STUDIES OF THE COMPLEX FORMATION OF SILVER (I) ION WITH 18-CROWN-6 IN H₂O–DMSO MIXTURES BY CALORIMETRY

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Abstract

The thermodynamic parameters ($\Delta_r G^0$, $\Delta_r H^0$, $T\Delta_r S^0$) of the reaction of $[Ag18C6]^+$ complex formation were obtained for a wide range of H₂O–DMSO mixtures from the calorimetric data at 298.15 K. The relation between the thermodynamic parameters of complex formation and solvation of each reagent was investigated.

Keywords: complex formation, 18-crown-6, enthalpy, silver (I) ion, mixed solvents

Introduction

The crown-ethers are analogous to some bio-ligands, able to selectively interact with metal-ions by including them in a cavity of the molecule [1]. This interaction is similar to the solvation process: the crown-ether molecule behaves like the first solvation shell of the cation [2]. The results of numerous investigations allow to conclude that the complexing properties of crown-ligands could be more effective in mixed and non-aqueous solvents rather than in water [3].

In the present work we have investigated the complex formation of Ag^+ ion with 18-crown-6 (18C6) in a wide range of H₂O–DMSO mixtures. Our study aimed to:

– simultaneous calorimetric determination of complex stability (lg$K$) and the heat effects ($\Delta_r H^0$) of complex formation in non-aqueous and mixed medium. Titration calorimetry is an especially important method when there is no other way to determine lg$K$,

– investigate the relation between the thermodynamic parameters of both complex formation and solvation of each reagent.

Experimental

Materials and methods

Silver nitrate was dried at 363 K under vacuum until constant mass is obtained [4]. The silver perchlorate was synthesized by the method described in [5]. The final pu-

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rity of the used reagents was checked by potentiometric titration and found to be 99.9% for $AgNO_3$ and 99.0% for $AgClO_4$. Crown-ether 18-crown-6 ('IREA', Moscow) was dried in a desiccator over P_2O_5 [6]. The elementary analysis has shown a carbon content of 99.97% in agreement with the chemical formula $C_{12}H_{24}O_6$. DMSO was purified by freezing and vacuum distillation. The presence of water in DMSO was determined by Fisher's method [7].

An isoperibolic calorimeter with mixing and titration cells was used. The enthalpy of the KCl dissolution in water, $\Delta_{sol}H^0_{298.15}$, was measured and its agreement with the standard SRM 1655 NBS [8] was about 0.4%.

The standard thermodynamic characteristics of the $[Ag18C6]^+$ complex formation ($\Delta_r G^0$, $\Delta_r H^0$, $\Delta_r S^0$) was calculated on the basis of the calorimetric data. The heat of mixing of the titrant with a solution of $AgNO_3$ or $AgClO_4$ (Q_{mix}) were experimentally measured at 298.15 K. The heat of the mixing process can be described as follows:

$$Q_{mix}=Q_{cmpl}+Q'_{dil}+Q''_{dil} \tag{1}$$

where Q_{cmpl} – heat of the complex formation, Q'_{dil} – heat of dilution of the added ligand solution (titrant), Q''_{dil} – heat of dilution of the solution contained in the cell.

During the experiment the volume of the solution in the cell was incremented approximately by 1% and the reagents' concentrations did not exceed 0.15 mol L^{-1}, thus the heat Q''_{dil} was negligible. The heat of dilution Q'_{dil} was determined by a mixing of a concentrate titrant solution and the corresponding solvent.

Therefore, the Eq. (1) can be written as:

$$\Delta_{cmpl}H_i=\Delta_{mix}H_i-\Delta_{dil}H_i \tag{2}$$

where $\Delta_{cmpl}H_i$, $\Delta_{mix}H_i$ and $\Delta_{dil}H_i$ – molar entalpies of the complex formation, mixing and dilution calculated for 1 mol of added ligand in the i-th experiment. We ave not found concentration dependence for the $\Delta_{dil}H$ values, so the average value obtained from 4–5 measurements made with different amounts of 18C6 was used for calculation.

For simultaneously calculating the values $\Delta_r H^0$ and lg$K$ the study of complex formation was carried out within a wide range of concentrations of the formed complex. This was achieved by the mathematical planning method of the experiment. The expected yield of the complex and also equilibrium concentrations of reagents were calculated before the experiment by using the most probable value lg$K$. The experimental concentrations could considerably change depending on the increasing or decreasing complex yield, and also the heat effect of the reaction. The primary experimental results are presented in Table 1.

