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Thermochemistry of the Silver(I) Complexation with 18-Crown-6 Ether in a Binary Solvent Methanol–Dimethylformamide

I. A. Kuz'mina, V. A. Sharnin, and A. N. Golikov

Ivanovo State University of Chemical Technology, pr. Engelsa 7, Ivanovo, 153000 Russia
e-mail: oxt703@isuct.ru

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Abstract—The effect of methanol–dimethylformamide solvent on the reaction enthalpy of the silver(I) complexation with the 18-crown-6 ether was studied using a calorimetric method. Increase in the DMF concentration was found to cause a decrease in the reaction exothermicity. The determining factor in the change of the reaction enthalpy is shown to be the increased solvation of the central ion.

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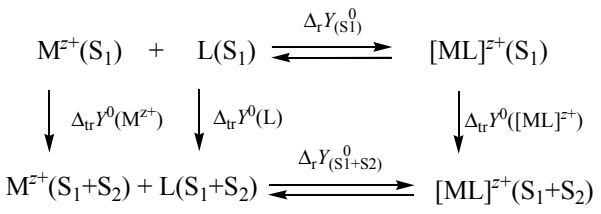
The determining role in a variety of chemical and physicochemical properties of solutions and processes occurring in them belongs to solvation [1,2]. Earlier [3] the effect of methanol (MeOH)–dimethylformamide (DMF) solvents composition (χ_{DMF} = 0.0 to 1.0 ppm) on the stability of $[Ag18C6]^+$ has been studied. In this study, by the calorimetric method the formation enthalpies of the silver(I) crown complexes were obtained over the entire range of compositions of binary nonaqueous solvents MeOH–DMF, and the contributions of the reagent into the $\Delta_r H$ variations were analyzed.

We discuss the results obtained basing on the solvation-thermodynamic approach [1], which allows us to consider the effect of solvent on the complexation reaction in terms of thermodynamic functions of the reagents solvation (transfer) ($\Delta_{tr}Y^0$). In accordance with the thermodynamic cycle:



The change in thermodynamic characteristics of the complexation reaction in a solvent (S_1) compared with the other solvent (S_2) can be represented as follows:

$$\Delta_{tr}Y^0_r = \Delta_{tr}Y^0([ML]^{z+}) - \Delta_{tr}Y^0(M^{z+}) - \Delta_{tr}Y^0(L), \qquad (1)$$

where $\Delta_{tr}Y^0_r$ are thermodynamic functions ($\Delta_{tr}G^0$, $\Delta_{tr}H^0$, $T\Delta_{tr}S^0$) of transfer of the reaction from one solvent to another; $\Delta_{tr}Y^0([ML]^{z+})$, $\Delta_{tr}Y^0(M^{z+})$, and $\Delta_{tr}Y^0(L)$ are the thermodynamic functions of transfer of the corresponding reagent.

Replacing the amphoteric MeOH by basic DMF causes a marked decrease in exothermicity of the reaction of the silver(I) crown complex formation (at 298.15 K):

χ_{DMF}, mole fraction	0.0	0.2	0.4	0.6	0.8	1.0
$\Delta_r H^0$, kJ mol^{-1}	–36.46	–30.58	–23.58	–18.13	–16.10	–15.86

The figure shows the dynamics of the solvation contributions of the reactants to the change in the enthalpy of the reaction of $[Ag18\text{-crown-}6]^+$ formation at replacing methanol by dimethylformamide.

The solvation state of the ligand is changed only slightly (see the figure), and it is not a dominant factor in changing the energy of the reaction complex. In contrast to the complex formation in aqueous-organic solvents [6–8], the change in the absolute value of the reaction enthalpy exceeds the $\Delta_{tr}H^0(18Crown6)_{MeOH\rightarrow DMF}$ value significantly.

It is obvious that the growth of exothermicity of the silver(I) solvation with increasing concentration of

DMF provides the strengthening of the donor–acceptor interaction of the solvent with the ion due to the higher donor capacity of DMF in comparison with methanol. Apparently, the solvation effect of the central ion is the determining factor in changing the reaction enthalpy. This is a significant distinguishing feature of the results obtained from the thermodynamic data of complexation of the *d*-metal ions with the ligands of the amine and carboxylate types in the water-organic solvents, where the reactions energetics is determined by the changes in the solvation state of the ligands at the full or partial compensation of the solvation contributions of central and complex ions [6–8].

At replacing methanol by dimethylformamide, the $\Delta_{tr}H^0(Ag^+)$ values are changed by about 30 kJ mol^{-1}, while the change in the solvation enthalpy of the complex ion does not exceed 10 kJ mol^{-1} (see the figure), and by the nature of the dependence is closer to a change in the solvate state of the ligand. Apparently, this is due to the fact that at the formation of the metal crownate the central ion is included in the coordination sphere formed by the ligand. The metal ion is located in the inner cavity of the crown ether, and therefore is largely unable to form solvate-comlexes with the solvent molecules. Hence, we can assume that the solvation state of the complex ion in solution is determined to a greater extent by the solvation state of the ligand.

