CONTRIBUTION TO THE THERMODYNAMICS OF COMPLEXES OF ALKALI METAL CATIONS WITH DIBENZO-18-CROWN-6 IN WATER–NITROBENZENE EXTRACTION SYSTEM

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The stability constants for the ML^+ complex species, where M^+ is an alkali metal cation and L is dibenzo-18-crown-6, in nitrobenzene saturated with water were calculated by employing published equilibrium data. The stability is found to increase in the cation order $Li^+ < Cs^+ < Rb^+ < K^+ < Na^+$. For the NaL^+, KL^+, RbL^+, and CsL^+ complex cations the individual extraction constants in the water–nitrobenzene system were determined; their values increase in the series $Na^+ < K^+ < Rb^+ < Cs^+$.

In 1967, Pedersen published his first paper[1] dealing with cyclic polyether compounds involving oxyethylene groups, —CH_2—CH_2—O— which with regard to their structure were given the name crowns. Electroneutral crown type compounds in non-aqueous solvents form rather stable complexes with alkali metal and alkaline earth cations, the cations being largely located within the ligand cavities. The size of the crown cavity with respect to the ionic radius of the central cation is a significant, if not decisive, factor governing the stability of the complex species in question[2]. It is particularly the complexing properties of crowns that have stimulated the recent rapid progress in their chemistry.

Based on the so-called „Ph_4AsBPh_4 assumption", *i.e.* the assumption that the change of the standard Gibbs energy of transfer from the aqueous phase into an organic phase (*e.g.*, nitrobenzene) is the same for the tetraphenylarsonium cation, Ph_4As^+, and the tetraphenylborate anion[3,4], BPh_4^-, the individual extraction constants have been determined for 22 univalent ions[5] and some dicarbolylcobaltate(III) anions[6] in the water–nitrobenzene system.

The aim of the present work was to determine the stability constants of complex ML^+ cations (M^+ stands for alkali metal cations, L is dibenzo-18-crown-6) in nitrobenzene saturated with water and their individual extraction constants in the water–nitrobenzene system, along with the corresponding changes in the standard Gibbs energies of transfer of the complex ions from the aqueous into the nitrobenzene phase in the equilibrium system.

THEORETICAL

Suppose that in the water–nitrobenzene two-phase system, the univalent cation M^+ and the electroneutral ligand L form a complex cation ML^+ both in the aqueous (aq) and the nitrobenzene (nb) phase. The system is then characterized by the stability constants $\beta_{aq}(ML^+)$ and $\beta_{nb}(ML^+)$ and the equilibrium distribution constant of the ligand in the two phases, $K_D(L)$:

$$M^+(aq) + L(aq) \rightleftharpoons ML^+(aq)\,; \quad \beta_{aq}(ML^+) \tag{A}$$

$$M^+(nb) + L(nb) \rightleftharpoons ML^+(nb)\,; \quad \beta_{nb}(ML^+) \tag{B}$$

$$L(aq) \rightleftharpoons L(nb)\,; \quad K_D(L) \tag{C}$$

The equilibrium constants then satisfy the relations

$$RT\ln \beta_{aq}(ML^+) = \mu^{0,aq}_{M^+} + \mu^{0,aq}_{L} - \mu^{0,aq}_{ML^+} \tag{1}$$

$$RT\ln \beta_{nb}(ML^+) = \mu^{0,nb}_{M^+} + \mu^{0,nb}_{L} - \mu^{0,nb}_{ML^+} \tag{2}$$

$$RT\ln K_D(L) = \mu^{0,aq}_{L} - \mu^{0,nb}_{L}\,, \tag{3}$$

where μ^0-s are the standard chemical potentials of the various species in the two phases concerned.

The changes in the standard Gibbs energies corresponding to the transfer of the M^+ and ML^+ ions from the aqueous into the nitrobenzene phase,

$$M^+(aq) \rightleftharpoons M^+(nb) \tag{D}$$

and

$$ML^+(aq) \rightleftharpoons ML^+(nb)\,, \tag{E}$$

are given by definitions

$$\Delta G^{0,tr}_{M^+} = \mu^{0,nb}_{M^+} - \mu^{0,aq}_{M^+} \tag{4}$$

and

$$\Delta G^{0,tr}_{ML^+} = \mu^{0,nb}_{ML^+} - \mu^{0,aq}_{ML^+}\,. \tag{5}$$

By combining Eqs (1)–(5) we obtain the following equation

$$\Delta G^{0,tr}_{M^+} = \Delta G^{0,tr}_{ML^+} + RT\ln\left[\beta_{nb}(ML^+)\,K_D(L)/\beta_{aq}(ML^+)\right] \tag{6}$$

which relates the thermodynamic parameters $\Delta G^{0,tr}_{M^+}$, $\Delta G^{0,tr}_{ML^+}$ characterizing quantitatively the transfer of the M^+ and ML^+ cations from the aqueous into the nitrobenzene phase under standard conditions, with the equilibrium constants $\beta_{aq}(ML^+)$,

$\beta_{nb}(ML^+)$, and $K_D(L)$ pertaining to the equilibria (*A*)–(*C*), respectively. Clearly, any one of the five quantities can be calculated from Eq. (*6*) if the remaining four are known.

