

Short communication

Synergistic Extraction of Some Univalent Cations into Nitrobenzene by Using Sodium Dicarbolylcobaltate and Dibenzo-21-crown-7

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Abstract

From extraction experiments and γ -activity measurements, the exchange extraction constants corresponding to the general equilibrium $M^+(aq) + 1 \cdot Na^+(nb) \rightleftharpoons 1 \cdot M^+(nb) + Na^+(aq)$ taking place in the two-phase water–nitrobenzene system ($M^+ = Li^+, H^+, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+$; $1 =$ dibenzo-21-crown-7; $aq =$ aqueous phase, $nb =$ nitrobenzene phase) were evaluated. Furthermore, the stability constants of the $1 \cdot M^+$ complexes in water – saturated nitrobenzene were calculated; they were found to increase in the series of $H^+ < Ag^+ < Li^+ < Cs^+ < K^+, Rb^+ < NH_4^+ < Tl^+$.

Keywords: Univalent cations, sodium dicarbolylcobaltate, dibenzo-21-crown-7, complexation, water–nitrobenzene system, extraction and stability constants

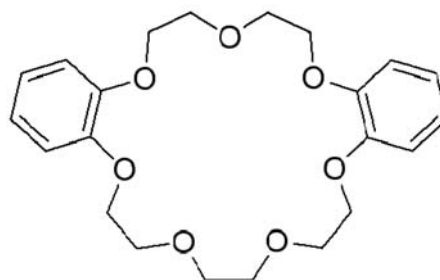
1. Introduction

In 1967, Pedersen published his first papers^{1,2} dealing with cyclic polyether compounds with oxyethylene groups $-CH_2-CH_2-O-$, that are called crowns owing to their structure. These electroneutral compounds form relatively stable complexes in nonaqueous solvents, especially with alkali and alkaline-earth metal cations, the cations being placed in the ligand cavities. The ratio of the size of the crown ligand cavity to the ion radius of the central cation is a decisive or at least an important factor in the stability of the complex species formed.³ It is the complexing properties of the crowns that are due to the rapid development of the chemistry of these cyclic polyethers that we have witnessed in recent decades. At this point it should be noted that several reviews have covered many aspects of their chemistry.^{3–6}

The dicarbolylcobaltate anion⁷ and some of its halogen derivatives are very useful reagents for the extraction of various metal cations (especially Cs^+ , Sr^{2+} , Ba^{2+} , Eu^{3+} and Am^{3+}) from aqueous solutions into a polar organic phase, both under laboratory conditions for purely

theoretical or analytical purposes,^{8–29} and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.^{30,31}

In the current work, the stability constant of the cationic complex species $1 \cdot M^+$, where $M^+ = Li^+, H^+, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+$ and 1 is dibenzo-21-crown-7 (see Scheme 1), in nitrobenzene saturated with water were determined.



Scheme 1. Structural formula of dibenzo-21-crown-7 (abbrev. 1).

2. Experimental

Dibenzo-21-crown-7 (abbrev. **1**) was supplied by Fluka. Cesium dicarbollylcobaltate, CsDCC, was synthesized by the method published by Hawthorne et al.³² A nitrobenzene solution of hydrogen dicarbollylcobaltate (HDCC)⁷ was prepared from CsDCC by the procedure described elsewhere.³³ The equilibration of the nitrobenzene solution of HDCC with stoichiometric NaOH yielded the corresponding NaDCC solution in nitrobenzene. The radionuclide ²²Na⁺ (DuPont, Belgium) was of standard radiochemical purity. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity.