The experimental data were calculated using the program HEAT [9] designed for calculation of enthalpies of reaction and equilibrium constants for systems having arbitrary signs of stoichiometry. The HEAT algorithm consists in the minimisation of the function F:

$$F=\sum_{i=1}^{N}\omega_i(\Delta_{cmpl}H-\Delta_{calc}H)_i^2 \tag{3}$$

where N – number of experimental points; ω_i – weighting factors taking into account unequal precision of measurements; $\Delta_{calc}H$ – enthalpies of process computed for the given stoichiometrical model.

Table 1 The primary calorimetric data at 298.15 K

X_{DMSO} mol. fr.	$C^{\circ}_{AgNO_3} \cdot 10^2/\text{mol L}^{-1}$	$C^{\circ}_{18C6} \cdot 10^3/\text{mol L}^{-1}$	$-\Delta_{cmpl}H/\text{kJ mol}^{-1}$ of ligand
	0.152	5.876	1.55
	1.330	10.70	2.38
	1.994	6.159	3.18
	2.807	5.504	4.21
0.0	5.100	10.20	5.77
	5.720	5.672	6.02
	9.635	5.856	7.45
	10.70	10.60	7.71
	13.18	5.500	7.72
	1.585	10.22	1.04
	2.967	9.870	2.13
	5.071	10.04	2.97
	6.983	9.963	4.08
	9.826	9.853	4.97
	15.25	10.23	6.88
	20.27	10.19	7.79
0.8	24.42	10.23	8.99
	0.892	5.865	0.64
	1.767	5.975	1.23
	2.675	5.379	1.49
	5.505	5.540	3.04
	7.267	4.812	4.79
	11.13	5.630	8.58

The $\Delta_{calc}H$ value for a 1:1 stoichiometry of complex formation was calculated as follows:

$$\Delta_{calc}H = \Delta[ML]\Delta_r H^0 / C_L^0 \tag{4}$$

where $\Delta_{calc}H$ – kJ (mol of ligand)$^{-1}$, C_L^0 – analytical concentration of the ligand, mol L^{-1}, $\Delta[ML]$ – change of equilibrium concentration of the complex during the experiment, calculated for current value lg$K$. The iterative procedure terminates, when the current values lg$K$ and $\Delta_r H^0$ yield minimum F. The HEAT algorithm described in work [9] finds a 'main' minimum F for any plausible starting values lg$K$, even if the function (3) has local minimums. The initiation of $\Delta_r H^0$ in computer calculation is not necessary, as it is calculated in each iteration.

During calculation the correlation between $\Delta_r H^0$ and lg$K$ values was observed. The true values correspond to a minimum of the function F (Fig. 1a) and agree with a principle of maximal statistical plausibility.
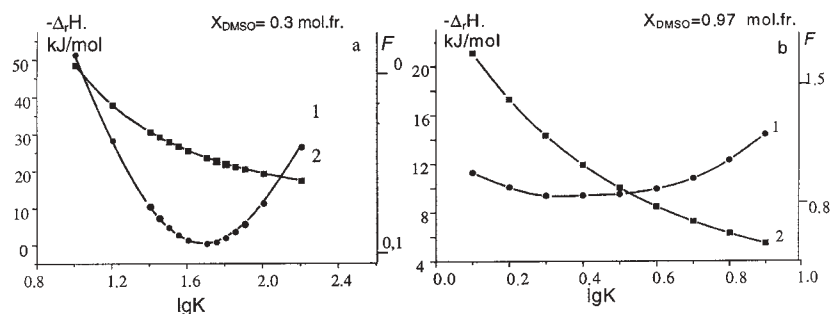
Fig. 1 a – b The correlation between $\Delta_r H^0$ and lg$K$ in a minimum of function F: 1 – F,
2 – $\Delta_r H$)

In the case of an indistinct minimum F there have been difficulties in calculation. Two processes are statistically equivalent: 1) reaction having high enthalpy and low equilibrium constants, 2) reaction having low enthalpy and high equilibrium constants (Fig. 1b).

The values $\Delta_r H^0$ and lg$K$, obtained from computer calculation were checked by using the Eq. (6). From the equation of material balance of reaction follows:

$$C_L^0 = [ML] + [L] \qquad (5)$$

where [ML] and [L] – equilibrium concentrations of complex and ligand.

