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Complex Formation of Silver(I) with 18-Crown-6 in Methanol–DMF Binary Mixtures

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Abstract—Dependence of the stability of the silver(I)–18-crown-6 complex on the composition of the binary methanol–DMF solvent was studied potentiometrically. It was found that the increase in DMF content in the binary mixture decreased the stability of the coordination compound. New approach to analysis of the solvation contributions of reagents in the variation of Gibbs energy while substitution of solvent with another one was suggested. It was shown that the shift in the complex formation equilibrium is determined by variation in the solvate state of the central ion.

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A series of our recent publications [1–3] permitted the establishment of certain rules describing the effect of water–organic solvents on complex formation of *d*-metal ions with the amine and carboxylate ligands. On this basis a conclusion was made about the possibility of performing the estimating calculation of the stability constants and heat effects of complex formation reactions while substitution occurs of water with organic solvent [4]. The predictive ability of the rules established was confirmed in [5–7] in the course of investigation of complex formation of the Ag^+ ion with 18-crown-6 in water–ethanol and water–DMSO mixtures. Data on the thermodynamic characteristics of complex formation and the solvation of the reagents for the mixtures of nonaqueous solvents are scarce. Performing the investigations in binary nonaqueous solvents and the classification of experimental data will permit to establish general principles of the effect of nature and composition of the medium on complex formation. It will be an important stage in the creation of scientific basis for solvent selection as the way of managing the liquid phase processes.

In the work presented the effect of composition of the mixed methanol–DMF solvents (χ_{DMF} 0.0–1.0 ppm) on the stability of silver(I) complexes with crown ethers was studied.

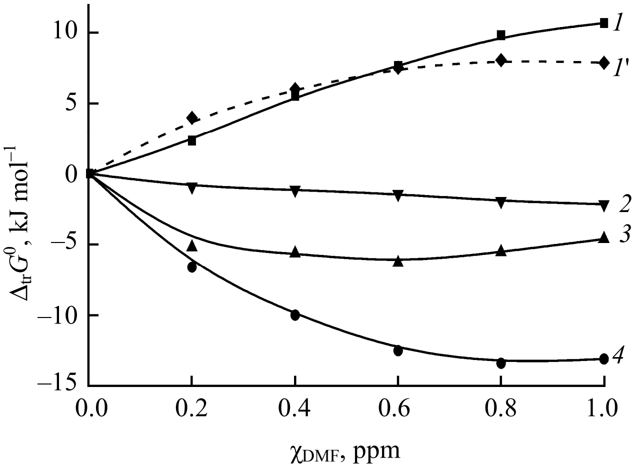
It was found that the transfer from methanol to DMF causes the significant decrease in the stability of the coordination compound formed. The corresponding stability constants of $[Ag(18\text{-crown-6})]^+$ in methanol–DMF mixtures at 298.15 K are as follows:

χ_{DMF}, ppm	0	0.2	0.4	0.6	0.8	1.0
$\log K^0 \pm 0.10$	4.33	3.92	3.36	2.99	2.61	2.46

The treatment of the experimental data was carried out from the position of the solvation approach based on thermodynamic characteristic of the solvation of each member of the chemical equilibrium [11]. According to the thermodynamic cycle of transfer of complex formation from the individual solvent (S_1) to the binary (S_1+S_2) the variations in Gibbs energy of reagents determine the changes in the stability of complex at the variation in composition of the mixed solvent [Eq. (1)].

$$\begin{tikzcd}
M(S_1) \arrow[d, "\Delta_{tr}Y^0(M)"] & + & L(S_1) \arrow[d, "\Delta_{tr}Y^0(L)"] \arrow[r, shift left, "\Delta_rY^0(S_1)"] & ML(S_1) \arrow[l, shift left] \arrow[d, "\Delta_{tr}Y^0(ML)"] \\
M(S_1+S_2) & + & L(S_1+S_2) \arrow[r, shift left, "\Delta_rY^0(S_1+S_2)"] & ML(S_1+S_2) \arrow[l, shift left]
\end{tikzcd}$$

Here $\Delta_rY^0(S_1)$ and $\Delta_rY^0(S_1+S_2)$ are standard thermodynamic characteristics (Δ_rG^0, Δ_rH^0, $T\Delta_rS^0$) of the reaction in the solvents S_1 and (S_1+S_2); $\Delta_{tr}Y^0(M)$, $\Delta_{tr}Y^0(L)$, $\Delta_{tr}Y^0(ML)$ are the variations in standard thermodynamic characteristics of reagents at the



The effect of composition of the methanol–DMF solvent on the variation in Gibbs energy of the reaction of formation of the Ag^+ complex with 18-crown-6: (*1*) $\Delta_{tr}G^0_r$(exp.), (*1′*) $\Delta_{tr}G^0_r$(calc.), (*2*) the solvation of reagents: 18-crown-6 (2) [9], (*3*) $[Ag18C6]^+$, and (*4*) Ag^+ [10].

