THERMOCHEMISTRY OF 18C6 COMPLEXATION WITH ALKALI, ALKALINE EARTH METAL CATIONS AND AMMONIUM ION

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Abstract

The object of the present study is to examine the factors governing the process of 18C6 complexation in aqueous solution by interpreting of thermodynamic parameters of the reaction in terms of observed selectivity and solvation characteristics under various temperature conditions.

Keywords: alkali, alkaline earth metal, 18C6 complexation, thermodynamic parameters

Introduction

Crown ethers are known as macrocyclic polyethers having the cavity adjusted to bind cations selectively forming complex compounds. Crown ethers were found to form complexes with alkali and alkaline earth metals regarded as nontypical central ions. The distinctive feature of crown ethers is their high conformational flexibility.

Experimental

All the reagents were of chemically pure grade. Crown ether 18C6 synthesized by the Institute of Chemical Reagents and Pure Substances, Moscow, was dried in an exsiccator over P_2O_5. The elemental analysis confirmed the content of carbon to be 99.94% of that calculated according to empirical formula $C_{12}O_6H_{24}$.

The standard salt solutions were made of recrystallized salts. The solutions of NaCl, RbCl and CsCl were made by dissolving the precise weights of the corresponding salts in bidistilled water. Ammonium chloride solution was standartized by the reverse titration with NaOH; $CaCl_2$ – complexonometrically and $SrCl_2$, $BaCl_2$ – gravimetrically in forms of $SrSO_4$ and $BaSO_4$, respectively.

Salt solutions were dosed by weighing. It allowed to exclude the intermediate dilutions and escape the application of the micropipette for the concentrated solutions with known mass content of the salt (mole/kg of the solution).

To determine the heat effects of 18C6 interaction with the corresponding salt (0.003–0.09 mole/l) was loaded into the calorimetric cell with the transfer pipette ($V = 50$ ml).

Concentration terms of the calorimetric experiments were chosen to provide the data at the broad range (30–80%) of the complex yield. These conditions were observed by varying crown ether and salt concentrations. The heat effects of the solutions of 18C6 with NaCl, RbCl, CsCl, NH_4Cl, $CaCl_2$, $SrCl_2$ and $BaCl_2$ were measured at 288.15 (for $CaCl_2$ only), 298.15, 308.15 and 318.15 K. In was assumed that the ionic strength of the solution has almost no effect on thermodynamic values being studied taking into account the low concentrations of the reagents and the same charge in the left and right parts of the equation:

$$M_{aq}^{n+} + L_{aq} \rightleftarrows ML_{aq}^{n+} \tag{I}$$

The heats of dilution of the solutions were calculated as an arithmetic mean of for parallel tests. Experimental heat effect of complexation was calculated as the difference:

$$\Delta H_{exp, i} = \Delta_{mix}H_i - \Delta_{dil}H_i \tag{1}$$

where $\Delta_{mix}H$ – is the heat effect of mixing of the salt and 18C6 solutions; $\Delta_{dil}H$ – is the heat of dilution of the salt solution in water.

The heat effect of the process (I) in the i-th experiment was calculated by the equation:

$$\Delta_r H_i = \Delta H_{exp, i} \frac{C_M^o i}{[ML^{n+}]_i} \tag{2}$$

The values of $\log\beta$ and $\Delta_r H$ were computed on the base of experimental data by minimization of the criterial function F on the target parameters ($\log\beta$ and $\Delta_r H$):

$$F = \sum_{i=1}^{N} w_i(\Delta H_{exp, i} - \Delta H_{cal, i})^2 \tag{3}$$

$$\Delta H_{cal,i} = \frac{1}{N} \frac{[ML^{n+}]_i}{C_M^o i} \sum_{i=1}^{N} \Delta_r H_i \tag{4}$$

where $\Delta H_{cal,\,i}$ – calculated heat effect at the given values of the general concentrations C_M^0, C_L^0 and current $\log\beta$; N – number of the experiments; w – weighing factor.