The enthalpies of complex formation can also be calculated through the Eqs 4 and 5 as follows:

$$1/\Delta_{cmpl}H = 1/\Delta_r H^0 + 1/(K\Delta_r H^0[Ag]) \qquad (6)$$

where $\Delta_{cmpl}H$ – experimental measured enthalpies of process; [Ag] – equilibrium concentration of Ag^+ ion.

Table 2 The stability constants of [Ag18C6]$^+$ in aqueous DMSO, T=298.15 K

X_{DMSO} mol. fr.	0.0	0.1	0.2	0.3	0.4	0.6	0.7	0.8	0.97
lg$K$	1.40	1.60	1.75	1.70	1.55	1.00	0.7±0.12	0.65	0.35
	±0.10	±0.10	±0.10	±0.10	±0.10	±0.10	0.70±0.12**	±0.15	±0.15
lg$K$	1.42	1.59	1.73	1.67	1.54	1.00	0.75	0.65	0.35
Ref. [10]*	±0.05	±0.05	±0.05	±0.05	±0.05	±0.05	±0.05	±0.05	±0.05

* – Potentiometrically determined by using AgClO$_4$
** – Calorimetrically determined by using AgClO$_4$
AgNO$_3$ was used in other cases

The Eq. (6) can be presented as linear dependence with the co-ordinates $Y \equiv 1/\Delta_{cmpl}H$, $X \equiv 1/[Ag]$ and slope $1/(K\Delta_r H^0)$. The example of $\Delta_r H^0$ and lg$K$ calculation by using the Eq. (6) are given in Fig. 2. The concentrations [Ag] were estimated by means of an initial
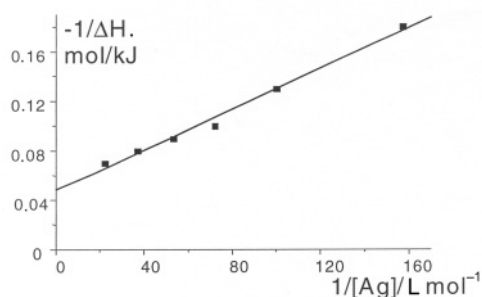
Fig. 2 $\Delta_r H^0$ and lg$K$ calculation by Eq. (6)

value of lg$K$ from Table 2. The data calculated by the Eq. (6) and by the program HEAT were coincident: $\Delta_r H^0 = -21.2 \pm 2$ kJ mol^{-1}, lg$K = 1.75$ ($X_{DMSO} = 0.2$ mol. Fr.).

The lg$K$ values calculated from the calorimetric data are in good agreement with those measured by potentiometry (Table 2). The calorimetric technique allowed us to obtain enough reliable formation constants and reaction enthalpies of weak complexes.

Results and discussion

The comparison of our lg$K$ and $\Delta_r H^0$ values for water with the appropriate literature data showed a satisfactory agreement (Table 3). However, in the case of a 0.97 mol. fr. DMSO (99.29 mass %), the lg$K$ value we have found out (0.35±0.15) was significantly different from the values given by Buschmann and Schollmeyer [11] and Izatt *et al.* [18]. Buschmann and Schollmeyer have found that the low negative enthalpy reaction, $\Delta_r H^0 = -1$ kJ mol^{-1}, results in formation of a relatively strong complex [Ag18C6]$^+$ due to its high positive entropy, $T\Delta_r S^0 = 7.9$ kJ mol^{-1}. We have found a higher heat effect of complexing and a lower complex stability in DMSO than in water. The correlation between $\Delta_r H^0$ and lg$K$ during calculation, as can be shown in Fig. 1b, could lead to the differences mentioned above.

The complex stability and exothermicity of complex formation of [Ag18C6]$^+$ recorded a maximum at $X_{DMSO} = 0.3$ mol. fr. The function lg$K = f(X_{DMSO})$ for Ag(I) complexes with benzoic or isonicotinic hydrazides [19] or 2,2'-dipyridyl [20] had also an extremum at 0.1–0.3 mol. fr. DMSO. The formation of a low stability hetero-solvate [Ag(DMSO)(H$_2$O)$_3$]$^+$ in mixed solvent could probably cause an extremum on the lg$K = f(X_{DMSO})$ plot.

