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Thermodynamics of Complexation of Ag^+ with 18-Crown-6 in Water–Dimethyl Sulfoxide Mixtures

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Abstract—The stability of complexes and enthalpy of interaction of Ag^+ ions with 18-crown-6 in water–dimethyl sulfoxide (DMSO) mixtures were determined by calorimetric titration in the range of mole fractions X_{DMSO} from 0.0 to 0.97 at 298.15 K. With increasing concentration of the nonaqueous component in the solvent to X_{DMSO} 0.3, the stability of the complex ion $[AgL]^+$ increases, which is followed by a decrease in $\log K(AgL^+)$ to 0.35 ± 0.15 at X_{DMSO} 0.97. The exothermic effect of the reaction shows a similar trend. The presence of the extremum in the $\log K$–X_{DMSO} and $\Delta_r H$–X_{DMSO} dependences is explained by the competition of two solvation contributions: destabilization of the ligand with decreasing water content in the solvent and formation of strong solvation complexes of Ag^+ with DMSO.

Crown ethers can be considered as analogs of natural biologically active ligands capable of binding metal ions with a high selectivity and incorporating them into the inner cavity of the molecule. Such interaction is an ideal model of solvation when the crown ether molecule is the first solvation shell of the complex-forming ion [1].

Shormanov *et al.* [2–5] found some relationships in the influence of the composition of aqueous solutions of acetone, acetonitrile, dimethyl sulfoxide (DMSO), propylene carbonate, and ethanol on the thermodynamics of complexation of the Ag^+ ion with pyridine and 2,2'-bipyridine. It was shown that the stability of silver(I) 2,2'-bipyridine complexes decreases with increasing concentration of DMSO owing to formation of strong solvation complexes of the central ion with DMSO and enhancement of ligand solvation [5].

In this work we studied calorimetrically the equilibrium constants and enthalpies of complexation of Ag^+ with 18-crown-6 (18C6, L) in water–DMSO mixtures of variable compositions.

The thermal effect of mixing of the solutions of the metal salt and ligand can be represented as the sum

$$Q_{mix} = Q_{comp} + Q'_{dil} + Q''_{dil}, \qquad (1)$$

where Q_{comp} is the heat of complexation, Q'_{dil} is the heat of dilution of the ligand solution in the course of mixing, and Q''_{dil} is the heat of dilution of the metal salt solution in the cell.

We have measured experimentally the heats of mixing Q_{mix} of aqueous-DMSO solutions of the ligand in the ampule with solutions of silver nitrate and the heats of dilution of the ligand solutions in the same solvent.

The experimental conditions were chosen so as to minimize the contribution of Q'_{dil} [Eq. (1)]. For this purpose, we took equal compositions of the solvent in the ampule and cell, and fairly low concentration of the ligand in the ampule. The solution volume in the cell increased in the course of the experiment by ~1%, and the concentration of the reagent in the cell did not exceed 0.15 M; therefore, Q''_{dil} was negligibly low.

Under these conditions, Eq. (1) can be transformed into (2):

$$\Delta_{comp}H_i = \Delta_{mix}H_i - \Delta_{dil}H_i, \qquad (2)$$

where $\Delta_{comp}H_i$, $\Delta_{mix}H_i$, and $\Delta_{dil}H_i$ are the molar enthalpies of complexation, mixing, and dilution per mole of the ligand in *i*th run.

Calculation of $\log K$ and $\Delta_r H$ consists in numerical minimization of the function F

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

where N is the number of experimental points, ω_i are the weight factors taking into account unequal accuracy of measurements, and $\Delta_{comp}H$ and $\Delta_{calc}H$ (kJ mol^{-1}) are, respectively, the experimental thermal

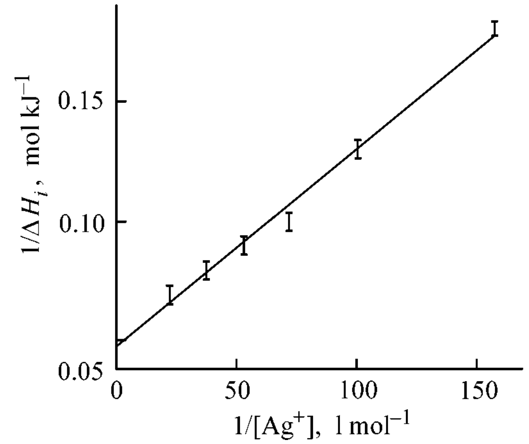

Fig. 1. Calculation of $\log K$ and $\Delta_r H$ by Eq. (6). Solvent water–DMSO (mole fraction of DMSO 0.2).