The individual extraction constant $K^i_{M^+}$ for the cation M^+ in the water–nitrobenzene system is defined by the relation[5]

$$\Delta G^{0,tr}_{M^+} = -RT \ln K^i_{M^+} . \tag{7}$$

Analogously, the individual extraction constant $K^i_{ML^+}$ for the ML^+ complex in the extraction system under study can be defined by

$$\Delta G^{0,tr}_{ML^+} = -RT \ln K^i_{ML^+} , \tag{8}$$

which combined with Eqs (*6*), (*7*) gives

$$K^i_{ML^+} = K^i_{M^+} \beta_{nb}(ML^+) K_D(L)/\beta_{aq}(ML^+) . \tag{9}$$

In this manner the $K^i_{ML^+}$ constant can be evaluated based on the known $K^i_{M^+}$, $\beta_{nb}(ML^+)$, $\beta_{aq}(ML^+)$, and $K_D(L)$ values.

Danesi and coworkers[7] have determined the extraction constants $K_{ex}(ML^+, A^-)$ corresponding to the chemical equilibria

$$M^+(aq) + A^-(aq) + L(nb) \rightleftharpoons ML^+(nb) + A^-(nb) , \tag{F}$$

where M^+ is an alkali metal cation (Li^+, Na^+, K^+, Rb^+, Cs^+), A^- is the picrate anion, and L is the dibenzo-18-crown-6 ligand. Since the individual extraction constants in the water–nitrobenzene system are known[5] both for the alkali metal cations and for the picrate anion, the $K_{ex}(M^+, A^-)$ constants which describe quantitatively the distribution of alkali picrates in the system in question according to

$$M^+(aq) + A^-(aq) \rightleftharpoons M^+(nb) + A^-(nb) \tag{G}$$

can readily be evaluated from the equation

$$\log K_{ex}(M^+, A^-) = \log K^i_{M^+} + \log K^i_{A^-} , \tag{10}$$

in which $K^i_{M^+}$ and $K^i_{A^-}$ are the individual extraction constants of the alkali metal cation and of the picrate anion ($\log K^i_{A^-} = 0{\cdot}8$, ref.[5]), respectively, in the water–nitrobenzene system. Knowing the $K_{ex}(ML^+, A^-)$ and $K_{ex}(M^+, A^-)$ values, the stability constants for the ML^+ species in the nitrobenzene phase (equilibrium (*B*)) can be evaluated simply as their ratio,

$$\beta_{nb}(ML^+) = K_{ex}(ML^+, A^-)/K_{ex}(M^+, A^-)\,. \qquad (11)$$

RESULTS AND DISCUSSION

The data obtained are summarized in Table I. As the values of the $\beta_{nb}(ML^+)$ constants (Eq. (*11*)) indicate, the stability of the complex cation in nitrobenzene saturated with water increases in the M^+ series of $Li^+ < Cs^+ < Rb^+ < K^+ < Na^+$. In the aqueous medium, the stability of the ML^+ complex is highest for $M^+ = K^+$, the series being $Li^+ < Cs^+ < Rb^+ < Na^+ < K^+$ (the $\beta_{aq}(ML^+)$ values in Table I, ref.[9]). Since the solvent molecules always compete with the ligand bonding sites for the central cation, the primary reason why the $\beta(ML^+)$ constants in nitrobenzene saturated with water are several orders of magnitude higher than in aqueous medium is to be sought in the higher basicity of water as compared with nitrobenzene. As

TABLE I

Equilibrium data for the two-phase extraction system water–nitrobenzene at 25°C. Symbols: M^+ alkali metal cation, A^- picrate anion, L dibenzo-18-crown-6 ligand; for the meaning of the constants see text