The enthalpy contribution in stability of complex prevalent at $X_{DMSO} = 0$ mol. fr. The increase of the concentration of DMSO up to ca. 0.4 mol. fr. DMSO was accompanied by a decrease in the entropy of reaction.

The thermodynamic characteristics we obtained have been considered on the basis of the solvation-thermodynamic approach [3, 21]. The transfer enthalpies of [Ag18C6]$^+$ from water to mixed solvents were calculated in the thermodynamic cycle as follows:

$$\Delta_{tr} H_r^0 = \Delta_r H^0 aq - \Delta_r H^0 s = \Delta_{tr} H^0([AgL]^+) - \Delta_{tr} H^0(Ag^+) - \Delta_{tr} H^0(L) \qquad (7)$$

The standard enthalpies of transfer, $\Delta_{tr} H^0(Ag^+)$ and $\Delta_{tr} H^0(L)$, were determined previously [22].

Table 3 Thermodynamic functions of $[Ag18K6]^+$ complex formation in individual solvents at T=298.15 K

Medium	Method	lg$K$	$-\Delta_r H^0$ /kJ mol^{-1}	$T\Delta S^0$ /kJ mol^{-1}	Ref.
Water	Cal+Pot	1.5±0.03	9.1±0.5	−0.5±0.6	[11]
	Cal+Pot	1.63±0.08	17	−	[12]
	Cal	1.5	9.07	−0.6	[6]
	Cal	1.5±0.03	9.08	−	[13]
	Cal	1.48±0.07	9.61	−	[14]
	Pot	1.60	−	−	[15, 16]
	Con	1.24	−	−	[17]
	Cal	1.40±0.1	10.2±0.8	−2.2±1	this work
DMSO	Cal+Pot	1.56±0.05	1.0±0.4	+7.9±0.7	[11]
	Pot	1.60	−	−	[18]
	Cal	0.35±0.15	13±2.5	−11±3	this work

The influence of the solvent composition on $\Delta_{tr} H^0([AgL]^+)$ was smaller than on $\Delta_{tr} H^0(Ag^+)$ and $\Delta_{tr} H^0(L)$. The plots presented in Fig .4 pointed out two main opposite contributions, $\Delta_{tr} H^0(L)$ and $\Delta_{tr} H^0(Ag^+)$, which change with the increase of DMSO concentration and determine the change of enthalpy of complex formation. The first contribution represents the desolvation of the ligand with the increase of DMSO concentration, meanwhile the second contribution represents the formation of solvo-complexes of Ag^+ ion with DMSO.
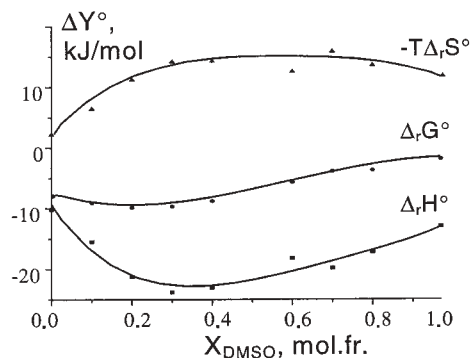

Fig. 3 The influence of composition of H$_2$O–DMSO solvent on the thermodynamic parameters of complex formation $[Ag18C6]^+$
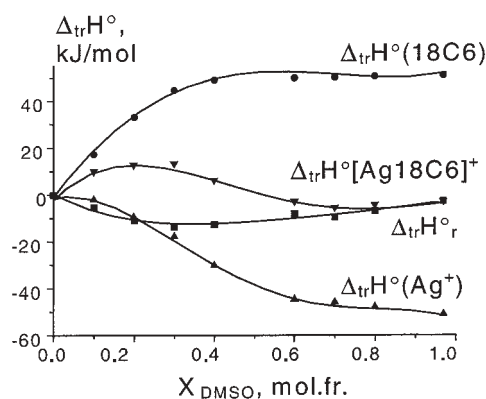
Fig. 4 Transfer enthalpies of the ligand 18C6, complex $[Ag18C6]^+$ and Ag^+ ion for H_2O–DMSO mixtures

The first contribution was predominating in the range $X_{DMSO}=0.0-0.3$ mol. fr. and determined an increment of the exothermicity of reaction. The second contribution determined a decrease of the exothermicity in the range $X_{DMSO}=0.3-0.97$ mol. fr.

We suppose that the solvation effects play the same role in the complex stability too.

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