
HYDRATION OF COMPLEXES OF SOME UNIVALENT CATIONS WITH POLYETHYLENE GLYCOL LIGANDS IN NITROBENZENE SATURATED WITH WATER

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The hydration numbers of the complexes ML^+ formed by some univalent cations ($M^+ = Li^+$, Na^+ , NH_4^+ , K^+ , Rb^+ and Cs^+) and polyethylene glycol ligands ($L = PEG\ 200$, $PEG\ 300$ and $PEG\ 400$) in nitrobenzene saturated with water were determined. The highest differences between the hydration numbers of the cations M^+ and the complexes ML^+ were found in the systems with the Na^+ cation.

In our previous paper¹, the extraction separations of dipicrylamines of alkali metal cations and NH_4^+ in the presence of some acyclic oxyethylene polyethers were studied in the two-phase water-nitrobenzene system.

Škarda and coworkers^{2,3} proved on the basis of the conductivity measurements that the salts of the type $M^+[(1,2-C_2B_9H_{11})_2Co]^-$, where M^+ is an alkali metal cation, Tl^+ , or $N(C_2H_5)_4^+$, and the other ion is a hydrophobic dicarbollylcobaltate anion (abbrev. B^-), are fully dissociated in nitrobenzene saturated with water. In this medium, they determined the hydration numbers of the mentioned cations.

The aim of the present communication is to evaluate the hydration numbers of the complex particles ML^+ ($M^+ = Li^+$, Na^+ , NH_4^+ , K^+ , Rb^+ , Cs^+ ; $L = PEG\ 200$, $PEG\ 300$, $PEG\ 400$) in nitrobenzene saturated with water.

EXPERIMENTAL

Polyethylene glycols PEG 200, PEG 300 and PEG 400 (Koch-Light) with the average relative molecular weight 200, 300 and 400, respectively, were employed without any further purification. Nitrobenzene and all other chemicals used of analytical grade purity were supplied by Lachema, Brno, Czechoslovakia.

The synthesis of cesium dicarbollylcobaltate, CsB, was described elsewhere⁴. In order to obtain the solution of HB in nitrobenzene, the solution of CsB in this medium ($0.2\ mol\ l^{-1}$) was twice equilibrated with equal volumes of 15% (v/v) propanol in diluted H_2SO_4 of the concentration of about $1\ mol\ l^{-1}$. H_2SO_4 and propanol were removed from the organic phase by

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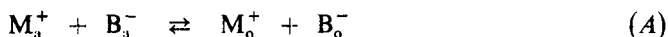
a ten-fold equilibration with the solution of H_2SO_4 in distilled water (about 1 mol l^{-1}) of an equal volume, followed by two equilibrations with distilled water. The concentration of HB in the nitrobenzene solution was determined by neutralization titration (NaOH, bromocresol green) after a ten-fold dilution with ethanol or acetone. The equilibration of the nitrobenzene solution of HB with stoichiometric MOH ($\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+$ and Cs^+), which was dissolved in the aqueous solution of MNO_3 (0.5 mol l^{-1}), yields a MB solution in nitrobenzene the concentration of which is equal to the initial concentration of HB. A NH_4B solution in nitrobenzene was prepared by a multiple equilibration of the nitrobenzene solution of HB with the aqueous solution of NH_4NO_3 (about 0.5 mol l^{-1}) till the absolute removal of the ions H^+ from the nitrobenzene phase.

15 ml probes with polyethylene stoppers were used in the extraction experiments concerning the two-phase water–nitrobenzene– $\text{MB}(\text{NH}_4\text{B})$ –L systems. The volume of each phase was 5 ml, the solutions were shaken for an hour (under the conditions used, 15 min is sufficient for the establishment of equilibrium) using a laboratory shaker ZK III (Chirana, Czechoslovakia) at a temperature of $25 \pm 2^\circ\text{C}$. After centrifugation, 3 ml of the nitrobenzene phase were always taken to determine the equilibrium concentration of water in the organic phase.

