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Formation of Molecular Complexes between 18-Crown-6 and Amino Acids in Aqueous-Organic Media

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Abstract—Data on the effect of aqueous-organic solvent composition on molecular complexes formation of 18-crown-6 with glycine, D,L-alanine, and L-phenylalanine have been generalized. The inncrease in ethanol, dimethylsulfoxide, or acetone fraction enhances the complexes stability. Amino acid solvation gives the major impact on the Gibbs free energy of complexes formation. It was demonstrated that stability of 18-crown-6 complexes with amino acids could be predicted basing on changes of the amino acid solvation state.

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Study of intermolecular interactions of solvated biomolecules with macrocyclic ligands can potentially resolve many topical issues of both fundamental and applied science. For instance, molecular complex formation is a clue to the vitally important biomolecules self-organization and their ability to recognize and response to external chemical factors. Molecular recognition in macrocycle-containing biological systems accompanies processes of enzymatic catalysis, membrane transport, and immune response [1–11]. Studies of complexing properties of synthetic macrocyclic molecules like crown ethers can provide simplified but applicable models of molecular recognition in biological systems; their results are also important for development of modern molecular devices and nanomaterials [3, 9, 10, 12].

Guest molecules are recognized by the *host* following the complementarity principle [1–3]; therefore, all the existing fields of synthetic macrocyclic crown ethers application are based on their unique feature to preferentially bind certain cations and neutral molecules. When the complex is formed in the medium other than water, the change of the components solvation state is the additional factor determining the components reactivity and thermodynamic parameters of the reaction [13].

Synthesis, study and application of macrocycles molecular complexes with amino acids and peptides in water are restricted by the hydrating properties of water as the medium of the proceeding processes, therefore the complex formation in water is often characterized by the low stability and poor solubility of the molecular complexes [14–24]. In nonaqueous solvents macrocycles generally form stable molecular complexes, and the complex formation reactions are highly exothermic [25–33].

The stabilizing effect of organic solvents is due to the changes in the solvation state of the components. Therefore, proper choice of the solvent can optimize the conditions so that a complex with certain predefined properties (stability or enthalpy of formation) is prepared. The solvent should not be necessarily a monocomponent liquid; moreover, using binary solvents with adjustable components ratio gives wider range of the solvent physicochemical properties, including the solvation ability.

Studies of the formation of *d*-metals complexes with amines, carboxylate ligands, and crown ethers have revealed some correlations between the reagents solvation state and the reaction thermodynamics [34–41], allowing prediction of the coordination compounds stability and their formation enthalpy in different media.

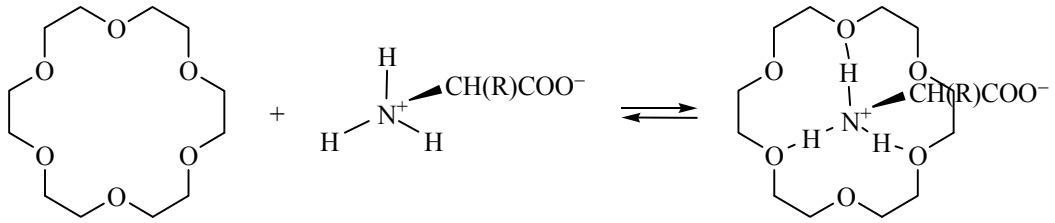
Hence, in order to choose proper solvent for providing of molecular complex formation reaction, it is necessary to investigate the effect of the solvation state of the components on the complex formation equilibrium and to find the main solvation factors

governing the thermodynamic parameters of the reaction at the change in the solvent composition.

In this work we present generalization of our own and published data on solvation effect on thermodynamic of the complex formation between selected amino acids and 18-crown-6 ether (18C6).

We have studied the influence of the mixed solvents (H_2O–EtOH, H_2O–DMSO, and H_2O–acetone) composition on the reactions of 18C6 with glycine (Gly), D,L-alanine (Ala), and L-phenylalanine (Phe). For these system the analysis was performed of the solvation-thermodynamic contribution of the reagents into the thermodynamic parameters of the reactions, and impact of the components solvation was revealed governing the changes in the complex stability and the ethalpy of complex formation.