transfer from the individual solvent S_1 to the binary one $[S_1+S_2)]$.

$$-RT\ln [K^0(S_1+S_2)/K^0(S_1)]$$
$$= \Delta_{tr}G^0_r = \Delta_{tr}G^0(ML) - \Delta_{tr}G^0(M) - \Delta_{tr}G^0(L), \quad (1)$$

where $\Delta_{tr}G^0_r$ are the Gibbs energy of transfer of the reaction from the individual solvent S_1 to the binary one (S_1+S_2).

Analogous thermodynamic relationships are used for analysis of the enthalpy and entropy characteristics of processes of the complex formation and the solvation of reagents in solutions within the frames of the solvation thermodynamic approach. While using this approach in thermodynamics of complex formation between metal ions and the amine or carboxylate ligands it was suggested [1] to present the solvation thermodynamic effect of solvent as a sum of two increments, namely, the solvation effect of ions $[\Delta_{tr}Y^0(ML) - \Delta_{tr}Y^0(M)]$ and the salvation effect of ligand $[\Delta_{tr}Y^0(L)]$. It resulted in establishing of a series of rules describing the variations in thermodynamic characteristics of the reaction and the solvation of reagents [4] permitting to predict the variation in stability of coordination compounds and the enthalpies of the reactions of their formation on the basis of variation of the solvate state of the ligand.

Such approach is based on the statement that in the reactions of formation of the amine and carboxylate complexes of *d*-metal ions coordination sphere $[ML]^{z+}$ is formed by the complex forming ion. In the course of formation of metal crown ether complexes the central ion enters the coordination sphere formed already by the ligand. The metal ion located in the inner cavity of crown ether can hardly form the solvatocomplexes with the molecules of solvent. On the basis of this statement it can be suggested that the solvate state of complex ion in solution is determined mainly by the solvate state of ligand. In this case the solvation thermodynamic effect of solvent [Eq. (1)] can be better described as the sum of contributions including the differences in solvation of complex ion and the ligand $[(\Delta_{tr}Y^0(ML) - \Delta_{tr}Y^0(L)]$ and the solvation effect of metal $[\Delta_{tr}Y^0(M)]$.

Dynamics of solvation contributions of reagents in the variation in stability of silver(I) crown ether complex at the transfer from methanol to DMF is shown in the figure. As seen, the variation in the composition of mixed solvent leads to the increase in the solvation of all the members of the chemical equilibrium.

The substitution of amphoteric MeOH with the basic DMF insignificantly changes the solvate state of the ligand and cannot be considered as a decisive factor in the variation in the stability of the obtained complex. Unlike the complex formation with the amine and carboxylate ligands [1–3], the variation in the absolute value of Gibbs energy of the reaction is significantly higher than $\Delta_{tr}G^0(18C6)_{MeOH\rightarrow DMF}$. The difference in the solvation of the complex ion and the ligand are not large and do not exceed the effect of variation in the solvate state of the complex-forming ion (see the figure). The contribution from the increase in the solvation of Ag^+ arising from the increase in the donor-acceptor interaction between the ion and the solvent [12] is only partially compensated by the solvation contribution of $[\Delta_{tr}G^0([Ag18C6]^+) - \Delta_{tr}G^0(18C6)]_{MeOH\rightarrow DMF}$. The solvation of the complex ion with DMF is to some extent stronger as compared to the ligand. It may be assumed that the additional contribution in solvation of the complex ion is provided by the interaction of Ag^+ with the molecules of solvent.

The variation in $\Delta_{tr}G^0(Ag^+)$ is practically the mirror image of the variation in $\Delta_{tr}G^0_r$ (see the figure). The effect of solvation of the central ion plays the main part in the stability variation of [Ag18C6]. Differences in the variation of the complex ion and the ligand solvation are proportional to the variation in the solvate state of Ag^+ ion. The proportionality coefficient calculated from the equation varies in the range 0.4±0.2.

$$k = [\Delta_{tr}G^0([\mathrm{Ag18C6}]^+) - \Delta_{tr}G^0(\mathrm{18C6})]/[\Delta_{tr}G^0(\mathrm{Ag}^+)].$$

Using the relationship obtained on the basis of Eq. (1) values of variation in Gibbs energies of complex formation of Ag^+ ion with 18-crown-6 taking place at the varying the solvent composition (MeOH→DMF) were calculated.

$$\Delta_{tr}G_r^0 = (k-1)\cdot[\Delta_{tr}G^0(\mathrm{Ag}^+)].$$

As seen from the figure, the results of $\Delta_{tr}G_r^0$ calculations give quite satisfactory description of the experimental data. Thus on the basis of variation in the solvate state of the starting reagents it is possible to predict the variation in thermodynamic functions of complex formation proceeding in binary mixtures of nonaqueous solvents. But for the establishing of general principles of the effect of nature and the composition of solvent on the processes of complex formation in solutions further studies of this problem must be performed.

