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Thermodynamics of Complex Formation and Solvation in the System NaCl–18-crown-6–Water–Dioxane

I. S. Zaitseva, N. Yu. Grigor'eva, S. V. El'tsov, and N. V. Bondarev

Kharkov State University, Kharkov, Ukraine

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Abstract — Stability constants of Na^+ complexes with 18-crown-6-ether and thermodynamic characteristics of the complex formation in water and mixed water–dioxane solvents (0.2, 0.4, 0.6, and 0.8 wt. fraction of dioxane, 283–318 K) were determined by the method of EMF of galvanic circuits without transfer. Comparative thermodynamic analysis of the complex 18-crown-6Na^+ formation reactions in water–dioxane, water–acetonitrile, water–acetone, water–methanol, and water–2-propanol mixtures was carried out. Contributions of the Gibbs energies of transfer (ΔG_t) of 18-crown-6Na^+, Na^+, and the ligand to the increase in the stability of the complexes on replacement of water by mixed water–dioxane solvents were estimated. It was shown that the increase in the stability of sodium crown ether complexes primarily depends on solvation of the complex cation and desolvation of the central cation. Changes in the conformational Gibbs energy of the ligand and quantitative parameters of selective solvation of the reagents were estimated.

To control chemical reactions in nonaqueous and mixed solvents, it is necessary to develop a scientific approach to selection of the solvents [1]. This is a complicated problem because of an exceptionally great variety and specificity of chemical reactions in solutions. One of the lines of attacking the problem involves a comprehensive study of solvent effects on similar reactions. An example of such reactions is complex formation of cations with uncharged and charged ligands in mixtures of water with various organic solvents [2].

Earlier we studied the thermodynamics of formation of Na^+ complexes with 18-crown-6 in mixtures of water with methanol, 2-propanol, acetone, and acetonitrile [3–6].

It is of interest to study this reaction in water–dioxane mixtures, where one of the components (dioxane) has a low dielectric constant (*D*), and the second (water), a high dielectric constant. It is known also that the K^+ cation is fully complementary to the electron-donor cavity of 18-crown-6, whereas the Na^+ cation is smaller than this cavity [7]. Therefore, it becomes possible to observe in this system a combined effect of topological and solvation factors on the thermodynamic characteristics of complex formation of K^+ and Na^+ with 18-crown-6.

The aim of this work was a thermodynamic study of complex formation of Na^+ with 18-crown-6 in water–dioxane mixtures with dioxane contents of 0, 0.2, 0.4, 0.6, and 0.8 wt fractions and in the temperature range 283–318 K by the method of electromotive forces, and to compare the resulting data with those in [3–6].

The logarithms of the stability constants of the sodium monocoronates are given in Table 1. It is evident from the table that the stability of these complexes decreases with increasing temperature and increases with increasing dioxane concentration in the mixed solvent. The role of solvent in complex-formation reactions is covenient to discuss in terms of relationships between the excess stability constants of the complexes and the compositions of the mixed solvents [8].

$$\log K^{\mathrm{ex}}_{\mathrm{NaL^+}} = \log K^{\mathrm{exp}}_{\mathrm{NaL^+}} - \log K^{\mathrm{ad}}_{\mathrm{NaL^+}}, \tag{1}$$

$$\log K^{\mathrm{ad}}_{\mathrm{NaL^+}} = \log K^{\mathrm{H_2O}}_{\mathrm{NaL^+}} + \frac{X_{\mathrm{S}}}{X^{\mathrm{max}}_{\mathrm{S}}}(\log K^{\mathrm{S,max}}_{\mathrm{NaL^+}} - \log K^{\mathrm{H_2O}}_{\mathrm{NaL^+}}). \tag{2}$$