Formation of the molecular complex of 18C6 with amino acids (AA, frequently present in the solution in the zwitter-ion form [42]) can be expressed by scheme (1).



$$18C6_{solv} + AA_{solv} \rightleftarrows [AA–18C6]_{solv}. \quad (1)$$

X-ray diffraction studies have shown that amino acid molecule interacts with 18C6 via the NH_3^+ group. In the crystalline state the binding occurs via three NH···O hydrogen bonds and three $N^+\cdots O^{\delta-}$ electrostatic (ion-dipole) bonds [29, 30, 43, 44].

Our own [45] and published NMR studies [15–17, 46, 47] and computer simulation results [30] have confirmed that the above-stated mechanism is operative in aqueous solutions as well. For example, in the ^1H NMR spectra of Phe aqueous solution, the H^2–H^8 signals have been resolved in the presence of 18C6 [45]. The chemical shifts of H^7 and H^8 have been changed the most significantly, thus pointing at Phe coordination with 18C6 via the NH_3^+ group (Fig. 1).

^{13}C NMR data [15–17] have additionally confirmed that the NH_3^+ group is the site of amino acids complex formation with 18C6 in aqueous solutions. The largest chemical shift changes have been observed in the cases of the COO^- group signal and that of the $C–NH_3^+$ carbon atom. However, carboxylate group is not involved in binding with the ether, and its signal change is due to solvation. Polar and aliphatic side groups of some amino acids are capable of interaction with the macrocycle and thus can sterically affect the NH_3^+ group coordination [15–17].

Review of the available literature has shown that no generalized correlations have as yet been found between the [AA–18C6] molecular complexes stability, the amino acid structure, and the solvent nature. Thermodynamics of complex formation between 18C6 and a series of amino acids in water and in alcohols has been studied in [15–17, 25, 27, 29, 30]. In ethanol and methanol [29, 30], the complexes stability constants have been close for all the studied systems; therefore, 18C6 is insensitive to the recognition of amino acid in alcoholic medium. However, enthalpies of the complex formation have been different; in other words, the binding is enthalpy-selective [29, 30]. In water, linear correlation has been observed between the molecular complex formation enthalpy and hydration enthalpy of the amino acid [17, 18].

Thermodynamics of the [Gly–18C6], [Ala–18C6], and [Phe–18C6] molecular complex formation in aqueous ethanol, dimethyl sulfoxide, and acetone has been studied by means of entropy titration in [45, 47–52]. Processing of the termochemistry method named calorimetric titration data using HEAT software [53] has allowed determination of several thermodynamic parameters ($\log K^0$, $\Delta_r G^0$, $\Delta_r H^0$, and $T\Delta_r S^0$) of the [Gly–18C6], [Ala–18C6], and [Phe–18C6] complexes formation. The experiments on titration were carried out on microcalorimeters TAM MOD 2277 (Thermometric, Sweden) and TAM III (TA Instruments, USA). Data on the [Gly–18C6], [Ala–18C6] and [Phe–18C6] complexes stability in H_2O–EtOH, H_2O–acetone and

