields the corresponding $Sr(DCC)_2$ solution in nitrobenzene.

The extraction experiments were carried out in 10 cm^3 glass test-tubes fitted with polyethylene stoppers.

2 cm^3 of the aqueous solution of $Pb(NO_3)_2$ of the concentration in the range from 2×10^{-4} to 2×10^{-3} mol dm^{-3} and microamounts of ^{85}Sr were added to 2 cm^3 of the nitrobenzene solution of 18-crown-6 and $Sr(DCC)_2$, whose initial concentrations varied from 1×10^{-4} to 1×10^{-3} mol dm^{-3} (in all experiments, the initial concentration of 18-crown-6 in nitrobenzene, $C_L^{in,nb}$, was always equal to the initial concentration of $Sr(DCC)_2$ in this medium, $C_{Sr(DCC)_2}^{in,nb}$). The test-tubes filled with the solutions were shaken for two hours at a temperature of 25 ± 2 °C using a laboratory shaker; under these conditions the equilibrium in the system under study has been established already after approximately 20 minutes of shaking. Then the phases were separated by centrifugation (5 min, 2 500 rpm). After centrifugation, 1 cm^3 samples were taken from each phase and their γ-activities were measured using a well-type NaI(Tl) scintillation detector connected with a single channel analyzer RFT Strahlungsmessgerät 20 026 (RFT, Dresden, Germany).

The equilibrium distribution ratio of strontium, D_{Sr}, was determined as a ratio of the measured radioactivities of the nitrobenzene and aqueous samples.

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Results and Discussion

With regard to the results of previous papers [6, 7], the two-phase water–$Pb(NO_3)_2$ –nitrobenzene–$Sr(DCC)_2$ extraction system can be described by the following equilibrium

$$Pb^{2+}(aq) + Sr^{2+}(nb) \rightleftharpoons Pb^{2+}(nb) + Sr^{2+}(aq);\ K_{ex}(Pb^{2+}, Sr^{2+}) \tag{1}$$

with the corresponding exchange extraction constant $K_{ex}(Pb^{2+}, Sr^{2+})$; aq and nb denote the presence of the particles in the aqueous and nitrobenzene phases, respectively.

The changes of the standard Gibbs energies corresponding to the transfer of Pb^{2+} and Sr^{2+} from the aqueous into the nitrobenzene phase, expressed by equilibria

$$Pb^{2+}(aq) \rightleftharpoons Pb^{2+}(nb) \tag{2}$$

$$Sr^{2+}(aq) \rightleftharpoons Sr^{2+}(nb), \tag{3}$$

are given by definitions

$$\Delta G^{o,aq\rightarrow nb}_{tr,Pb^{2+}} = \mu^{o,nb}_{Pb^{2+}} - \mu^{o,aq}_{Pb^{2+}} \tag{4}$$

$$\Delta G^{o,aq\rightarrow nb}_{tr,Sr^{2+}} = \mu^{o,nb}_{Sr^{2+}} - \mu^{o,aq}_{Sr^{2+}} \tag{5}$$

Here μ^0-s are the standard chemical potentials of Pb^{2+} and Sr^{2+} in the two phases concerned.

The individual extraction constants $K^{i}_{Pb^{2+}}$ and $K^{i}_{Sr^{2+}}$ for Pb^{2+} and Sr^{2+}, respectively, in the water–nitrobenzene system are defined by [6]

$$\Delta G^{o,aq\rightarrow nb}_{tr,Pb^{2+}} = -RT \ln K^{i}_{Pb^{2+}} \tag{6}$$

$$\Delta G^{o,aq\rightarrow nb}_{tr,Sr^{2+}} = -RT \ln K^{i}_{Sr^{2+}} \tag{7}$$

Combination of the relation

$$-RT \ln K_{ex}\left(Pb^{2+}, Sr^{2+}\right) = \mu^{o,nb}_{Pb^{2+}} + \mu^{o,aq}_{Sr^{2+}} - \mu^{o,nb}_{Pb^{2+}} - \mu^{o,aq}_{Sr^{2+}} \tag{8}$$

corresponding to equilibrium (1) with equations (4) – (7) yields

$$\log K_{ex}\left(Pb^{2+}, Sr^{2+}\right) = \log K^{i}_{Pb^{2+}} - \log K^{i}_{Sr^{2+}} \tag{9}$$

Knowing $\log K^{i}_{Pb^{2+}} = -10.6$ [8] and $\log K^{i}_{Sr^{2+}} = -10.7$, which was inferred from previous results [6, 9], the exchange extraction constant $K_{ex}(Pb^{2+}, Sr^{2+})$ was simply calculated from equation (9):

$$\log K_{ex}(Pb^{2+}, Sr^{2+}) = 0.1 \tag{10}$$

With respect to previous papers [7, 10], the two-phase water–$Pb(NO_3)_2$–nitrobenzene–L–$Sr(DCC)_2$ (L = 18-crown-6) extraction system (see Experimental section), chosen for determination of stability of the complex PbL^{2+} in water-saturated nitrobenzene, can be characterized by the main chemical equilibrium