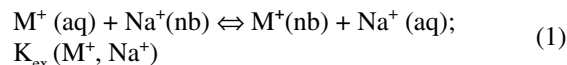
The extraction experiments were carried out in 10 mL glass test-tubes with polyethylene stoppers: 2 mL of an aqueous solution of MNO₃ (M⁺ = Li⁺, H⁺, NH₄⁺, Ag⁺, K⁺, Rb⁺, Tl⁺, Cs⁺) of the concentration in the range from 5 × 10⁻³ to 5 × 10⁻² mol/L and microamounts of ²²Na⁺ were added to 2 mL of a nitrobenzene solution of **1** and NaDCC, whose initial concentrations varied also from 5 × 10⁻³ to 5 × 10⁻² mol/L (in all experiments, the initial concentration of **1** in nitrobenzene, C₁^{in,nb}, was equal to the initial concentration of NaDCC in this medium, C_{NaDCC}^{in,nb}). The test-tubes filled with the solutions were shaken for 2 h at 25 ± 1 °C, using a laboratory shaker. Under these conditions, the equilibria in the systems under study were established after approximately 20 min of shaking. Then the phases were separated by centrifugation. Afterwards, 1 mL samples were taken from each phase and their γ-activities were measured by means of a well-type NaI(Tl) scintillation detector connected to a γ-analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of sodium, D_{Na}, were determined as the ratios of the corresponding measured radioactivities of ²²Na⁺ in the nitrobenzene and aqueous samples.

3. Results and Discussion

Regarding the results of previous papers,^{7,34,35} the two-phase water–MNO₃ (M⁺ = Li⁺, H⁺, NH₄⁺, Ag⁺, K⁺,

Rb⁺, Tl⁺, Cs⁺)–nitrobenzene–sodium dicarbollylcobaltate (NaDCC) extraction system can be described by the following equilibrium

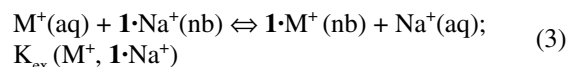


with the corresponding exchange extraction constant K_{ex}(M⁺, Na⁺); aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively. For the constant K_{ex}(M⁺, Na⁺) one can write^{34,35}

$$\log K_{ex}(M^+, Na^+) = \log K_{M^+}^i - \log K_{Na^+}^i \quad (2)$$

where K_{M⁺}ⁱ and K_{Na⁺}ⁱ are the individual extraction constants for M⁺ and Na⁺, respectively, in the water–nitrobenzene system.^{34,35} Knowing the values log K_{M⁺}ⁱ (M⁺ = Li⁺, H⁺, NH₄⁺, Ag⁺, K⁺, Rb⁺, Tl⁺, Cs⁺),^{34,35} the single exchange extraction constants K_{ex}(M⁺, Na⁺) were simply calculated on the basis of Eq. (2). The corresponding data are given in Table 1.

In terms of previous results,^{7,36–40} the two-phase water–MNO₃ (M⁺ = Li⁺, H⁺, NH₄⁺, Ag⁺, K⁺, Rb⁺, Tl⁺, Cs⁺)–nitrobenzene–**1** (**1** = dibenzo-21-crown-7)–NaDCC extraction system (see Experimental), chosen for determination of the stability constant of the complex **1**·M⁺ in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium



with the general equilibrium constant K_{ex}(M⁺, **1**·Na⁺):

$$K_{ex}(M^+, \mathbf{1} \cdot Na^+) = \frac{[\mathbf{1} \cdot M^+]_{nb} [Na^+]_{aq}}{[M^+]_{aq} [\mathbf{1} \cdot Na^+]_{nb}} \quad (4)$$

It is necessary to emphasize that **1** is a very hydrophobic ligand, practically present in the nitrobenzene phase only, where this ligand forms the relatively stable complexes **1**·M⁺ and **1**·Na⁺ with the univalent cations mentioned. Taking into account the conditions of electroneutrality in

Table 1. Equilibrium data for the M⁺ and **1**·M⁺ cations in the two-phase water–nitrobenzene extraction system at 25 °C (M⁺ = Li⁺, Na⁺, H⁺, NH₄⁺, Ag⁺, K⁺, Rb⁺, Tl⁺, Cs⁺; **1** = dibenzo-21-crown-7; for the meaning of the constants see text).