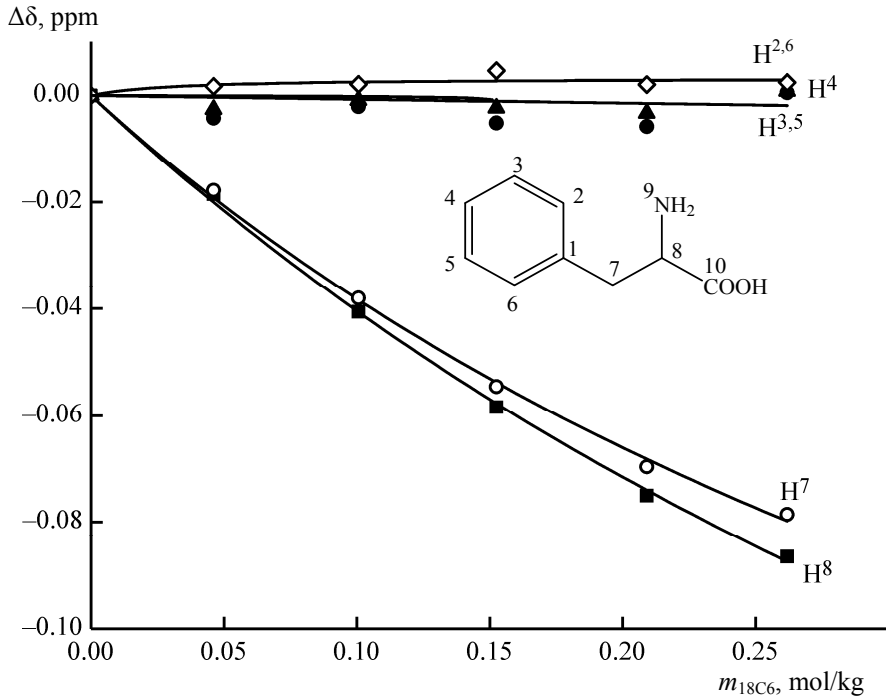


Fig. 1. Change in the chemical shifts of H^{2-8} protons of Phe as a function of 18C6 concentration (deuterated water, 298.15 K) [45].

H_2O–DMSO media of varied composition is collected in Tables 1–3.

In water, complexes of 18C6 with glycine are more stable than those with D,L-alanine or L-phenylalanine (Figs. 2–4). With increasing fraction of the non-aqueous component in the reaction medium, the stability of the [Gly–18C6], [Ala–18C6], and [Phe–18C6] molecular complexes in general increases. Noteworthily, the relative stability order is preserved: $\log K^0$[Ala–18C6] < $\log K^0$ [Gly–18C6] in H_2O–EtOH, H_2O–acetone, and H_2O–DMSO media and $\log K^0$[Phe–18C6] ≤ $\log K^0$[Ala–18C6] < $\log K^0$[Gly–18C6] in H_2O–EtOH medium.

In H_2O–EtOH (Fig. 2) and H_2O–DMSO (Fig. 4) media, at x_2 = 0.0–0.2 (hereinafter, x_2 stands for the molar fraction of organic cosolvent) the [Phe–18C6] complex stability is comparable with that of the [Ala–18C6] complex. Increasing ethanol fraction in the H_2O–EtOH medium destabilizes the [Phe–18C6] complex in comparison with the [Ala–18C6] one. In anhydrous ethanol, $\log K^0$[Ala–18C6] is equal to $\log K^0$[Gly–18C6] within thw experimental accuracy.

In H_2O–DMSO medium, increasing DMSO fraction above $x_2 \approx 0.2$ does not significantly change the [Phe–18C6] complex stability. Similarly to the case of the H_2O–EtOH medium, at all studied compositions of H_2O–DMSO solvent, $\log K^0$[Phe–18C6] < $\log K^0$[Gly–18C6].

The comparison of the [Gly–18C6] and [Ala–18C6] complexes stability in H_2O–EtOH, H_2O–acetone, and H_2O–DMSO mixed solvents (Figs. 2–4) shows that the $\log K^0$[Gly–18C6] – $\log K^0$[Ala–18C6] difference is constant irrespectively of water fraction, and its value expressed in log units is 0.26±0.03 (H_2O–EtOH, x_2 = 0.00–0.60), 0.34±0.05 (H_2O–acetone, x_2 = 0.00–0.22),

Table 1. Stability of the [Gly–18C6] complex in H_2O–EtOH, H_2O–acetone, and H_2O–DMSO[a] media at 298.15 K

H_2O–EtOH		H_2O–acetone [47]	
x_2	$\log K^0$	x_2	$\log K^0$
0.00	0.63±0.02 [16]	0.08	1.02±0.05
	0.73±0.03 [47]	0.14	1.29±0.05
0.12 [47]	1.20±0.05	0.21	1.51±0.05
0.25 [47]	1.64±0.05	H_2O–DMSO [48]	
0.50 [47]	2.29±0.07	0.1	1.28±0.10
0.74 [47]	3.01±0.08	0.2	1.80±0.10
0.91 [47]	3.50±0.10	0.25	1.92±0.10
1.0 [30]	3.81±0.12		

[a] Hereinafter x_2 is the organic cosolvent molar fraction.

