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Variation of Thermodynamic Parameters of Crown Ether–Metal Complex Formation and Reactant Solvation in Binary Nonaqueous Solvent Mixtures

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Abstract—General trends in the variation of thermodynamic parameters of complex formation of crown ethers with *d*-metal ions in binary nonaqueous solvent mixtures were determined. An equation was proposed for predicting variation of the stability of coordination compounds upon replacement of one nonaqueous solvent by another on the basis of the change in the Gibbs energy of solvation of the central ion. Calculation of the Gibbs energies for the formation of the $[Ag18C6]^+$ ion in acetonitrile and a number of nonaqueous solvents confirmed the predictive ability of the proposed equation.

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Solvent not only acts as a medium in liquid-phase reactions but also actively participates in interactions with the dissolved reactants (various types of solvation); on the other hand, the solute affects the solvent structure [1, 2]. Solvent may displace equilibrium in complex formation processes and essentially affect their rate and mechanism. Therefore, it is impossible to understand complicated processes occurring in solution without studying solvation of the reacting and resulting species.

In terms of the solvation–thermodynamic approach [3], transfer of a complexation reaction from a pure solvent to a binary mixture may be represented by the following scheme.

$$\begin{tikzcd}
M^{Z+}(S_1) \arrow[d, "\Delta_{tr}Y(M^{Z+})"] & + & L(S_1) \arrow[d, "\Delta_{tr}Y(L)"] \arrow[r, shift left, "\Delta_{r}Y_{S1}"] & {[ML]^{Z+}(S_1)} \arrow[l, shift left] \arrow[d, "\Delta_{tr}Y([ML]^{Z+})"] \\
M^{Z+}(S_1 + S_2) & + & L(S_1 + S_2) \arrow[r, shift left, "\Delta_{r}Y_{S1+S2}"] & {[ML]^{Z+}(S_1 + S_2)} \arrow[l, shift left]
\end{tikzcd}$$

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

Variations of the complexation thermodynamic parameters $\Delta_{tr}Y_r$ in one solvent (S_1) relative to those in another solvent (S_2) may be expressed through the change of the thermodynamic parameters of solvation of the reactants [Eq. (1)].

$$\Delta_{tr}Y_r = \Delta_{tr}Y([ML]^{z+}) - \Delta_{tr}Y(M^{z+}) - \Delta_{tr}Y(L). \quad (1)$$

As shown previously for the formation of amine nickel(II) complexes in mixed aqueous–organic medium [4], the range of $\Delta_{tr}Y_r$ values does not exceed the range of variation of the corresponding thermodynamic function for ligand transfer $\Delta_{tr}Y(L)$, taken with the opposite sign. It was found later [5] that such relationship is general for the thermodynamics of the formation of amine and carboxylate complexes of *d*-metals (Ni^{2+}, Cu^{2+}, Cd^{2+}, Ag^+), as well of some *s*-, *p*-, and *f*-elements in aqueous–organic solvent mixtures. This relationship may be written as follows.

$$0 \le |\Delta_{tr}Y_r| \le |\Delta_{tr}Y(L)| \text{ and } (\Delta_{tr}Y_r)\,[\Delta_{tr}Y(L)] \le 0.$$

It was also found [5] that the differences in the variation of the solvation parameters of the central ion and the complex $[\Delta_{tr}Y([ML]^{z+}) - \Delta_{tr}Y(M)^{z+}]$ in absolute value are proportional to $\Delta_{tr}Y(L)$ [Eq. (2)].

$$\{\Delta_{tr}Y([ML]^{z+}) - \Delta_{tr}Y(M)^{z+}\} = f[\Delta_{tr}Y(L)] = \alpha_d[\Delta_{tr}Y(L)]. \quad (2)$$

Here, the proportionality coefficient α_d ranges from 0 to 1, depending on the metal and ligand nature, and it