Quantity	M ⁺								
	Li ⁺	Na ⁺	H ⁺	NH ₄ ⁺	Ag ⁺	K ⁺	Rb ⁺	Tl ⁺	Cs ⁺
log K _{M⁺} ^a	-7.6	-6.0	-5.7	-4.7	-4.5 ^b	-4.1	-3.4	-3.4 ^b	-2.7
log K _{ex} (M ⁺ , Na ⁺) ^c	-0.7	–	0.3	1.3	1.5	1.9	2.6	2.6	3.3
log K _{ex} (M ⁺ , 1 ·Na ⁺) ^d	-0.4	–	-0.8	2.6	1.2	3.1	3.8	4.2	3.9
log β _{nb} (1 ·M ⁺) ^e	6.0	5.7 ^f	4.6	7.0	5.4	6.9	6.9	7.3	6.3

^a Ref. 34. ^b Ref. 35. ^c Calculated from Eq. (2) using data from Refs 34 and 35. ^d Calculated from Eq. (5). ^e Calculated from Eq. (6) using data from Refs 34, 35 and 41. ^f Ref. 41.

the organic and aqueous phases of the system under study, the mass balances of the considered univalent cations at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium ratio of sodium, $D_{\text{Na}} = [\mathbf{1}\cdot\text{Na}^+]_{\text{nb}} / [\text{Na}^+]_{\text{aq}}$, combined with Eq. (4), we gain the final expression for $K_{\text{ex}}(\text{M}^+, \mathbf{1}\cdot\text{Na}^+)$ in the form

$$K_{\text{ex}}(\text{M}^+, \mathbf{1}\cdot\text{Na}^+) = \frac{1}{D_{\text{Na}}} \frac{C_{\text{NaDCC}}^{\text{in,nb}}}{(1 + D_{\text{Na}}) C_{\text{MNO}_3}^{\text{in,aq}} - C_{\text{NaDCC}}^{\text{in,nb}}} \quad (5)$$

where $C_{\text{MNO}_3}^{\text{in,aq}}$ ($\text{M}^+ = \text{Li}^+, \text{H}^+, \text{NH}_4^+, \text{Ag}^+, \text{K}^+, \text{Rb}^+, \text{Tl}^+, \text{Cs}^+$) is the initial concentration of MNO_3 in the aqueous phase and $C_{\text{NaDCC}}^{\text{in,nb}}$ denotes the initial concentration of NaDCC in the nitrobenzene phase of the system under consideration.

In this study, from the extraction experiments and γ -activity measurements (see Experimental) by means of Eq. (5), the logarithms of the constants $K_{\text{ex}}(\text{M}^+, \mathbf{1}\cdot\text{Na}^+)$ ($\text{M}^+ = \text{Li}^+, \text{H}^+, \text{NH}_4^+, \text{Ag}^+, \text{K}^+, \text{Rb}^+, \text{Tl}^+, \text{Cs}^+$) were determined, as given in Table 1.

Moreover, with respect to References 36–40, for the extraction constants $K_{\text{ex}}(\text{M}^+, \text{Na}^+)$ and $K_{\text{ex}}(\text{M}^+, \mathbf{1}\cdot\text{Na}^+)$ defined above, as well as for the stability constants of the complexes $\mathbf{1}\cdot\text{M}^+$ and $\mathbf{1}\cdot\text{Na}^+$ in nitrobenzene saturated with water, denoted by $\beta_{\text{nb}}(\mathbf{1}\cdot\text{M}^+)$ and $\beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+)$, respectively, one gets

$$\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{M}^+) = \log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+) + \log K_{\text{ex}}(\text{M}^+, \mathbf{1}\cdot\text{Na}^+) - \log K_{\text{ex}}(\text{M}^+, \text{Na}^+) \quad (6)$$