The equilibrium concentrations of water in the nitrobenzene extracts were determined by biamperometric titration with the Fischer agent (Lachema, Brno, Czechoslovakia) using the "Dead-Stop Titrimeter" OP 402 (Radelkis, Budapest, Hungary).

RESULTS AND DISCUSSION

With regard to the results of previous papers¹⁻³ the two-phase water–nitrobenzene– MB –L extraction system chosen for determination of the hydration numbers h_{ML^+} of the complex particles ML_o^+ in the nitrobenzene phase can be described by the equilibria



to which the following equilibrium constants

$$K_{\text{ex}}(\text{M}^+, \text{B}^-) = [\text{M}^+]_o [\text{B}^-]_o / [\text{M}^+]_a [\text{B}^-]_a \quad (1)$$

$$\beta_o(\text{ML}^+) = [\text{ML}^+]_o / [\text{M}^+]_o [\text{L}]_o \quad (2)$$

$$K_{\text{D}} = [\text{L}]_o / [\text{L}]_a \quad (3)$$

correspond. The indices a and o denote the presence of the particles in the aqueous and organic phases, respectively.

As the hydrophobic dicarbollyl-cobaltate anion B^- is not hydrated in the nitrobenzene phase^{2,3}, the equilibrium concentration of water in this phase $[\text{H}_2\text{O}]_o$, can be written in the form

$$[\text{H}_2\text{O}]_o = h_{\text{M}^+} [\text{M}^+]_o + h_{\text{ML}^+} [\text{ML}^+]_o + h_{\text{L}} [\text{L}]_o + [\text{H}_2\text{O}]_s, \quad (4)$$

where h_{M^+} , h_{ML^+} and h_L are the hydration numbers of the particles M^+ , ML^+ and L in the organic phase, respectively, and $[H_2O]_s$ denotes the equilibrium molar concentration of "freely" dissolved water in nitrobenzene ($[H_2O]_s = 0.16 \text{ mol l}^{-1}$ at a temperature of 25°C – see ref.³).

In the present paper it was experimentally found that the presence of the polyethylene glycol ligand L ($L = \text{PEG 200, PEG 300, PEG 400}$) in the two-phase water–nitrobenzene– L extraction system in the concentration range of $0.01 - 1.20 \text{ mol l}^{-1}$ in the initial aqueous phase (at the equal volumes of the aqueous and organic phases) does not show within the limits of experimental errors any effect on the equilibrium concentration of water in the nitrobenzene phase; in any case this water concentration in the organic phase attains a value of 0.16 mol l^{-1} . This fact is apparently due to low values of $K_D \approx 10^{-3}$ (ref.¹) and hence to extremely low equilibrium concentrations $[L]_o$ in the systems under study. For these reasons the product $h_L[L]_o$ is negligible in comparison with the other terms of the right-hand side of Eq. (4), so that this equation has the form

$$[H_2O]_o = h_{M^+}[M^+]_o + h_{ML^+}[ML^+]_o + [H_2O]_s. \quad (5)$$

If we denote the ratio $[ML^+]_o/[M^+]_o$ by the symbol k , i.e.

$$[ML^+]_o/[M^+]_o = \beta_o(ML^+) [L]_o = k, \quad (6)$$

then by simple rearrangements of the relations (7)–(10) expressing the conditions of electroneutrality of the organic and aqueous phases

$$[M^+]_o + [ML^+]_o = [B^-]_o. \quad (7)$$

$$[M^+]_a = [B^-]_a, \quad (8)$$

the mass balance of the dicarbollylcobaltate salt MB at the equal volumes of the aqueous and organic phases

$$c_{MB} = [M^+]_a + [M^+]_o + [ML^+]_o = [B^-]_a + [B^-]_o. \quad (9)$$

and the mass balance of the ligand L

$$c_L = (1 + K_D^{-1}) [L]_o + [ML^+]_o. \quad (10)$$

and with regard to Eqs (1)–(3) we obtain the following relations

$$[M^+]_o = c_{MB}/\{k + 1 + [(k + 1)/K_{ex}(M^+, B^-)]^{1/2}\} \quad (11)$$

$$[M^+]_a = [M^+]_o [(k + 1)/K_{ex}(M^+, B^-)]^{1/2} \quad (12)$$

$$c_L = k(1 + K_D^{-1})/\beta_o(ML^+) + kc_{MB}/\{k + 1 + [(k + 1)/K_{ex}(M^+, B^-)]^{1/2}\}. \quad (13)$$