Quantity	Value for M^+ =				
	Li^+	Na^+	K^+	Rb^+	Cs^+
log $K^{i}_{M^+}$[a]	−6·7	− 6·0	− 4·1	− 3·4	− 2·7
$\Delta G^{0,tr}_{M^+}$[b], kJ mol^{-1}	38·2	34·2	23·4	19·4	15·4
log $K_{ex}(M^+, A^-)$[c]	−5·9	− 5·2	− 3·3	− 2·6	− 1·9
log $K_{ex}(ML^+, A^-)$[d]	−1·5	1·9	3·6	3·2	3·0
log $\beta_{nb}(ML^+)$[e]	4·5	7·1	6·9	5·8	4·9
log $\beta_{aq}(ML^+)$[f]	<0	1·2	1·7	1·1	0·8
log $K^{i}_{ML^+}$[g]	—	4·3	5·5	5·7	5·8
$\Delta G^{0,tr}_{ML^+}$[h], kJ mol^{-1}	—	−24·5	−31·4	−32·5	−33·1
h_{M^+}[j]	6·5	3·9	1·5	0·8	0·5
h_{ML^+}[k]	2·9	1·2	0·1	0·1	0·1

[a] Ref.[5]; [b] calculated from Eq. (*7*) using data of ref.[5]; [c] calculated based on Eq. (*10*) using data of ref.[5]; [d] average values of ref.[7] to one decimal point; [e] calculated from Eq. (*11*) using data of refs[5,7]; [f] average values of ref.[9]; to one decimal point; [g] calculated from Eq. (*9*) using data of refs[5,7,9,11]; [h] calculated from Eq. (*6*) or (*8*) using data of refs[5,7,9,11]; [j] ref.[10]; [k] ref.[12].

shown in Fig. 1, the dependence of $\log \beta_{nb}(ML^+)$ on the crystallographic radius of the cation M^+ displays a maximum for $M^+ = Na^+$. The occurrence of such maxima seems to be a general feature of the alkali metal complex formation with cyclic as well as acyclic polyethers in organic solvents[8].

Škarda, Rais and Kyrš have proved[10] that alkali metal cations in the equilibrium nitrobenzene phase of the water–nitrobenzene system are present in the hydrated state. This is true also of complex species constituted by alkali metal or alkaline earth cations and electroneutral ionophores of the crown or cryptand type, and even of the crown or cryptand ligands themselves[11,12]. The average number of water molecules bonded to a species i in the nitrobenzene phase is expressed quantitatively by the hydration number h_i (Table I). For complex species constituted by alkali metal cations and crown type ligands the hydration numbers in the nitrobenzene phase are considerably lower than for the alkali metal cations themselves[10,12] (Table I only includes data for the particular case of dibenzo-18-crown-6). This indicates that these cyclic polyethers (similarly as cryptand type ligands) displace a fraction of the co-extracted water from the hydration shell of the alkali metal cation.

Using the requisite data published in papers[5,7,9,11] and equation (9) ($\log K_D(L) = 4{\cdot}4$ for dibenzo-18-crown-6, ref.[11]), the logarithms of the individual extraction constants for the ML^+ complex cation in the water–nitrobenzene system at 25°C were evaluated as given in Table I; they are found to increase in the order $Na^+ < K^+ < Rb^+ < Cs^+$, *i.e.* in the order of increasing crystallographic radii of the alkali metal cations. The corresponding $\Delta G^{0,tr}_{ML^+}$ values are also given in Table I. For Li^+ the above quantities could not be evaluated because of a lack of a sufficiently accurate value of the $\beta_{aq}(LiL^+)$ constant.

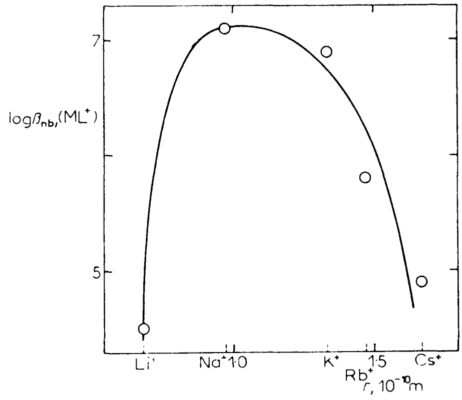

FIG. 1

Dependence of the logarithm of the stability constant of the ML^+ complex cation in the nitrobenzene phase on the crystallographic radius of the alkali metal cation M^+

The individual extraction constant of an ion can be looked upon as a quantitative measure of its hydrophobicity in the two-phase system in question; so, taking into account our data in combination with those of Rais[5], it can be claimed that with respect to their hydrophobic nature in the water–nitrobenzene system, the NaL^+, KL^+, RbL^+, and CsL^+ species (L = dibenzo-18-crown-6) lie between the tetrabutylammoniom cation (TBA^+; $\log K^i_{TBA^+} = 4{\cdot}2$, ref.[5]) and the tetraphenylarsonium cation (Ph_4As; $\log K^i_{Ph_4As^+} = 6{\cdot}3$, ref.[5]).

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