Here $K^{\mathrm{exp}}_{\mathrm{NaL^+}}$ is the experimental stability constant of the sodium coronate in a mixture with the mole fraction X_{S} of a nonaqueous solvent, $K^{\mathrm{ex}}_{\mathrm{NaL^+}}$ is the excess stability constant, $K^{\mathrm{ad}}_{\mathrm{NaL^+}}$ is the additive stability constant, $K^{\mathrm{H_2O}}_{\mathrm{NaL^+}}$ is the stability constant of the complex in water, $K^{\mathrm{S,max}}_{\mathrm{NaL^+}}$ is the stability constant in the nonaqueous (mixed) solvent with the maximum fraction of the nonaqueous component, and $X^{\mathrm{max}}_{\mathrm{S}}$ is the maximum mole fraction the nonaqueous solvent in the mixture, where $K^{\mathrm{exp}}_{\mathrm{NaL^+}}$ was determined.

It is of interest to compare the energies of complex formation of Na^+ with 18-crown-6 in various mixed

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Table 1. Stability constants (log K_{NaL}, molal scale) of the sodium coronate 18-crown-6Na^+ in water–dioxane mixtures

Weight fraction of dioxane	Temperature, K				
	283	288	298	308	318
0.00	0.99 ± 0.06	0.96 ± 0.04	0.87 ± 0.05	0.82 ± 0.04	0.74 ± 0.03
0.20	1.07 ± 0.12	1.08 ± 0.10	1.04 ± 0.10	1.00 ± 0.09	0.83 ± 0.09
0.40	1.65 ± 0.11	1.62 ± 0.11	1.53 ± 0.07	1.44 ± 0.07	1.35 ± 0.06
0.60	2.07 ± 0.02	2.02 ± 0.01	1.94 ± 0.02	1.87 ± 0.03	1.75 ± 0.01
0.80	2.58 ± 0.03	2.53 ± 0.02	2.40 ± 0.02	2.27 ± 0.03	2.14 ± 0.04

solvents. We studied mixtures containing an aprotic and a protic solvents (water–acetone and water–acetonitrile) and two protic solvents (water–methanol and water–2-propanol. As seen from Fig. 1a, the plots of log $K^{ex}_{NaL^+}$ against concentration of the nonaqueous component in water–aprotic solvent mixtures are qualitatively similar to each other up to 0.5 mole fraction of the organic component.

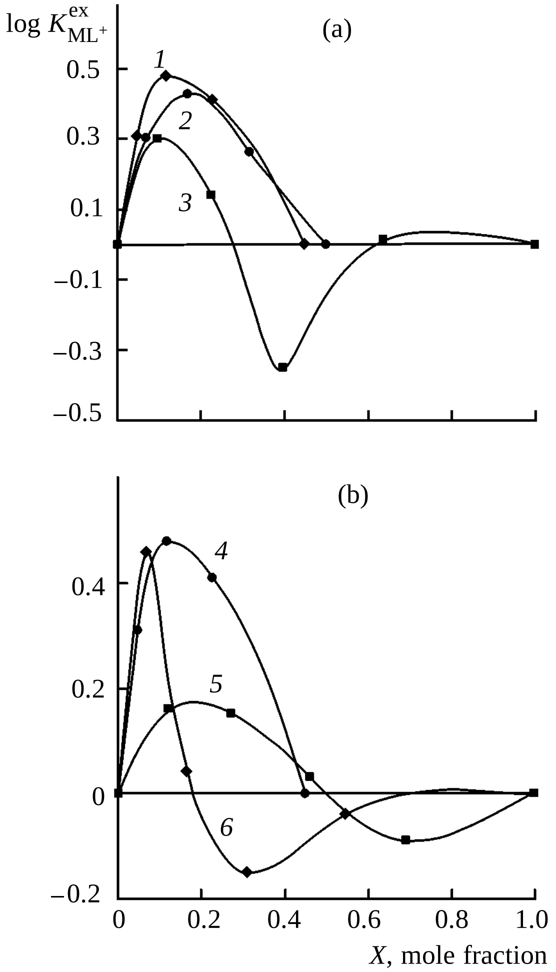

Fig. 1. Dependence of the excess stability constant of the 18-crown-6Na^+ complex on the composition of the mixed solvent. Solvent: (a): (*1*) water–dioxane, (*2*) water–acetone, and (*3*) water–acetonitrile and (b): (*4*) water–dioxane, (*5*) water–methanol, and (*6*) water–2-propanol.