Table 2. Stability of the [Ala–18C6] complex in H_2O–EtOH, H_2O–acetone, and H_2O–DMSO media at 298.15 K

H_2O–EtOH		H_2O–acetone [50]	
x_2	$\log K^0$	x_2	$\log K^0$
0.0	0.32 [49]	0.08	0.63
	0.32±0.16 [50]	0.17	1.07
	0.40±0.20 [16]	0.22	1.33
0.1 [49]	0.81±0.16	0.30	1.35
0.2 [49]	1.15±0.16	H_2O–DMSO [51]	
0.4 [49]	1.73±0.16	0.08	0.74
0.6 [49]	2.12±0.16	0.17	1.35
1.0 [30]	3.69±0.10	0.25	1.40
		0.30	1.58

Table 3. Stability of the [Phe–18C6] complex in H_2O–EtOH and H_2O–DMSO media at 298.15 K

H_2O–EtOH		H_2O–DMSO [52]	
x_2	$\log K^0$	x_2	$\log K^0$
0.0	0.23±0.05 [44]	0.05	0.76±0.20
	0.67±0.10 [16]	0.15	1.29±0.20
0.1 [45]	0.78±0.15	0.25	1.20±0.16
0.2 [45]	1.20±0.13	0.30	1.34±0.16
0.4 [45]	1.46±0.13	0.40	1.10±0.16
0.6 [45]	1.94±0.10		
1.0 [30]	3.36±0.04		

and 0.51±0.05 (H_2O–DMSO, x_2 = 0.00–0.25). Lower stability of the [Ala–18C6] complex as compared with that of the [Gly–18C6] one is likely due to the steric hindrance towards interaction with the macrocycle caused by D,L-alanine methyl group [15–17]. The (log K^0[Gly–18C6] – log K^0[Ala–18C6]) difference most likely reflects the impact of methyl group as confirmed by its constant value over wide range of the solvents composition.

In H_2O–DMSO medium at $x_2 \approx 0.2$–0.4, the observed relation $\log K^0$[Phe–18C6] < $\log K^0$[Ala–18C6] points at the differentiating effect of phenyl group solvation state on the [Phe–18C6] molecular complex stability.

In H_2O–EtOH and H_2O–DMSO media, difference in the [Ala–18C6] and [Phe–18C6] complexes stability (Figs. 2 and 4) is within experimental accuracy. In these media the solvation impact of phenyl group in log K^0[Phe–18C6] is likely comparable to that of methyl group. We assume that the $\log K^0$[Phe–18C6] ≈ $\log K^0$[Ala–18C6] relation is due to the mechanism of amino acid binding with the macrocycle: the major

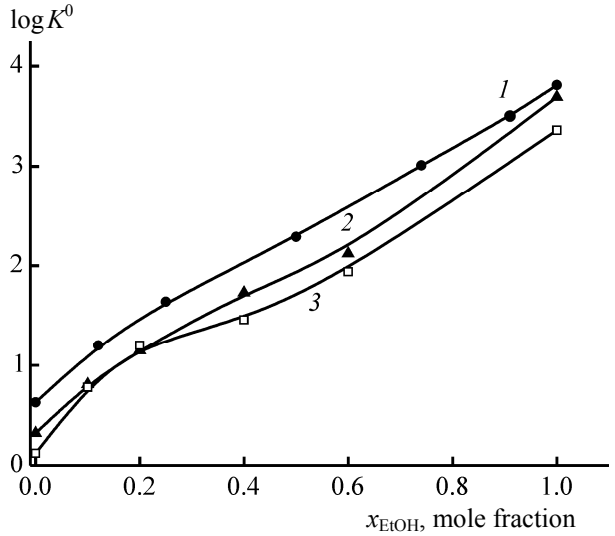


Fig. 2. Stability of the [Gly–18C6] [16, 30, 47] (*1*), [Ala–18C6] [16, 30, 49, 50] (*2*), and [Phe–18C6] [30, 45] (*3*) complexes in H_2O–EtOH medium.