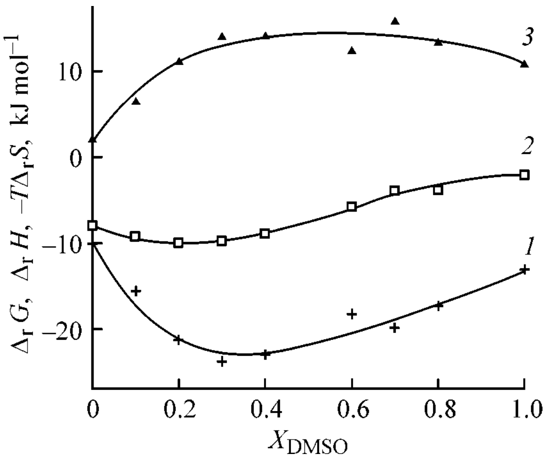

Fig. 2. Thermodynamic parameters of complexation of Ag^+ with 18-crown-6 as functions of the composition of the water–DMSO solvent: (*1*) $\Delta_r H$, (*2*) $\Delta_r G$, and (*3*) $-T\Delta_r S$. T = 298 K.

effect and that calculated by the model at the given total concentrations of the initial components and current values of $\Delta_r H$ and $\log K$.

For the simplest complexation model, the thermal effect of interaction of solutions per mole of the ligand is given by

$$\Delta_{calc}H = \Delta[AgL]^+\Delta_r H/C^0_L, \qquad (4)$$

where C^0_L is the total (analytical) concentration of the ligand, and $\Delta[AgL]^+$ is the change in the equilibrium concentration of the complex in the experiment, calculated for the current values of $\log K$.

The experimental data were processed using the HEAT program [6] developed for calculating the reaction enthalpies and equilibrium constants in systems of arbitrary stoichiometry.

The enthalpy of reaction (5) can be calculated graphically from relation (6) [7]:

$$Ag^+ + L = [AgL]^+, \qquad (5)$$

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

where K is the stability constant of the complex, and $[Ag^+]$ is the equilibrium concentration of Ag^+.

Relation (6) is the equation of a straight line in the coordinates $1/\Delta_{comp}H_i$–$1/[Ag^+]$ with a slope equal to $1/(K\Delta_r H)$. Figure 1 gives an example of graphical calculation of $\log K$ and $\Delta_r H$.

Silver nitrate in aqueous solution is partly associated ($\log K_{as}$ 0.29) [8]; in decimolar solution, about 5% of silver is in the form of the nitrate complex. Data on the stability of Ag^+ nitrate complexes in DMSO are lacking. Presumably, the presence of associates of the type $[AgNO_3]$ and, possibly, $[AgLNO_3]$, and also of solvation-separated ion pairs has no appreciable effect on the thermodynamics of the process under consideration. This assumption is confirmed by results of the calorimetric experiment: In the range of the $C_{Ag^+} : C_L$ ratios from 24 : 1 (at X_{DMSO} 0.0–0.97) to 1 : 28 (at X_{DMSO} 0.7 and 0.97), calorimetric data are adequately described by the model assuming $[AgL]^+$ as the only complex species.

In the solvent with X_{DMSO} 0.7, instead of $AgNO_3$ we used $AgClO_4$ whose tendency to association is considerably weaker [9]. The $\log K(AgL^+)$ and $\Delta_r H$ values calculated in this case are quite consistent with the data obtained for the other H_2O–DMSO solvents with $AgNO_3$ (Fig. 2). In the range of $AgNO_3$ concentrations 0.008–0.25 M, possible variations of the activity coefficient had no appreciable effect on the deviation of separate points or sum of squared deviations of F [Eq. (3)].

Example of primary experimental data is given in Table 1. The values of $\log K(AgL)$ and $\Delta_r H$ for reaction (5) in H_2O–DMSO solvents are listed in Table 2. The calculated values of $\log K$ and $\Delta_r H$ mutually correlate (Fig. 3): The most reliable values correspond to the minimum of F.

Our thermodynamic functions for aqueous solutions (Table 2) agree well with published data: $\log K$ 1.5 [10], 1.6 [11, 12]; $\Delta_r H$ 9.7 kJ mol^{-1} [10].