During the minimization procedure the $\Delta_r H$ values were calculated as an arithmetic mean of $\Delta_r H_i$ estimated by the Eq. (2). The low (0.2–0.6%) values of the $\Delta_r H_i$ relative deviations and their alternating sign confirmed the adequacy of the mathematic model to the experimental data.

The values of $\log\beta$ at 288.15 (for $CaCl_2$), 308.15, 318.15 K were calculated from the $\log\beta$ data for 298.15 K by the equation:

$$\log\beta_T = \log\beta_{298.15} + \frac{\Delta_r H_{298.15}\,(T - 298.15)}{5708.72T} \tag{5}$$

The results of the study are compiled in the Table.

Table 1 Thermochemical characteristics of 18C6 complexation with alkali, alkaline-earth cations and ammonium ion

Cation	T /K	$\log\beta$	$\Delta_r H^o/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_r S^o/\text{J(mol}\cdot\text{K)}^{-1}$	$\Delta_r C_p^o/\text{J(mol}\cdot\text{K)}^{-1}$
Na^+	298.15	0.80±0.20	9.40±0.42	15.4±3.6	
Rb^+	298.15	1.56±0.02	16.09±0.03	24.0±0.4	
	308.15	1.47±0.02	15.30±0.17	21.7±0.7	68±6
	318.15	1.38±0.02	14.70±0.12	19.9±0.5	
Cs^+	298.15	0.95±0.06	16.08±0.04	35.8±1.1	
	308.15	0.89±0.06	15.00±0.15	31.6±1.2	107±24
	318.15	0.77±0.06	13.95±0.06	29.1±1.9	
NH_4^+	298.15	1.23±0.07	9.82±0.06	9.4±0.3	
	308.15	1.17±0.07	9.52±0.06	8.5±0.3	33±5
	318.15	1.12±0.07	9.16±0.09	7.4±0.4	
Ca^{2+}	288.15	0.49±0.11	10.60±0.40	27.5±2.5	
	298.15	0.43±0.11	10.10±0.12	25.8±2.2	
	308.15	0.37±0.11	9.80±0.36	24.6±2.4	
Sr^{2+}	298.15	2.72±0.02	14.93±0.03	–1.9±0.4	
	308.15	2.64±0.02	13.85±0.03	–5.6±0.4	97±4
	318.15	2.56±0.02	13.10±0.07	–7.8±0.4	
Ba^{2+}	298.15	3.85±0.04	30.44±0.09	28.5±0.7	
	308.15	3.68±0.04	29.30±0.19	24.7±0.9	118±20
	318.15	3.52±0.04	28.10±0.39	21.1±1.4	

Results and discussion

The studied arrays of alkali and alkaline earth metal cations given in the order of ML^{n+} stability growth match the principle of structure correspondence. The data in Fig. 1 show that for both alkali and alkaline earth metal ions the maximum stability for complexes with 18C6 occurs when the metal ion to ligand cavity ratio is approximately unity as is the case with K^+ and Ba^{2+} $(R(18C6)=130-168$ pm, $R(K^+)=133$ pm, $R(Ba^{2+})=143$ pm).
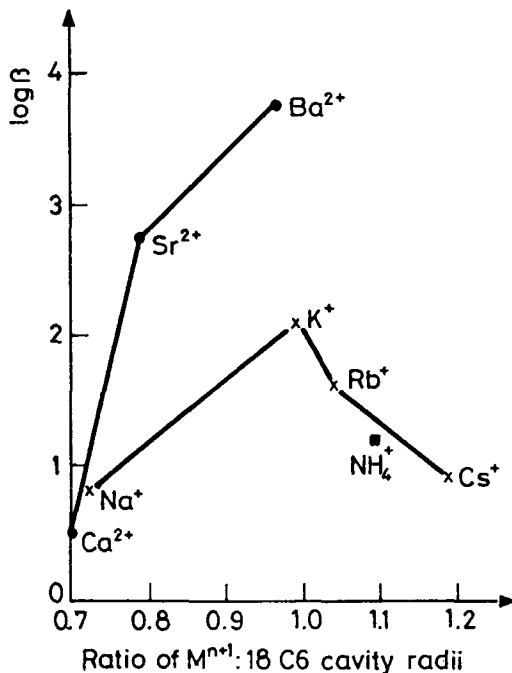