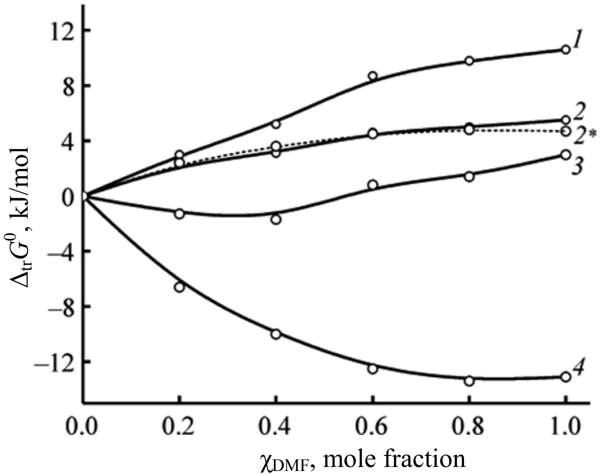

Fig. 1. Plots of the Gibbs energies of formation of $[AgDipy]^+$ and solvation of the reactants versus mole fraction of DMF in binary methanol–DMF mixtures: (*1*) $\Delta_{tr}G^0_{bipy}$ [19], (*2*) $\Delta_{tr}G^0_{r1exp}$ [7], (*2′*) $\Delta_{tr}G_{r1calc}$, (*3*) $\Delta_{tr}G^0([Agbipy]^+)$; (*4*) $\Delta_{tr}G^0(Ag^+)$ [20]. Curve *3* was plotted for the data calculated by Eq. (1).

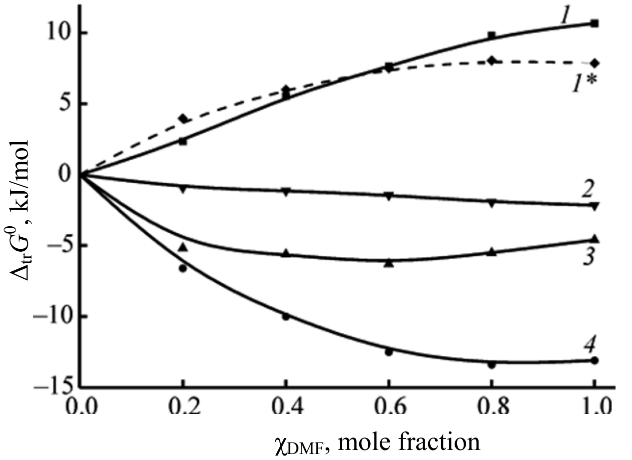

Fig. 2. Plots of the Gibbs energies of (*1*, *1′*) formation of $[Ag18C6]^+$ and (*2*–*4*) solvation of the reactants versus mole fraction of DMF in binary methanol–DMF mixtures: (*1*) $\Delta_{tr}G^0_{r\,exp}$, (*1′*) $\Delta_{tr}G_{r\,calc}$, (*2*) $\Delta_{tr}G^0(18C6)$, (*3*) $\Delta_{tr}G^0([Ag18C6]^+)$, (*4*) $\Delta_{tr}G^0(Ag^+)$ [9].

generally does not depend on the composition of aqueous–organic solvent.

Analysis of our own and published data allowed us to determine the most probable ranges of the α_d values for the complexation of *d*-metals with amine and carboxylate ligands [6]. This made it possible to estimate the stability constants of the complexes and enthalpies of their formation in aqueous–organic solvent mixtures from variations of the thermodynamic parameters for ligand solvation according to equations like Eq. (3).

$$\Delta_{tr}Y_r = (\alpha_d - 1)\Delta_{tr}Y(L). \quad (3)$$

At present, studies on the relationships between the thermodynamic parameters for complexation and reactant solvation in binary nonaqueous solvent mixtures are confined to accumulation of experimental data.

Table 1. Gibbs energies for Ag^+ ion transfer from acetonitrile to some organic solvents at 298.15 K

Solvent	$\Delta_{tr}G(Ag^+)$,[a] kJ/mol	
	Ph_4AsBPh_4	bis(biphenyl)-chromium(I)/(0)
Dimethylformamide	5	8
Dimethyl sulfoxide	–12	–7 (–9.9)[b]
Ethanol	29	24
Methanol	30	30
Propylene carbonate	38	47
Acetone	30	28
2,2,2-Trifluoroethanol	71	

[a] The $\Delta_{tr}G(Ag^+)$ values were obtained by division of stoichiometric ion mixtures into ion constituents on the basis of tetraphenylarsonium tetraphenylborate (Ph_4AsBPh_4) and bis(biphenyl)chromium(I)/(0) assumptions [11]. [b] Potentiometric data [12].