The influence of the solvent composition on the stability of the complex $[AgL]^+$ and the enthalpy and entropy characteristics of its formation is sophisticated. In the range of DMSO mole fractions 0.2–0.4, the stability of the complex and the exothermic effect of the reaction pass through a maximum. Increase in the stability of the complex in the binary solvent as compared to the individual solvents was noted previously for complexes of Ag(I) with 2,2'-bipyridine in H_2O–DMSO solvents [5].

To understand the observed variation in stability of the complexes, it is appropriate to use a versatile approach based on thermodynamic characteristic of the reagent solvation [13], in which the stability of the complex is considered as a function of thermodynamic characteristics of solvation of the main reaction participants:

$$-RT\ln(K_{sol}/K_{H_2O}) = \Delta_{tr}G_{comp} = \Delta_{tr}G(ML^+) - \Delta_{tr}G(M^+) - \Delta_{tr}G(L), \qquad (7)$$

where $\Delta_{tr}G(ML^+)$, $\Delta_{tr}G(M^+)$, and $\Delta_{tr}G(L)$ are, respectively, the Gibbs energies of transfer of the complex species, metal, and ligand from water to aqueous-organic solvent.

The enthalpy of transfer of the reaction from the aqueous to binary solvent is determined similarly:

$$\Delta_{tr}H_r = \Delta_r H_{sol} - \Delta_r H_{H_2O} = \Delta_{tr}H(ML^+) - \Delta_{tr}H(M^+) - \Delta_{tr}H(L), \qquad (8)$$

where $\Delta_{tr}H(M^+)$, $\Delta_{tr}H(L)$, and $\Delta_{tr}H(ML^+)$ are, respectively, the enthalpies of transfer from water to aqueous-organic solvent of M^+, L, and $[ML]^+$.

We found that in water, which is a proton-donor solvent (AN_{H_2O} 54.8), 18-crown-6 is mainly solvated by hydrogen bonding of H_2O with oxygen atoms of the macrocycle [14]. With increasing concentration of DMSO, the proton-donor properties of the medium decrease (AN_{DMSO} 19.3). In DMSO, the major contribution to solvation of the crown ether is made by the van der Waals forces whose energy is considerably lower than that of hydrogen bonds. Therefore, we can assume that, as the DMSO concentration in the mixed solvent is increased, the solvation of the ether weakens (destabilization). It is known [15] that DMSO forms solvation complexes with the central ion, which are more stable than the aqua complexes of Ag(I) ($\Delta_{tr}G_{H_2O-DMSO}(Ag^+)$ –34.8 kJ mol^{-1}).

Table 1. Molar enthalpies determined calorimetrically at 298 K[a]

C^0_{18C6}, M	$C^0_{Ag^+}$, M	$\Delta_{comp}H$, kJ mol^{-1}
$-\Delta_{dil}H$ 1.25 kJ mol^{-1}		
5.86×10^{-3}	8.92×10^{-3}	0.64
5.98×10^{-3}	1.77×10^{-2}	1.23
5.38×10^{-3}	2.68×10^{-2}	1.49
5.54×10^{-3}	5.50×10^{-2}	3.04
4.81×10^{-3}	7.27×10^{-2}	4.79
5.63×10^{-3}	1.11×10^{-1}	8.58
$-\Delta_{dil}H$ 1.85 kJ mol^{-1}		
1.02×10^{-2}	1.59×10^{-2}	1.04
9.87×10^{-3}	2.97×10^{-2}	2.13
1.00×10^{-2}	5.07×10^{-2}	2.97
9.96×10^{-3}	6.98×10^{-2}	4.08
9.85×10^{-3}	9.83×10^{-2}	4.99
1.02×10^{-2}	1.52×10^{-1}	6.88
1.02×10^{-2}	2.03×10^{-1}	7.79
1.02×10^{-2}	2.44×10^{-1}	8.99

[a] Cell volume 72.3 ml; ligand concentration in the ampule 0.4131 mol kg^{-1} solution; solvent: mole fractions of H_2O 0.2, DMSO 0.8.

Table 2. Thermodynamic parameters of complexation of Ag^+ with 18-crown-6 in H_2O–DMSO at 298 K

X_{DMSO}	$\log K$	$-\Delta_r H$, kJ mol^{-1}
0.0	1.40 ± 0.10	10.2 ± 0.8
0.1	1.60 ± 0.10	15.5 ± 1.5
0.2	1.75 ± 0.10	21.2 ± 2.0
0.3	1.70 ± 0.10	23.8 ± 2.0
0.4	1.55 ± 0.10	23.0 ± 2.0
0.6	1.00 ± 0.10	18.2 ± 2.0
0.7[a]	0.70 ± 0.12	19.8 ± 2.5
0.8	0.65 ± 0.15	17.2 ± 2.5
0.97	0.35 ± 0.15	13.0 ± 2.5

[a] With $AgClO_4$.