The plots of the logarithms of the excess stability constants of the sodium coronate in water–organic solvents containing both protic (water, methanol, and 2-propanol) and aprotic (dioxane) components, against the mole fraction X_S of the organic components are shown in Fig. 1b. As seen, the log $K^{ex}_{NaL^+} - f(X_S)$ plots are sharply different at X_S greater than 0.15. The presence of extrema in these plots points to a different nature of solvation of the Na^+ and NaL^+ cations and the ligand L.

The thermodynamic characteristics (ΔG, ΔH, and $T\Delta S$) of the complex formation, calculated from the temperature dependences of the stability constants, are given in Table 2. The Gibbs energy of the complex formation monotonically varies with the composition of water–organic solvents and thus provides little information on interparticle interactions because of the entropy–enthalpy compensation [9]. Physically this means that the enthalpy and entropy components of the Gibbs energy directly reflect specifics of reagent–solvent interactions and characterize qualitative and quantitative distinctions of systems and processes under comparison [9].

The changes in the enthalpy and entropy of formation of the sodium coronates in water–dioxane mixtures (Fig. 2) point to an enthalpy control of the stability of the crown ether complexes, whereas in the mixed solvent containing 0.049–0.4 mole fraction of dioxane stability increase is also controlled by the entropy of the complex formation.

Entropy-stabilized complexes of Na^+ with 18-crown-6 are formed in water–2-propanol mixtures [4], which is also characteristic of the complex formation in the water–methanol solvent [3]. At the same time, the value and sign of the entropy contribution to the Gibbs energy of the sodium coronate formation ap-

Table 2. Thermodynamic parameters (kJ/mol) of complex formation of 18-crown-6 with Na^+ in water–dioxane mixtures (molal scale)

Parameter	Temperature, K				
	283	288	298	308	318
Water					
$-\Delta G \pm 0.15$	1.53	1.44	1.23	1.08	0.85
$-\Delta H \pm 2.5$	7	7	7	7	7
$-T\Delta S \pm 2.5$	5	6	6	6	6
0.2 mole fraction of dioxane					
$-\Delta G \pm 0.3$	5.80	5.96	5.94	5.90	5.06
$-\Delta H \pm 2.0$	11	11	11	11	11
$-T\Delta S \pm 2.0$	5	5	6	6	6
0.4 mole fraction of dioxane					
$-\Delta G \pm 0.2$	8.94	8.94	8.73	8.50	8.22
$-\Delta H \pm 1.7$	15	15	15	15	15
$-T\Delta S \pm 1.7$	6	6	6	7	7
0.6 mole fraction of dioxane					
$-\Delta G \pm 0.15$	11.19	11.12	11.07	11.03	10.66
$-\Delta H \pm 1.2$	15	15	15	15	15
$-T\Delta S \pm 1.2$	4	4	4	4	4
0.8 mole fraction of dioxane					
$-\Delta G \pm 0.08$	13.98	13.95	13.69	13.39	13.09
$-\Delta H \pm 0.7$	22	22	22	22	22
$-T\Delta S \pm 0.7$	8	8	8	9	9

preciably depend on the composition of the mixed solvent water–2-propanol, whereas in water–methanol mixtures containing up to 0.7 mole fraction of the alcohol the complex is entropy-stabilized. In the water–acetone solvent [5], the stability of the 18-crown-6Na^+ complexes is determined by enthalpy and entropy contributions. In water–acetonitrile mixtures [6], the stability of such complexes is mainly controlled by entropy.