EXPERIMENTAL

18-Crown-6 (Merck, chemically pure grade) was dried in a vacuum at room temperature for seven days. Silver perchlorate was prepared according to [12]. The substance obtained was dried in a vacuum at 60–70°C for 10 days. $K[Ag(CN)_2]$ was prepared according to [13]. Methanol of the superfine grade and DMF of the chemically pure grade were dried according to the procedures described in [14]. Water content in solvents was evaluated by Fischer method: methanol contained 0.009 wt %, and DMF, 0.01 wt % of water.

The evaluation of the stability constants of silver(I) crown ether complexes in the mixed nonaqueous MeOH–DMF solvents was carried out potentiometrically without the salt background using the following the electrochemical circuit consisting of two silver electrodes. Their electrochemical potential was reproduced in nonaqueous media with the accuracy ±0.1 mV.

$$\begin{array}{c|c||c|c} \mathrm{Ag} & \text{MeOH–DMF,} & \text{MeOH–DMF,} & \mathrm{Ag} \\ & \mathrm{AgClO_4}, \text{18C6} & \mathrm{AgClO_4} & \end{array}$$

Silver electrodes were prepared by coating the platimun net with silver by its electrochemical precipitation from the $K[Ag(CN)_2]$ solution. Working capacity of the electrode system was checked by its calibration with $AgClO_4$ solutions in the concentration range 1.5×10^{-3}–7.8×10^{-2} mol l^{-1} for each composition of the mixed solvent. The choice of concentration conditions for potentiometric measurements and calculation of the stability constants for $[Ag18C6]^+$ from the experimental data were carried out by means of the PHMETR program. The average from the obtained values of the stability constants of silver(I) crown ether complex at the ion force ~5×10^{-3}–1.0×10^{-2} created by silver perchlorate and complex ion was accepted as the standard meaning of this value. The largest log K^0 error was no more than 0.1 logarithmic unit. It was determined as the standard mean square deflection with the consideration of Student criterion at the confidence probability 0.95 for the series of experiments (3) and (4) for each composition of each solvent.

REFERENCES

1. Shormanov, V.A. and Sharnin, V.A., *Dostizheniya i problemy teorii solvatatsii: Strukturno-termodinamicheskie aspekty* (Achievements and Problems of the Solvation Theory: Structural and Thermodynamic Aspects), Moscow: Nauka, 1998, p. 172.
2. Sharnin, V.A., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 9, p. 1421.
3. Sharnin, V.A., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 9, p. 1452.
4. Sharnin, V.A., *Koord. Khim.*, 1996, vol. 22, no. 5, p. 418.
5. Usacheva, T.P., Ledenkov, S.F., Gzheidzyak, A., and Sharnin, V.A., *Izv. Vysshikh Uchebnykh Zavedenii, Ser. Khim., Khim. Tekhnol.*, 2000, vol. 43, no. 5, p. 87.
6. Usacheva, T.R., Ledenkov, S.F., Sharnin, V.A., and Gzheidzyak, A., *Koord. Khim.*, 2001, vol. 27, no. 3, p. 222.
7. Usacheva, T.R., Sharnin, V.A., and Ledenkov, S.F., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 5, p. 754.
8. Ignaczak, M. and Grzejdziak, A., *Monatsh. Chem.*, 1984, vol. 115, p. 943.
9. Brown, A.S., *J. Am. Chem. Soc.*, 1934, vol. 56, p. 646.
10. Golikov, A.N., Kuz'mina, I.A., and Sharnin, V.A., *Izv. Vysshikh Uchebnykh Zavedenii, Ser. Khim., Khim. Technol.*, 2007, vol. 50, no. 12, p. 18.
11. Krestov, G.A., *Termodinamika ionnykh protsessov* (Thermodynamics of Ionic Processes), Leningrad: Khimiya, 1984.
12. Moshorin, G.V., Repkin, G.I., and Sharnin, V.A.*, Zh. Fiz. Khim.*, 2006, vol. 80, no. 2, p. 215.
13. Golikov, A.N., Kuz'mina I,.A., and Sharnin, V.A., *Izv. Vysshikh Uchebnykh Zavedenii, Ser. Khim., Khim. Tekhnol.*, 2007, vol. 50, no. 9, p. 38.
14. Stroka, J. and Schneider, H., *Polish J. Chem.*, 1980, vol. 54, p. 1805.