Fig. 1

However, the factors governing the stability of 18C6 complexes are not limited by the geometry correspondence only. The comparison of stability constants for the most stable complexes of alkali and alkaline earth metal cations of the · close size reveals the increase of stability with the charge raise $(\log\beta(KL^+)=2.03$, $\log\beta(BaL^{2+})=3.85)$. Complexes formed by large dipositive ions usually have higher stabilities than those formed by monopositive ions of similar size, while the opposite is true for small cations of differing changes. For example 18C6 as ligand prefers Na^+ over Ca^{2+} (at almost similar ionic radii) while in the large cation range Ba^{2+} is preferred over K^+.

For the large alkali and alkaline earth metal ions cation size seems to be responsible primarily for the complexing characteristics. The smaller cations in

these series are solvated strongly due to the higher charge density. Generally their complexes with 18C6 are less stable than those formed by the larger cations of the same family. It proved the solvation factor to be important for interpreting of 18C6 selectivity at complexation. This effect takes place in the case of Na^+ and Ca^{2+} complexes with 18C6 (Table 1).

The lower stability of ammonium complex with 18C6 comparing with that of RbL^+ at actually coinciding sizes of NH_4^+ and Rb^+ central ions proved the principle of structure correspondence to be unsufficient for the interpreting of complex stability data.
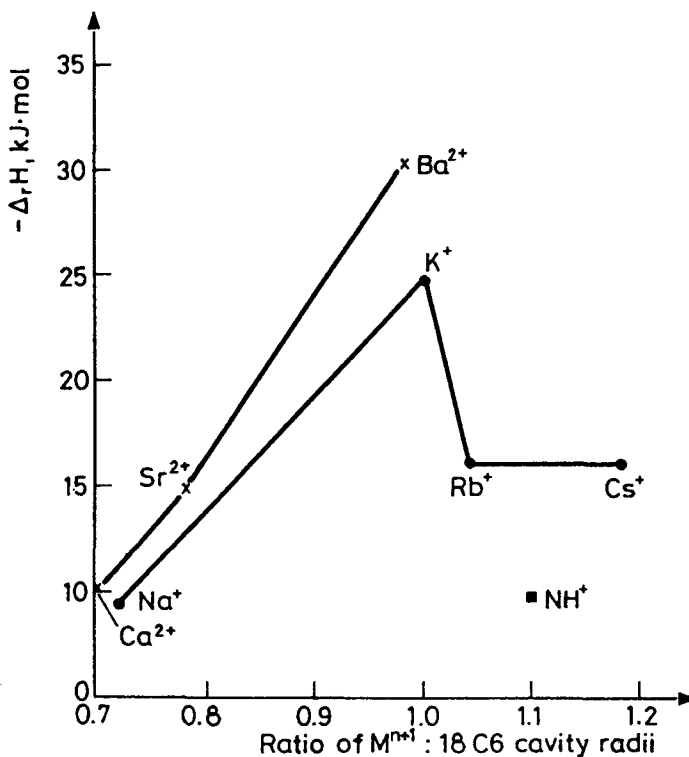

Fig. 2

Tetrahedron structure of the ammonium ion causes certain stereochemical limitations to the interacting with oxygen donor atoms of the macrocycle [3]. Resulting H–O bonds in NH_4L^+ complex appeared to be less strong than those in RbL^+ as rubidium ion has spherical symmetry.

The affinity of the cation towards 18C6 and their solvation abilities are reflected on the value of complexation enthalpy. According to the Table data the studied reactions are exothermic. The heat effect value of the studied processes

is known to involve the cation-macrocycle binding energy and difference of the solvation energies of the reagents and the complex.