Finally, using the constants $\log K_{\text{ex}}(\text{M}^+, \text{Na}^+)$ and $\log K_{\text{ex}}(\text{M}^+, \mathbf{1}\cdot\text{Na}^+)$ given in Table 1, the value $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+) = 5.7$,⁴¹ determined from the distribution of sodium picrate in the water–nitrobenzene system containing the ligand **1**, and applying Eq. (6), we obtain the stability constants of the complexes $\mathbf{1}\cdot\text{M}^+$ ($\text{M}^+ = \text{Li}^+, \text{H}^+, \text{NH}_4^+, \text{Ag}^+, \text{K}^+, \text{Rb}^+, \text{Tl}^+, \text{Cs}^+$) in water-saturated nitrobenzene. These data are also listed in Table 1. Thus, the $\beta_{\text{nb}}(\mathbf{1}\cdot\text{M}^+)$ values from this table indicate that the stability of the complex species $\mathbf{1}\cdot\text{M}^+$ in nitrobenzene saturated with water increa-

ses in the following cation order: $\text{H}^+ < \text{Ag}^+ < \text{Na}^+ < \text{Li}^+ < \text{Cs}^+ < \text{K}^+, \text{Rb}^+ < \text{NH}_4^+ < \text{Tl}^+$.

In conclusion, Table 2 summarizes the stability constants of the cationic complexes ML^+ , where $\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$, with eight crown ligands L, denoted by the symbols 18C6, B18C6, DB18C6, DCH18C6, DB21C7, DB24C8, DCH24C8 and DB30C10, in nitrobenzene saturated with water at 25 °C. In this context it is necessary to emphasize that the most stable complexes ML^+ are mostly the NaL^+ or KL^+ cationic species, respectively, for the crown ligands L presented in Table 2.

4. Acknowledgements

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Table 2. Stability constants of the complexes ML^+ [$\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$; L = 18-crown-6 (18C6), benzo-18-crown-6 (B18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 (DCH18C6), dibenzo-21-crown-7 (DB21C7), dibenzo-24-crown-8 (DB24C8), dicyclohexano-24-crown-8 (DCH24C8), dibenzo-30-crown-10 (DB30C10)] in nitrobenzene saturated with water at 25 °C.

L	$\log \beta_{\text{nb}}(\text{LiL}^+)$	$\log \beta_{\text{nb}}(\text{NaL}^+)$	$\log \beta_{\text{nb}}(\text{KL}^+)$	$\log \beta_{\text{nb}}(\text{RbL}^+)$	$\log \beta_{\text{nb}}(\text{CsL}^+)$	Ref.
18C6	7.9	8.0	9.5	8.1	7.0	39
B18C6	7.0	7.4	7.6	6.3	5.5	42
DB18C6	4.5	7.1	6.9	5.8	4.9	36
DCH18C6	8.1	7.8	8.2	7.5	6.3	43
DB21C7	6.0	5.7 ^a	6.9	6.9	6.3	This work
DB24C8	5.5	7.7	6.6	6.3	5.4 ^b	44
DCH24C8	8.0	8.4	7.7	6.7	6.4	45
DB30C10	6.9	6.5	7.3	6.6	5.9	46

^a Ref. 41. ^b Ref. 47.

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Povzetek

Z ekstrakcije in meritvami γ -aktivnosti smo določili ravnotežne konstante ekstrakcije za ravnotežja $M^+(aq) + 1 \cdot Na^+(nb) \rightleftharpoons 1 \cdot M^+(nb) + Na^+(aq)$ v dvofaznem sistemu voda-nitrobenzen ($M^+ = Li^+, H^+, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+$; $1 =$ dibenzo-21-21-crown-7; aq = vodna faza, nb = nitrobenzen). Ugotovili smo, da konstante stabilnosti $1 \cdot M^+$ kompleksov v vodi, nasičeni z nitrobenzenom, naraščajo v zaporedju $H^+ < Ag^+ < Li^+ < Cs^+ < K^+, Rb^+ < NH_4^+ < Tl^+$.