The interrelation between the energy parameters of stability of the sodium crown ether complexes ($\Delta G_{NaL^+} = -RT\ln K_{ML^+}$, $F = G, H, S$) and the energy characteristics of solvation (transfer) of the reagents $\Delta F_{t,Na^+}$, $\Delta F_{t,NaL^+}$, and $\Delta F_{t,L^+}$ is determined by the following thermodynamic cycle [10, 11].

$$\begin{tikzcd}
M^+ + L \arrow[r, "\Delta F^{H_2O}_{t,M^+}"] \arrow[d, "\Delta F_{t,M^+}"'] & ML^+ \text{ water} \arrow[d, "\Delta F_{t,M^+}"] \\
M^+ + L \arrow[r, "\Delta F^{S}_{t,M^+}"] & ML^+ \text{ solvent S}
\end{tikzcd}$$

(the middle vertical arrow from L to L is labelled $\Delta F_{t,M^+}$)

$$\Delta F^{H_2O}_{NaL^+} + \Delta F_{t,NaL^+} = \Delta F_{t,L} + \Delta F_{t,Na^+} + \Delta F^{S}_{NaL^+}, \quad (3)$$

$$\Delta\Delta F_{NaL^+} = \Delta F^{S}_{NaL^+} - \Delta F^{H_2O}_{NaL^+} = \Delta F_{t,NaL^+} - \Delta F_{t,Na} - \Delta F_{t,L}. \quad (4)$$

Using published Gibbs energies of transfer of sodium cations $\Delta G_{t,Na^+}$ [12] and the ligand $\Delta G_{t,L}$ [7], we estimated the Gibbs energies of transfer of the sodium coronate $\Delta G_{t,NaL^+}$. The plots of ΔG_t and $\Delta\Delta G_{NaL^+}$ against the composition of the water–dioxane mixed solvent are given in Fig. 3.

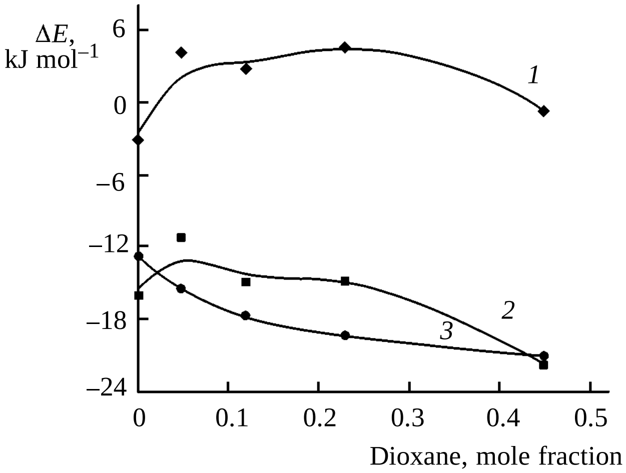

Fig. 2. Effect of the water–dioxane solvent on the (*1*) entropy $T\Delta S_{NaL^+}$, (*2*) enthalpy ΔH_{NaL^+}, and (*3*) Gibbs energy ΔG_{NaL^+} of complex formation of Na^+ with 18-crown-6 (rational scale).

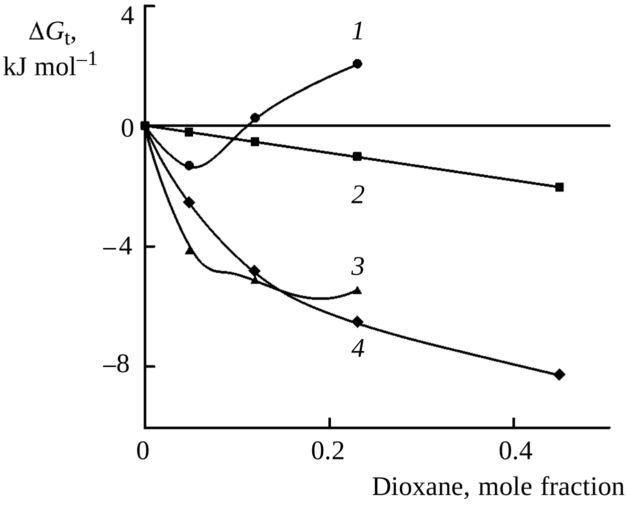

Fig. 3. Effect of the water–dioxane solvent on the Gibbs energy of transfer of the reagents and of fomation of the sodium crown ether complexes. (*1*) $\Delta G_{t,Na^+}$, (*2*) $\Delta G_{t,L}$, (*3*) $\Delta G_{t,NaL^+}$, and (*4*) $\Delta\Delta G_{NaL^+}$.