The value of c_L resulting from Eq. (13) can be regarded as the initial concentration of the polyethylene glycol ligand L in the aqueous phase, required for the ratio $[ML^+]_o/[M^+]_o$ to be equal to the value k .

Assuming that the hydration numbers h_{M^+} and h_{ML^+} permit mutual comparison and $k \geq 100$, then the product $h_{M^+}[M^+]_o$ in Eq. (5) may be neglected with regard to the sum $h_{ML^+}[ML^+]_o + [H_2O]_s$.

As the inequality $K_{ex}(M^+, B^-) > 100$ holds (its validity results from refs⁵⁻⁷), then for the chosen $k = 100$ the inequality

$$[M^+]_o, [M^+]_a < c_{MB}/100 \quad (14)$$

follows from Eqs (11) and (12).

Finally, by summing up the facts given above and assuming that the initial concentration c_L in the aqueous phase fulfils the following inequality

$$\begin{aligned} c_L &\geq 100(1 + K_D^{-1})/\beta_o(ML^+) + 100c_{MB}/\{101 + [101/K_{ex}(M^+, B^-)]^{1/2}\} \approx \\ &\approx 100(1 + K_D^{-1})/\beta_o(ML^+) + c_{MB}, \end{aligned} \quad (15)$$

then Eq. (5) can be rewritten more simply as

$$[H_2O]_o = h_{ML^+}[ML^+]_o + [H_2O]_s, \quad (16)$$

where $[ML^+]_o \approx c_{MB}$ is aggravated by an error of less than 2% as follows from Eqs (9) and (14).

The example of graphic determination of h_{ML^+} by means of Eq. (16) is shown in Fig. 1. All the determined values h_{ML^+} are summarized in Table I together with the values of h_{M^+} obtained by a method published in ref.². It is necessary to note that these h_{M^+} values are in good agreement with previous results^{2,8,9}.

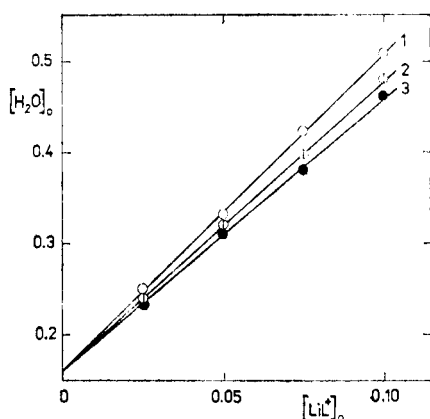


FIG. 1
Equilibrium concentration of water in the organic phase as a function of the $[LiL^+]_o$ concentration for the system water-nitrobenzene-polyethylene glycol- LiL^+ -dicarbollycobaltate: 1 PEG 200; 2 PEG 300; 3 PEG 400

By comparing the values h_{M^+} with h_{ML^+} (see Table I) it follows that the presence of the polyethylene glycol ligand L (PEG 200, PEG 300, PEG 400) in all the systems under study (with the exception of those containing Cs^+) decreases the equilibrium water content in the nitrobenzene phase. In the case of Cs^+ it is very probable that an expected analogous decrease of the equilibrium concentration of water in the organic phase exceeds the possibility of experimental determination.