$$Pb^{2+}(aq) + SrL^{2+}(nb) \rightleftharpoons PbL^{2+}(nb) + Sr^{2+}(aq);\ K_{ex}(Pb^{2+}, SrL^{2+}) \tag{11}$$

to which the equilibrium constant

$$K_{ex}(Pb^{2+}, SrL^{2+}) = \frac{\left[PbL^{2+}\right]_{nb}\left[Sr^{2+}\right]_{aq}}{\left[Pb^{2+}\right]_{aq}\left[SrL^{2+}\right]_{nb}} \tag{12}$$

corresponds; aq and nb refer to the aqueous and nitrobenzene phases, respectively. It is necessary to emphasize that the 18-crown-6 ligand forms – with Pb^{2+} and Sr^{2+} – the very stable complexes PbL^{2+} and SrL^{2+} in the nitrobenzene phase [10].

Following the conditions of electroneutrality of the organic and aqueous phases

$$\left[SrL^{2+}\right]_{nb} + \left[PbL^{2+}\right]_{nb} = C^{in,nb}_{Sr(DCC)_2} \tag{13}$$

$$\left[Sr^{2+}\right]_{aq} + \left[Pb^{2+}\right]_{aq} = C^{in,aq}_{Pb\left(NO_3\right)_2} \tag{14}$$

the mass balances of lead and strontium at equal volumes of the nitrobenzene and aqueous phases

$$\left[Pb^{2+}\right]_{aq} + \left[PbL^{2+}\right]_{nb} = C^{in,aq}_{Pb\left(NO_3\right)_2} \tag{15}$$

$$\left[Sr^{2+}\right]_{aq} + \left[SrL^{2+}\right]_{nb} = C^{in,nb}_{Sr(DCC)_2} \tag{16}$$

and the measured equilibrium distribution ratio of strontium

$$D_{Sr} = \frac{\left[SrL^{2+}\right]_{nb}}{\left[Sr^{2+}\right]_{aq}} \tag{17}$$

then combination of previous relationships (12) – (17) gives the final expression for the extraction constant $K_{ex}(Pb^{2+}, SrL^{2+})$:

$$K_{ex}\left(Pb^{2+}, SrL^{2+}\right) = \frac{1}{D_{Sr}} \frac{C^{in,nb}_{Sr(DCC)_2}}{\left(1 + D_{Sr}\right) C^{in,aq}_{Pb\left(NO_3\right)_2} - C^{in,nb}_{Sr(DCC)_2}} \tag{18}$$

In this study, from the extraction experiments and γ-activity measurements (see Experimental section) by using equation (18), the following value of the constant $\log K_{ex}(Pb^{2+}, SrL^{2+})$ was determined:

$$\log K_{ex}(Pb^{2+}, SrL^{2+}) = 1.5 \tag{19}$$

Further, for the extraction constant $K_{ex}(Pb^{2+}, SrL^{2+})$ we can formulate – on the basis of equilibrium (11) – the following thermodynamic relation

$$-RT \ln K_{ex}\left(Pb^{2+}, SL^{2+}\right) = \mu^{o,nb}_{PbL^{2+}} + \mu^{o,aq}_{Sr^{2+}} - \mu^{o,aq}_{Pb^{2+}} - \mu^{o,nb}_{SrL^{2+}} \tag{20}$$

Similarly, for the stability constants of the PbL^{2+} and SrL^{2+} complexes in water saturated nitrobenzene, denoted by β_{nb} (PbL^{2+}) and β_{nb} (SrL^{2+}), it can be written

$$-RT \ln \beta_{nb}\left(PbL^{2+}\right) = \mu^{o,nb}_{PbL^{2+}} - \mu^{o,nb}_{Pb^{2+}} - \mu^{o,nb}_{L} \quad (21)$$

$$-RT \ln \beta_{nb}\left(SrL^{2+}\right) = \mu^{o,nb}_{SrL^{2+}} - \mu^{o,nb}_{Sr^{2+}} - \mu^{o,nb}_{L} \quad (22)$$

Finally, by combining equations (8) and (20) – (22) one obtains

$$\log \beta_{nb}(PbL^{2+}) = \log \beta_{nb}(SrL^{2+}) + \log K_{ex}(Pb^{2+}, SrL^{2+}) - \log K_{ex}(Pb^{2+}, Sr^{2+}) \quad (23)$$

Using the constants $\log K_{ex}(Pb^{2+}, Sr^{2+})$ and $\log K_{ex}$ (Pb^{2+}, SrL^{2+}) given above, the value $\log \beta_{nb}$ (SrL^{2+}) = 11.5 (L = 18-crown-6) [10] and applying equation (23), we get the stability constant of the 18-crown-6 – lead complex in water saturated nitrobenzene at 25 °C:

$$\log \beta_{nb} (PbL^{2+}) = 12.9 \quad (24)$$

The stability constant of the 18-crown-6 complex of lead in water is $\log \beta_{aq}$ (PbL^{2+}) = 4.27 [11]. Since the formation of an arbitrary complex is assumed to be accompanied by competition for the respective cation between solvent molecules and ligand bonding sites, the previous results are obviously a consequence of the decrease in basicity and solvating power of the medium as one proceeds from the aqueous phase to the nitrobenzene one.

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