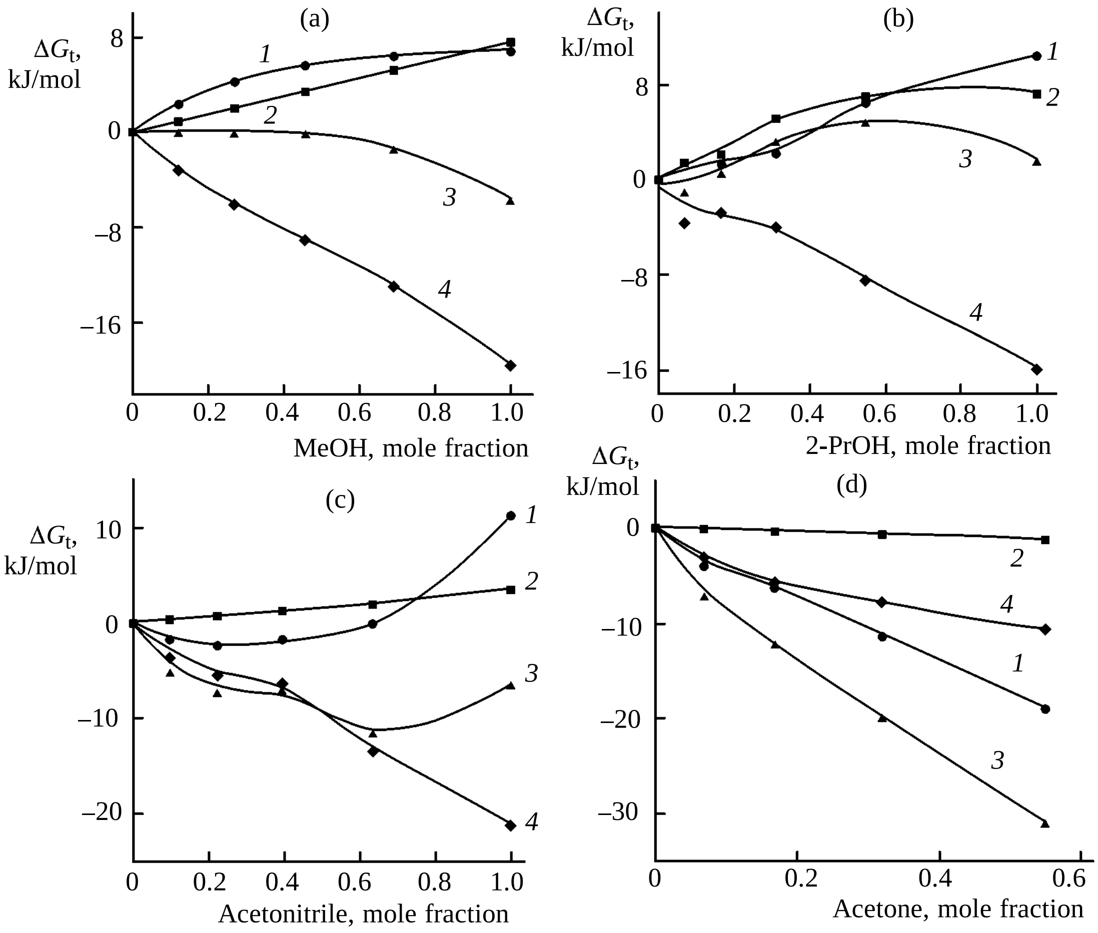

Fig. 4. Effects of the (a) water–methanol, (b) water–2-propanol, (c) water–acetonitrile, and (d) water–acetone solvents on the Gibbs energy of transfer of the reagents and of formation of the sodium crown ether complexes. (*1*) $\Delta G_{t,Na^+}$, (*2*) $\Delta G_{t,L}$, (*3*) $\Delta G_{t,NaL^+}$, and (*4*) $\Delta\Delta G_{NaL^+}$.