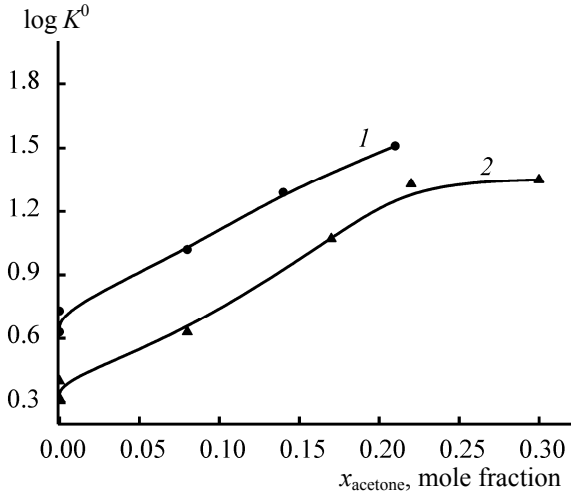


Fig. 3. Stability of the [Gly–18C6] [16, 47] (*1*) and [Ala–18C6] [16, 49, 50] (*2*) complexes in H_2O–acetone medium.

role is played by the hydrogen bonds formed by amino group protons, whereas participation of the side groups in the coordination is negligibly low [15–17, 30, 43–46].

Following the solvation-thermodynamic concept [13, 34–38], the change of thermodynamic parameters of the reaction with variation of the medium composition can be related to the changes of the components solvation (2).

$$\Delta_{tr}Y^0_r = \Delta_{tr}Y^0([AA–18C6]) – \Delta_{tr}Y^0(AA) – \Delta_{tr}Y^0(18C6). \quad (2)$$

In Eq. (2), $\Delta_{tr}Y^0$([AA–18C6]) stands for the change in a thermodynamic function (ΔG^0, ΔH^0, or $T\Delta S^0$) of the complex formation in going from water to the mixed solvent [Eq. (5)], whereas $\Delta_{tr}Y^0$(AA) and $\Delta_{tr}Y^0$(18C6) are the changes in the components solvation function [Eqs. (4)–(5)].

$$\Delta_{tr}Y^0_r = \Delta_rY^0_{sol} – \Delta_rY^0_{H_2O}, \quad (3)$$

$$\Delta_{tr}Y^0(AA) = \Delta_rY^0(AA)_{sol} – \Delta_rY^0(AA)_{H_2O}, \quad (4)$$

$$\Delta_{tr}Y^0(18C6) = \Delta_rY^0(18C6)_{sol} – \Delta_rY^0(18C6)_{H_2O}. \quad (5)$$

In Eqs (3)–(5), the subscript "H_2O" points at pure water as solvent, and the subscript "sol" marks the mixed solvent.

$$\Delta_{tr}Y^0([AA–18C6]) = \Delta_{tr}Y^0_r + \Delta_{tr}Y^0(AA) + \Delta_{tr}Y^0(18C6). \quad (6)$$

Equation (2) rewritten in the form (6) allows calculation of change in the thermodynamic parameters of the [AA–18C6] complex solvation upon transfer from water to mixed solvent without additional experiments.

Our own [45, 49, 54, 55] and published data [30, 56, 57] on the change of Gibbs free energy of amino acids and 18C6 solvation upon transfer to the mixed solvents allows analysis of the reagents solvation impact on the formation of the [Gly–18C6], [Ala–18C6], and [Phe–18C6] complexes in the case of H_2O–EtOH system (Figs. 5a–5c) and of the [Gly–18C6] complex in the case of H_2O–DMSO system (Fig. 6).

The observed trends in the changes of the reagents solvation impact on Gibbs energy of the complex formation shown in Figs. 5 and 6 are identical for all the studied systems.

Transfer from water to aqueous EtOH or DMSO impedes solvation of the amino acids and 18C6, as reflected by positive values of $\Delta_{tr}G^0$(AA) and $\Delta_{tr}G^0$(18C6) at the growing fraction of nonaqueous solvent component.