Table 2. Experimental and calculated Gibbs energies for the transfer of the complexation of Ag^+ with 18C6 from acetonitrile to some organic solvents at 298.15 K

Solvent	$\Delta_{tr}G_r$, kJ/mol	
	experimental	calculated
Dimethylformamide	8.32 [9, 13]	–2.9, –4.64
Dimethyl sulfoxide	3.25 [13]	6.96, 4.06, 5.75
Ethanol	–14.91 [13, 14], –13.49 [13, 15]	–16.82, –13.92
Methanol	–18.97 [9, 13]	–17.40, –17.40
Propylene carbonate	–34.77 [13, 14], –33.46 [13, 17]	–22.04, –27.26
Acetone	–24.33 [13, 14], –21.64 [13, 18]	–17.40, –16.24
2,2,2-Trifluoroethanol	–41.16 [13, 14]	–41.18

We previously [7–9] analyzed thermodynamic parameters of the complexation of silver(I) ions with 2,2′-bipy-ridine (bipy) and 18-crown-6 (18C6) in methanol–dimethylformamide mixtures and revealed a number of differences from the corresponding data obtained in aqueous–organic mixtures. In particular, we found that the solvation of the complex ion is largely determined by the solvation of the ligand and that the difference in the variation of the Gibbs energy of solvation of the complex ion and ligand in the complexation of Ag^+ with 18C6 is smaller than in the complexation with the heterocyclic amine (Figs. 1, 2). This may be rationalized by essential desolvation of the metal ion as a result of its interaction with crown ether in solution. The coordination sphere in the crown ether complex is relatively large, and it completely or partially isolates the metal ion from the solvent, acting as structured solvate shell. Desolvation of the central ion by the crown ligand is also favored by almost perfect conformity of the crown ether cavity (2.6–3.2 Å [10]) to the Ag^+ ion diameter (2.52 Å [10]).

It was also found that the difference in the variation of the Gibbs energy of solvation of the complex ion and ligand in going from one nonaqueous solvent to another does not exceed $\Delta_{tr}G$ for the metal ion and that the difference $(\Delta_{tr}G(ML^+) - \Delta_{tr}G(L)$ in absolute value is proportional to $\Delta_{tr}G(Ag^+)$:

$$\{\Delta_{tr}G([ML]^+) - \Delta_{tr}G(L)\} = f[\Delta_{tr}G(Ag^+)] = k\Delta_{tr}G(Ag^+). \quad (4)$$

Here, the coefficient k depends only slightly on the binary solvent composition and is 0.42±0.18 for the formation of $[Ag18C6]^+$ and 0.64±0.05 for the formation of $[Agbipy]^+$. Therefore, by analogy with [5], rearrangement of the reactant solvation contributions in Eq. (1) leads to Eq. (5):

$$\Delta_{tr}Y_r = k\Delta_{tr}Y(Ag^+) - \Delta_{tr}Y(Ag^+) = (k-1)\Delta_{tr}Y(Ag^+). \quad (5)$$

Using Eq. (5) we calculated variations of the Gibbs energies of complex formation of Ag^+ with 18-crown-6 and 2,2′-bipyridine upon increase of the DMF fraction in binary MeOH–DMF mixtures. Figures 1 and 2 demonstrate quite satisfactory agreement between the calculated $\Delta_{tr}G_r$ values and experimental data. Thus, Eq. (5) possesses predictive power, i.e., change of the stability of complex ions formed by d-metals and large heterocyclic ligands upon replacement of one nonaqueous solvent by another may be estimated on the basis of variation of the Gibbs energy of solvation of the central ion.

Using published data on the Gibbs energies of silver(I) ion transfer from acetonitrile to dimethyl sulfoxide [11, 12], dimethylformamide [11], ethanol [11], methanol [11], propylene carbonate [11], acetone [11], and 2,2,2-trifluoroethanol [11] (Table 1) we calculated by Eq. (5) variations of the Gibbs energies for the complexation of Ag^+ with 18-crown-6 in going from acetonitrile to another organic solvent. The coefficient k was assumed to be equal to 0.42. The calculated values ($\Delta_{tr}G_{r\,calc}$) are collected in Table 2. From our experimental data on the Gibbs energies of formation of $[Ag18C6]^+$ in acetonitrile [13], DMSO [13], MeOH [9], and DMF [9] and $\Delta G_r([Ag18C6]^+)$ values in EtOH, propylene carbonate, acetonitrile, and 2,2,2-trifluoroethylene, calculated from the stability constants of $[Ag18C6]^+$ in these solvents [14–18], we obtained the experimental Gibbs energies $\Delta_{tr}G_{r\,exp}$ for the transfer of the complexation reaction from acetonitrile to the corresponding organic solvent. As follows from the data in Table 2, fairly good correlation is observed in most cases between the experimental $\Delta_{tr}G_r$ values and those calculated by Eq. (5), despite the use of different $\Delta_{tr}G(Ag^+)$ values.

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