The decrease of the equilibrium concentration of water in the nitrobenzene extracts of alkali metal dipicrylamines by means of cyclic polyether ligands was also proved by Iwachido et al.¹⁰. However, it is remarkable that the hydration numbers h_{ML^+} ($M^+ = K^+, Rb^+, Cs^+$ and L is the mentioned cyclic polyether ligand), varying from 0.1 to 0.4 (ref.¹⁰), are substantially lower than the values of the hydration numbers h_{ML^+} of the complexes formed by K^+, Rb^+ or Cs^+ and the polyethylene glycol ligands, evaluated here (see Table I). On the other hand, it was found¹⁰ that the hydration numbers h_{NaL^+} for the majority of the cyclic polyether ligands

TABLE I

Hydration numbers of some univalent cations and the complexes of these cations with polyethylene glycol ligands in nitrobenzene saturated with water

Ligand	Cation					
	Li^+	Na^+	NH_4^+	K^+	Rb^+	Cs^+
—	6.3	3.8	2.0	1.5	0.8	0.5
PEG 200	3.5	1.3	1.1	0.9	0.7	0.5
PEG 300	3.2	1.1	1.0	0.8	0.6	0.5
PEG 400	3.0	1.0	0.9	0.8	0.6	0.5

TABLE II

Logarithms of stability constants of the complexes of some univalent cations with polyethylene glycol ligands in nitrobenzene saturated with water (taken from ref.¹)

Ligand	Cation					
	Li^+	Na^+	NH_4^+	K^+	Rb^+	Cs^+
PEG 200	5.36	5.98	5.06	5.09	4.98	4.86
PEG 300	6.13	6.83	6.09	6.11	5.58	5.04
PEG 400	6.59	7.37	6.67	6.79	6.13	5.49

studied in ref.¹⁰ are in the range of 0.8–1.2 so that these numbers do not differ essentially from the values h_{NaL^+} given in Table I.

Furthermore, it is necessary to emphasize that the relatively highest decrease of the water content bonded in the complex ML_o^+ as compared with the hydrated particle M_o^+ was proved for the systems containing the cation Na^+ (see Table I), which forms the most stable complexes NaL_o^+ in the nitrobenzene phase with the ligands PEG 200, PEG 300 and PEG 400 (see Table II). It is interesting that approximately the same relative water decreases were found in the systems with the particles LiL^+ , NH_4L^+ and KL^+ (for PEG 400 this decrease is about 50% – see Table I), the stabilities of which in nitrobenzene saturated with water are roughly the same (see Table II).

If Cs^+ is not taken into account, then the water content in the nitrobenzene phase decreases with the increasing stability of the complex ML_o^+ for every cation under study. In the case of K^+ and Rb^+ , however, this tendency was not proved experimentally when one proceeds from PEG 300 to PEG 400 as in the other cases because the expected similar changes of the hydration numbers, proved for the remaining alternatives, could not be obviously found out with the experimental techniques used.

Finally, from Table I it follows that with the same ligand in the system, the differences between the successive hydration numbers h_{ML^+} in the sequence Na^+ , NH_4^+ , K^+ , Rb^+ , Cs^+ are 0.1–0.2 only in contrast to the pair Li^+/Na^+ where the values of the differences $h_{\text{LiL}^+} - h_{\text{NaL}^+}$ vary in the range of 2.0–2.2 for the same ligand L. From here and from the previously discussed influence of the polyethylene glycol ligand L on extraction selectivity¹, a relatively close connection between separation selectivity of the pair $\text{M}_1^+/\text{M}_2^+$ in the presence of this ligand and the corresponding difference of the hydration numbers $h_{\text{M}_1\text{L}^+} - h_{\text{M}_2\text{L}^+}$ results, which can be characterized by the fact that a greater difference of the two mentioned hydration numbers implies a greater selectivity of extraction separation. But one must realize that this statement is rather of a qualitative character or at most of a semi-quantitative character because the fact must be taken into account that the accuracy of determination of the values h_{ML^+} (± 0.1) in most cases does not differ significantly from the considered differences of the “neighbouring” hydration numbers given in Table I.

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