As seen from Fig. 3, the stability of the 18-crown-6Na^+ complexes increases with increasing dioxane concentration, which is mainly due to enhanced solvation (stabilization) of the complex ions. It should be noted that the stability of the complexes in the mixed solvents water–methanol, water–2-propanol, water–acetone, and water–acetonitrile (Fig. 4) also increases with increasing contents of the nonaqueous solvents [3–6].

In the water–methanol (Fig. 4a) and water–2-propanol (Fig. 4b) solvents, the stability of the sodium coronate results from destabilization of the ligand and the central ion, i.e., from the decrease in the Gibbs energy of solvation of the ligand and the cation with increasing alcohol concentration in the mixed solvent.

The increase in the stability of the 18-crown-6Na^+ complexes in aqueous acetonitrile (Fig. 4c) up to an 0.6 mole fraction of acetonitrile is associated with increased solvation energy of the complex ion and also from destabilization of the ligand. In mixtures containing more than 0.65 mole fraction of acetonitrile, Na^+ is destabilized, and the stability of the complex increases.

An increase in the acetone concentration in water–acetone mixtures (Fig. 4d) increases the Gibbs energy of solvation of the crown ether L, the complex-forming ion Na^+, and the complex cation NaL^+; therewith, the stabilizing contribution of the complex cation overrides the destabilizing effects of the first two factors.

The interaction of the Na^+ cation with the electron-donor cavity of the macroring gives rise to a large organic cation with a structure depending on the composition of the water–organic mixture [13]. A change in the composition of the mixed solvent entails a change in the macroscopic properties of the medium, such as its dielectric constant. The interaction of the complex and free cations with the primary solvation shell is mostly electrostatic in nature, as demonstrated by linear dependences of the Gibbs energies of complex formation and transfer of the Na^+ and NaL^+ ions on the reciprocal of the dielectric constant of the mixed solvent (Fig. 5). The inflection in the $\Delta G_{\mathrm{NaL}^-}$ – $f(1/D)$ plot may be explained by changes in the radii of solvated Na^+ and NaL^+ in going from water to mixed solvents.

Ions and molecules in solutions are almost always solvated. Therefore, most reactions are accompanied by changes in the solvation shells of the reagents (liberation and replacement of solvent molecules and even increase in their number). The composition of the solvation shells of reagents in a binary solvent can considerably differ from the overall composition of the solution owing to selective solvation. The Gibbs energy of solvation of reagents in a mixed solvent is described by Eq. (5) (DO is dioxane) [14].

$$\Delta G_\mathrm{S}(\mathrm{DO{-}H_2O}) = \Delta G_\mathrm{h} m_\mathrm{h} + \Delta G_\mathrm{S} m_\mathrm{S}. \tag{5}$$

Here m_h and m_S are the weight statistical factors determining the contributions of the Gibbs energies of hydration and solvation of a particle in the nonaqueous solvent to the total Gibbs energy of solvation in the binary solvent.

$$m_\mathrm{h} + m_\mathrm{S} = 1, \tag{6}$$

$$\frac{m_\mathrm{h}}{m_\mathrm{S}} = \frac{X_{\mathrm{H_2O}}}{X_\mathrm{DO}} \exp(-x), \tag{7}$$

$$x = -\frac{\Delta G_{\mathrm{t},i}}{RT}. \tag{8}$$

Here $\Delta G_{\mathrm{t},i}$ is the Gibbs energy of transfer of the reagents from water into the nonaqueous solvent. Thus, the greater is the difference in the Gibbs energies of hydration and solvation of particles, the stronger is the effect of selective solvation on physicochemical properties of solutions.