The maximum absolute value of the heat effect for the array of alkali metals (Fig. 2) is observed for KL^+ and for BaL^{2+} within the alkaline earth metals range, being the highest for BaL^{2+} complex. Probably it is the result of some enhancement of the ion-dipole interaction occurring with the increase of cation charge. Hence, the energy of cation-oxygen donor atoms bond raises. With the increase of the difference between the sizes of the cation and macrocyclic cavity the absolute values of the complexation heat effect are declining. Notably, this trend seems to be more pronounced in the case of dipositive alkaline earth cations reflecting the growth of solvation effect contribution.

Less exothermic heat effect of NH_4L^+ formation compared with that value for RbL^+ probably is the result of more intensive solvation of the ammonium ion able to form hydrogen bonds with water molecules. So, more energy is required for the withdrawal of the solvent off the ammonium ion shell during the complexation.

Minimum $\Delta_r S$ values are observed for KL^+ complex in the range of alkali metals and for BaL^{2+} in the range of alkaline earth metals (Table). The comparison of the obtained $\Delta_r H$ and $\Delta_r S$ data reveals the prevalence of enthalpy contribution to the free energy of complexation with 18C6. While enthalpy contribution is unfavourable at almost every case.

Exothermic character of the process becomes less pronounced with the temperature growth (Table), correspondingly $\Delta_r C_p > 0$. This is valid for many complexes of mono- and polydentative ligands (as NH_3, EDTA, etc.).

For 18C6 complexation $\Delta_r C_p$ value may provide information on the character of its ring deformation and central ion encapsulation.

It is notable that for the arrays of alkali and alkaline earth metals the maximum $\Delta_r C_p$ values were found for the most stable complexes KL^+ (135 ± 20 J/mol·K) and BaL^{2+} (118 ± 20 J/mol·K). It probably proved the 18C6 complex formation in these complexes to be less strained. For 18C6 complexation with K^+ and Ba^{2+} ions the corresponding $\Delta_r C_p$ values despite of the charge increase were almost the same taking into account their estimated errors. The best structural correspondence of Ba^{2+} ion and 18C6 cavity facilitates the cation coordination and therefore leads to certain increase of BaL^{2+} complex rigidity. At the same time $\Delta_r C_p$ value decreases as the ML^{n+} stability goes down (Table). This parameter appears to indicate the growth of the complex system rigidity as 18C6 molecule undergoes deformation adjusting its free form to the coordinated one. So, the structural differences of the studied complexes are expected to contribute to the regularities observed for the $\Delta_r C_p$ trend.

The obtained $\Delta_r C_p$ values confirmed the structure of 18C6 complexes to be closely linked with the character of its central ion encapsulation from the sol-

vent. The planar conformation reported for KL^+ and BaL^{2+} complexes [4] provides less screening of the cations from the solvation than the twisted form of macrocycle occurring in NH_4L^+ and NaL^+ complexes [3, 4]. Therefore the more intensive solvation in the cases of KL^+ and BaL^{2+} compounds provides more degrees of freedom to the resulting system and hence larger values of $\Delta_r C_p$ (exp. $\Delta_r C_p(BaL^{2+}) = 118\pm20$ J/mol·K; $\Delta_r C_p(NH_4L^+) = 33\pm5$ J/mol·K).

The obtained thermodynamic characteristics of 18C6 complexation proved cation selectivity of polyether to be affected by the conformational transition of ligand as well as by the solvation of the reagents and the complex.

The data on temperature dependence of 18C6 complexation appear to be helpful for further evaluating of the optimum terms of cation extraction at various temperatures and solvents.

References

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Zusammenfassung — Gegenstand vorliegender Arbeit ist die untersuchung jener Faktoren, die die Komplexierung von 18C6 in wäßriger Lösung beherrschen, indem die thermodynamischen Parameter der Reaktion hinsichtlich der beobachteten Selektivität und Solvatationscharakteristik unter verschiedenen Temperaturbedingungen interpretiert werden.