A difference in solvation of the silver(I) crown ether complex and the crown ether itself leads to some decrease in the solvation effect of the central ion, but to a lesser extent than the change in $\Delta_{tr}H^0(Ag^+)$. The values $\{\Delta_{tr}H^0([ML]^{z+}) - \Delta_{tr}H^0(L)\}$ vary proportionally to the solvation state of Ag^+ with the proportionality coefficient *k*:

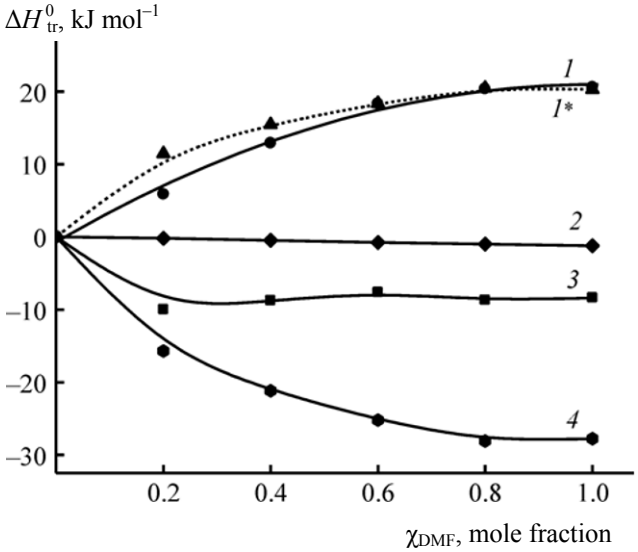
$$\{\Delta_{tr}H^0([Ag18K6]^+) - \Delta_{tr}H^0(18K6)\} = k\Delta_{tr}H^0(Ag^+). \quad (2)$$

In the region of DMF concentration above 0.4 ppm the proportionality factor is equal to 0.27±0.04 and varies little with the solvent composition.

Based on the above, taking into account relation (2), and by analogy with [8], the solvatothermodynamic solvent effect (1) can be represented as a function of two variables: the coefficient of proportionality, and the enthalpy change of the central ion transfer:

$$\Delta_{tr}H^0_r = k\Delta_{tr}H^0(Ag^+) - \Delta_{tr}H^0(Ag^+) = (k-1)\Delta_{tr}H^0(Ag^+). \quad (3)$$

Using relation (3), we calculated change of the enthalpy in the reactions of Ag^+ complexation with 18-crown-6 at the replacing the solvent MeOH → DMF. As can be seen from the figure, the results of calculation of $\Delta_{tr}H^0_r$ give a satisfactory description of the experimental data with pairing correlation coefficient 0.96. Hence, the relation (3) has a predictive character, which allows the evaluation of the change in exothermicity of the complexation reaction at the replacing one solvent by another, proceeding from the changes in the solvation enthalpy of the complexed ion. It can be assumed that similar patterns can be revealed in the analysis of the Gibbs energy of complexation reactions and solvation of reagents in binary mixtures of non-aqueous solvents.



Effect of composition of the methanol–dimethylformamide bitary solvent on the change in the formation enthalpy of $[Ag18\text{-crown-}6]^+$, (*1*) $\Delta_{tr}H^0_{r\,exo}$, (*1**) $\Delta_{tr}H^0_{r\,calc}$, and solvation of the reagents: (*2*) 18-crown-6 [4], (*3*) $[Ag18\text{-crown-}6]^+$, and (*4*) Ag^+ [5].

EXPERIMENTAL

To determine the heat effects of complexation reaction we used a variable temperature calorimeter with an isothermal jacket, similar to that described in [9]. During the experiment, we measured the magnitude of the heat of mixing (q_{mix}) of the 18C6 solution (C^0 ~5×10^{-1} M) in an ampule with a solution of $AgClO_4$ (C^0 ~2×10^{-2} M) placed in the reaction vial in the cell (solutions in the ampule and the reaction vial have identical binary compositions). In a separate experiment we measured the heat of dilution of the solution of the ligand in the binary solvent of the same composition (q'_{dil}). Heat of mixing solutions of metal

salt and ligand contains the following thermal contribution: $q_{mix} = q_r + q'_{dil} + q''_{dil}$, where q_r is the heat of the complexation reaction, J; q'_{dil} is the heat of dilution of the solution of the ligand in the mixture, J; q''_{dil} is the heat of dilution of the $AgClO_4$ solution, located in the calorimetric vial, with the solution of ligand, J.

The solution volume in the reaction vial increased during the experiment by about 1%, so the value of q''_{dil} was negligible, which allowed us to exclude it from the equation for calculating the complexation reaction enthalpy. On this basis, the molar enthalpy of complexation ($\Delta_r H_i^m$) can be calculated using the following Eq. (4):

$$\Delta_r H_i^m = \Delta_{mix} H_i^m - \Delta_{dil} H_i^{m'}, \quad (4)$$

where $\Delta_{mix} H_i^m$ and $\Delta_{dil} H_i^{m'}$ are molar enthalpies of mixing and dilution, respectively, per 1 mol of the ligand in the ith experiment.

The complexation enthalpies were calculated using the HEAT software [10] taking into account the reaction incompleteness. In the calculations the values of stability constants of the silver(I) crown complexes were used obtained by potentiometric method [3].

In the course of the calorimetric measurements, the solution ionic strength created by the reactants was 2×10^{-2} to 3×10^{-1} M and did not change. For such small values of the ionic strength the effect of the ion environment on the reaction of $[Ag18C6]^+$ is negligible, so the thermodynamic functions ($\Delta_r H$) obtained were considered to be standard values for these quantities. The maximum error in the $\Delta_r H$ did not exceed ±0.9 kJ mol^{-1}, it was determined as the standard mean square deviation based on the Student's test at a confidence probability of 0.95 for a series of experiments with each composition of the mixed solvent.

The procedures for the preparing the reagents are similar to those described in [3].

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