Table 3 lists the weight statistical factors calculated by Eqs. (6)–(8) from the Gibbs energies of transfer of the particles. Analysis of these values shows that the Na^+ cation and the ligand preserve their hydration shells even at high concentrations of the nonaqueous component in mixed solvents, except for water–dioxane (for the ligand) and water–acetone (for the cation and the ligand). The Gibbs energy of solvation of the sodium coronate depends mainly on the solvate environment (m_h 0.29–0.0), except for water–2-propanol mixtures. As the concentration of the organic component in a mixture increases, the contribution of the Gibbs energy of hydration to the total Gibbs energy of solvation in the binary solvent decreases.

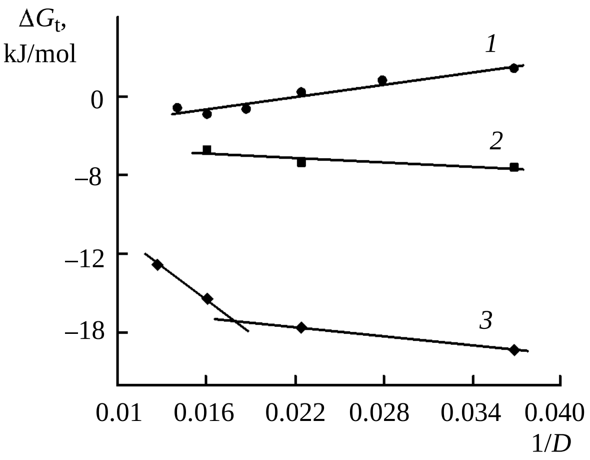

Fig. 5. Dependence of the Gibbs energies of transfer of the Na^+ and NaL^+ ions and of formation of the sodium coronate on the reciprocal of the dielectric constant of the water–dioxane solvent. (*1*) $\Delta G_{\mathrm{t,Na}^+}$, (*2*) $-\Delta G_{\mathrm{t,NaL}^+}$, and (*3*) $\Delta G_{\mathrm{NaL}^+}$.

It is known [15] that the formation of a crown ether complex with a cation in solution is accompanied by conformational preadaptation of the macroring, the energy of which (ΔG_conf) depends on the properties of the cation and the ligand and on the reaction conditions. In can be assumed the total Gibbs energy of the complex formation ΔG_{ML^+} involves a conformational contribution [8] which is a part of the Gibbs energy of solvation of the ligand. In terms of the linear free energy principle [16], the Gibbs energy of the complex formation in solution has Eq. (9):

$$\Delta G_{\mathrm{ML}^+} = \Delta G^\mathrm{vac}_{\mathrm{ML}^+} + \Delta G_{\mathrm{S,ML}^+} - [b(\Delta G_{\mathrm{S,M}^+} + \Delta G_\mathrm{S,L}) + \Delta G_\mathrm{conf}]. \tag{9}$$

Here $\Delta G^\mathrm{vac}_{\mathrm{ML}^+}$ is the Gibbs energy of the complex formation in a vacuum, b is a factor reflecting the contribution of solvation of the ligand and the cation to the change in the Gibbs energy of solvation of the coronate without inclusion of the conformation component. Change in the conformational Gibbs energy of the ligand can be estimated by Eq. (10):

$$\Delta G_{\mathrm{t,ML}^+} = \Delta\Delta G_\mathrm{conf} + b(\Delta G_{\mathrm{t,M}^+} + \Delta G_\mathrm{t,L}). \tag{10}$$

Here $\Delta\Delta G_\mathrm{conf}$ are the changes in the Gibbs energy of solvation, resulting from the different conformational preadaptations of the ligand in water and in a nonaqueous solvent [17]. When $b = 0$, $\Delta G_{\mathrm{t,ML}^+} = \Delta\Delta G_\mathrm{conf}$, i.e., the solvation energy of the cationic complex on changing the solvent is determined only by differences in the energy of conformational preadaptation of the ligand.