These data suggest that the maximum in the dependence of the stability of $[AgL]^+$ on the content of DMSO is due to competition of two solvation contributions: destabilization of the ligand with decreasing concentration of water and formation of strong solvation complexes of Ag^+ with DMSO. Presumably, at small additions of DMSO prevails the first factor, and at $X_{DMSO} > 0.3$, the second factor.

Figure 2 shows the dependence of the thermodynamic characteristics of complexation on the composition of the water–dimethyl sulfoxide solvent. In water, the major contribution to stability of the complex is made by the enthalpy component of the Gibbs energy, whereas in DMSO-rich solvents the enthalpy and entropy contributions to the Gibbs energy become comparable.

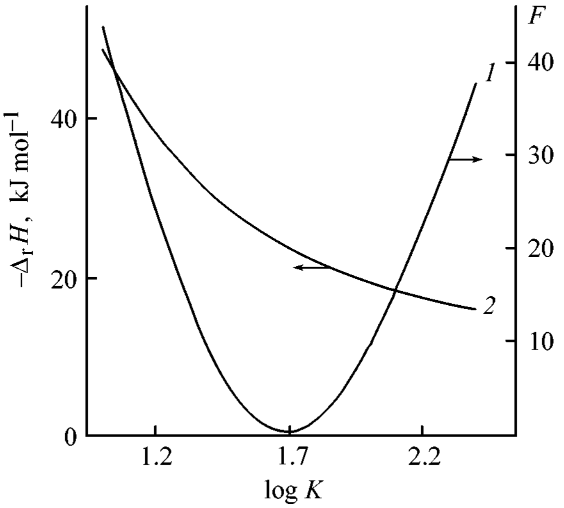

Fig. 3. (*1*) Variation of the target function *F* at log*K* varied in the course of iterations; (*2*) mutual correlation of the calculated values of log*K* and $\Delta_r H$ in the vicinity of the minimum of *F* (X_{DMSO} = 0.3).

It should be noted that the range of solvent compositions in which the absolute values of $\Delta_r H$, $\Delta_r G$, and $T\Delta_r S$ are maximal (X_{DMSO} 0.2–0.3) coincides with the range of maximal deviations from additivity of the physicochemical properties of the H_2O–DMSO system [16]. According to [17], DMSO forms a stable solvate DMSO · $3H_2O$ with the enthalpy of formation of about –18.9 kJ mol^{-1} [17]. In the range of the mole fractions of DMSO from 0.0 to 0.25, accumulation of the associates DMSO · $3H_2O$ affects the solvation characteristics of L^+, M^+, and $[ML]^+$.

EXPERIMENTAL

18-Crown-6 (Institute of Chemical Reagents and Ultrapure Substances, Moscow) was dried in a desiccator over P_2O_5 [10]. The carbon content determined by elemental analysis was 99.97% relative to the theoretical content for $C_{12}H_{24}O_6$. Pure grade DMSO was purified by vacuum distillation. The moisture content of DMSO was determined by Fischer titration [18]. Silver perchlorate was prepared according to [19], dried in a vacuum, and stored over P_2O_5. Silver nitrate (analytically pure grade) was used without additional purification. The content of the main substance in $AgNO_3$ and $AgClO_4$ was checked by potentiometric titration. Solutions were prepared gravimetrically in double-distilled deaerated water.

Measurements were performed in an ampule calorimeter with an isothermal jacket, similar in design to that described in [20]. The operation of the calorimeter was checked by measuring the heat of solution of KCl in water. The obtained value of $\Delta_{sol}H$(KCl, ∞H_2O) = 17.27 ± 0.5 kJ mol^{-1} agrees well with the value of $\Delta_{sol}H$(KCl, ∞H_2O) = 17.243 ± 0.018 kJ mol^{-1} given by the SRM 1655 NBS standard [21]. The measured thermal effects were 0.5–9.0 J, which corresponded to the optimal working range of the cell. The concentration conditions of the experiments were preliminarily calculated so as to ensure the maximally wide range of the complex yield. The equilibrium concentrations of reactants were determined by the RRSU program [22].

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