The impact of amino acids desolvation, $\Delta_{tr}G^0$(AA), prevails over that of other components, $\Delta_{tr}G^0$(18C6) and $\Delta_{tr}G^0$([AA–18C6]). It means that the weakening of the solvation shell of the amino acid governs the changes in the Gibbs energy of reactions at transfer from water to solvents H_2O–EtOH and H_2O–DMSO. Indeed, $\Delta_{tr}G^0_r$ is close to $\Delta_{tr}G^0$(AA) by the absolute value but has the opposite sign.

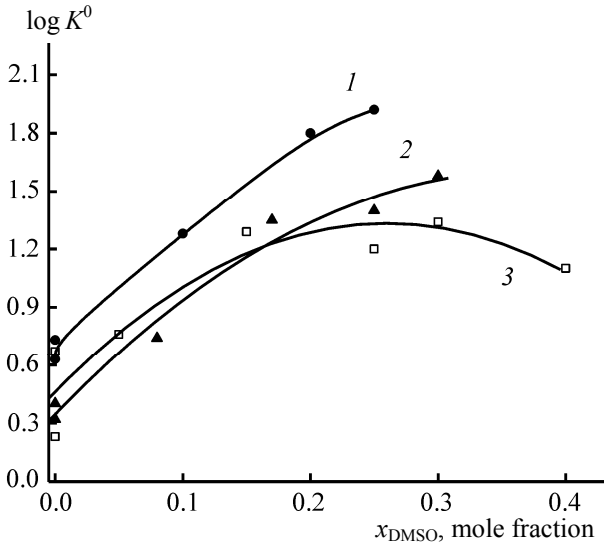


Fig. 4. Stability of the [Gly–18C6] [16, 47, 48] (*1*), [Ala–18C6] [17, 50–52] (*2*), and [Phe–18C6] [16, 45, 52] (*3*) complexes in H_2O–DMSO medium.

The changes in the solvation states of complexes [AA–18C6] − $\Delta_{tr}G^0$([AA–18C6] are small and close to zero value of $\Delta_{tr}G^0$(18C6) indicating the determining role of the macrocycle in the formation of the solvation shall of the complex [AA–18C6]. Therefore it is possible to conclude that the changes in the solvation state of the carboxy, methyl, and phenyl groups of the studied amino acids do not make a significant contribution into the changes in the solvation state of the complex [AA–18C6].

According to the above cited regularity of the influence of solvents H_2O–EtOH and H_2O–DMSO on the formation of molecular complexes [Gly–18C6], [Ala–18C6], and [Phe–18C6] and in keeping with Eq. (2) the changes in Gibbs energies of reactions (1) depends mainly on the changes in the solation state of amino acid $\Delta_{tr}G^0$(AA). Therefore the changes in the stability of the 18C6 complexes with amino acids in H_2O–EtOH and H_2O–DMSO media may be predicted basing on the changes in the solvation state of amino acids.