Table 3. Gibbs energies of transfer of particles from water into water–organic mixtures and the weight statistical factors m_h and m_S of Eq. (5)

Parameter	Mole fractions of solvent S											
	0.20			0.40			0.60			0.80		
	NaL^+	Na^+	L	NaL^+	Na^+	L	NaL^+	Na^+	L	NaL^+	Na^+	L
Water–dioxane (S)–18-crown-6Na^+												
$\Delta G_{t,i}$	–7.1	5.7	–4.5	–7.1	5.7	–4.5	–7.1	5.7	–4.5	–7.1	5.7	–4.5
m_h	0.19	0.97	0.39	0.08	0.94	0.20	0.04	0.87	0.10	0.01	0.71	0.04
Water–acetone (S)–18-crown-6Na^+												
$\Delta G_{t,i}$	–43.0	–26.0	–2.3	–43.0	–26.0	–2.3	–43.0	–26.0	–2.3	–43.0	–26.0	–2.3
m_h	0.0	0.0	0.61	0.0	0.0	0.37	0.0	0.0	0.21	0	0	0.09
Water–methanol (S)–18-crown-6Na^+												
$\Delta G_{t,i}$	–5.7	6.4	7.5	–5.7	6.4	7.5	–5.7	6.4	7.5	–5.7	6.4	7.5
m_h	0.29	0.98	0.99	0.13	0.95	0.97	0.06	0.90	0.93	0.02	0.77	0.84
Water–2-propanol (S)–18-crown-6Na^+												
$\Delta G_{t,i}$	1.6	10.4	7.2	1.6	10.4	7.2	1.6	10.4	7.2	1.6	10.4	7.2
m_h	0.88	0.99	0.99	0.74	0.99	0.97	0.56	0.98	0.92	0.32	0.94	0.82
Water–acetonitrile (S)–18-crown-6Na^+												
$\Delta G_{t,i}$	–6.6	11.2	3.5	–6.6	11.2	3.5	–6.6	11.2	3.5	–6.6	11.2	3.5
m_h	0.22	0.99	0.94	0.10	0.99	0.86	0.05	0.94	0.73	0.02	0.96	0.51

Table 4. Parameters of Eq. (10)

System	ΔG_{ML^+}	$\Delta G_{t,M^+}$	$\Delta G_{t,L}$	*b*	$\Delta\Delta G_{conf}$	r^a
$H_2O–CH_3OH–Na^+$–18-crown-6	<0	>0	>0	–0.46	2.55	0.945
H_2O–2-PrOH–Na^+–18-crown-6	>0	>0	>0	0.51	–1.55	0.980
$H_2O–C_4H_8O_2–Na^+$–18-crown-6	<0	>0, <0	<0	–0.5	–5.01	0.990
$H_2O–CH_3CN–Na^+$–18-crown-6	<0	<0	>0	–0.01	–6.50	0.991
$H_2O–(CH_3)_2CO–Na^+$–18-crown-6	<0	<0	<0	1.43	–2.18	0.997

[a] (*r*) Correlation coefficient.

The values of $\Delta\Delta G_{conf}$ and *b*, calculated by Eq. (10) are given in Table 4. These values show that, except for the water–methanol solvent, conformational transformations of crown ethers are thermodynamically preferred in nonaqueous media (2-propanol, acetonitrile, acetone, and dioxane) compared to water ($\Delta\Delta G_{conf} < 0$), thus stabilizing coronates. The stability of sodium coronates in passing from water to water–acetonitrile mixtures predominantly depends on conformational transformations of the ligand ($b \approx 0$).

The negative values of the factor *b* indicate that an increase in the concentration of the nonaqueous component in the systems under consideration is accompanied by stabilization of certain of the reagents and destabilization of the others.

EXPERIMENTAL

The stability constants of NaL^+ complexes were determined using galvanic circuits without transfer:

$$\text{Glass electrode } (Na^+)\,|\,NaCl + L\,|\,AgCl,\ Ag$$

Glass electrodes reversible to Na^+ ions (ESL-51-07) were used as indicator electrodes.

The technique of potentiometric experiments, the purification and preparation of salts and crown ethers, and the procedure for calculating thermodynamic constants and energetic parameters of complex formation were described earlier [3–6].

Dioxane was purified according to [18]. The purity of the product was controlled by densimetry. Mixed water–dioxane solvents were prepared by the gravimetric method.

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