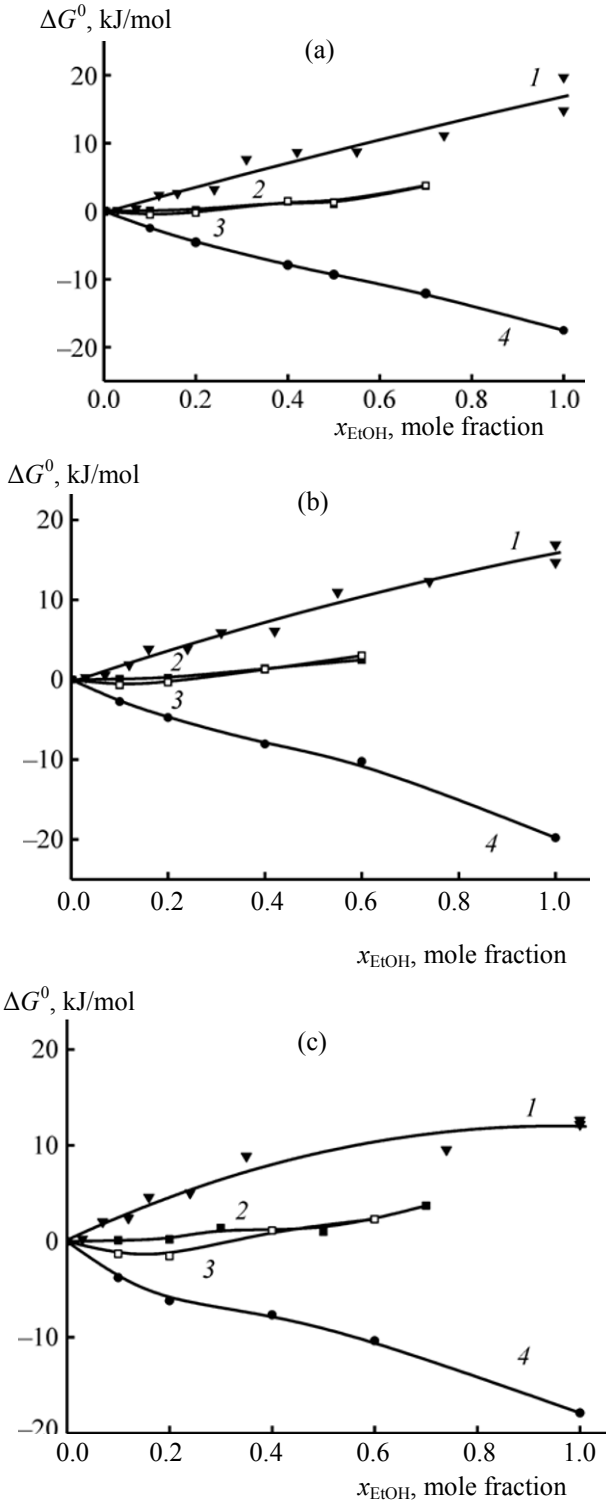


Fig. 5. Change in the components solvation contribution in Gibbs free energy upon transition of the [Gly–18C6] (a), [Ala–18C6] (b), and [Phe–18C6] (c) complexes formation reaction from water to H_2O–EtOH medium. (*1*) $\Delta_{tr}G^0$(Gly) (a), $\Delta_{tr}G^0$(Ala) (b), $\Delta_{tr}G^0$(Phe) (c) [45, 49]; (*2*) $\Delta_{tr}G^0$(18C6) [54]; (*3*) $\Delta_{tr}G^0$ ([Gly–18C6]) (a), $\Delta_{tr}G^0$([Ala–18C6]) (b), $\Delta_{tr}G^0$([Phe–18C6]) (c); (*4*) $\Delta_{tr}G^0_r$ [47] (a), [49] (b), [45] (c).

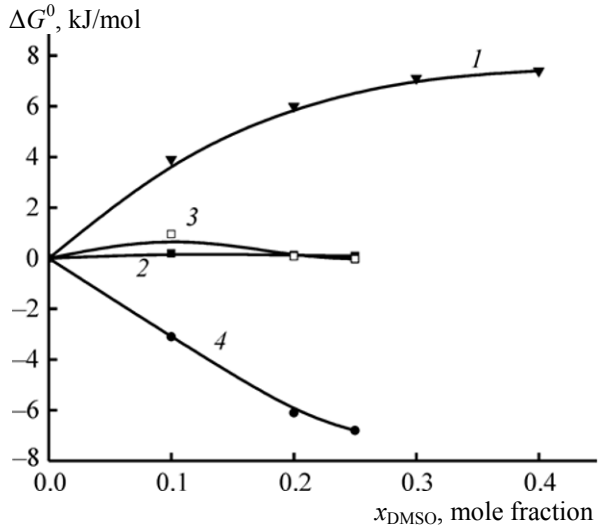


Fig. 6. Change in the components solvation contribution in Gibbs free energy upon transition of the [Gly–18C6] complex formation reaction from water to H_2O–DMSO medium. (*1*) $\Delta_{tr}G^0$(Gly) [57]; (*2*) $\Delta_{tr}G^0$(18C6) [55]; (*3*) $\Delta_{tr}G^0$([Gly–18C6]), (*4*) $\Delta_{tr}G^0_r$ [48].

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