Russian Journal of General Chemistry, Vol. 73, No. 7, 2003, pp. 1021–1026. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 7, 2003, pp. 1079–1084.

Correlation Analysis of the Solvent Effects on the Thermodynamic Functions of Complexation of Sodium and Potassium Ions with 18-Crown-6 Ether in Aqueous-Organic Solvents

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Received May 25, 2001

Abstract — The effect of dielectric and chemical (donor–acceptor interactions, cohesion energy density) properties of aqueous-organic solvents (water–methanol, water–2-propanol, water–acetonitrile, water–acetone, water–dioxane) on the thermodynamic functions of complexation of sodium and potassium cations with 18-crown-6 ether at 298 K was subjected to overall correlation analysis.

In analysis of the solvent effects on the thermodynamic functions of equilibrium processes in solution, electrostatic and chemical models of solvation are widely used for quantitative evaluation of the solvating power of solvents [1].

Electrostatic theories allow the effect of the solvent permittivity ε on the equilibrium (dissociation, association, complexation, homoconjugation) constants to be revealed on the basis of the following relationships:

$$\Delta G = 2.303RT\mathrm{p}K = A + B/\varepsilon.$$

In chemical models of solvation, the solvent activity manifested in molecule–molecule, ion–ion, and ion–molecule interactions is evaluated by such parameters as donor numbers (*DN*), accceptor numbers (*AN*), and empirical parameters of the solvent polarity. The polarity parameters characterize certain properties common for all solvents, whereas donor and acceptor numbers characterize the donor–acceptor power of solvent molecules in a certain model reaction in an inert medium [2]. Therefore, to describe the solvent effects on the thermodynamic functions of reactions in aqueous-organic solvents, it is preferable to use in correlation analysis the polarity parameters.

The goal of this study is overall correlation analysis of the influence exerted by the dielectric properties of the medium, solute–solvent donor–acceptor interactions, and cohesion energy density on the thermodynamics of complexation in the systems water–organic solvent–cation–18-crown-6 ether.

Quantitative consideration of the solvation features, governing the thermodynamic functions of complexation of sodium and potassium cations with 18-crown-6 in aqueous-organic solvents (water–methanol, water–2-propanol, water–acetonitrile, water–acetone, water–dioxane) was performed using a multiparameter equation of the following general form:

$$\log K(\Delta G) = A_0 + bE_T^N + cB_{KT} + d\varepsilon^{-1} + k\delta^2, \quad (1)$$

where A_0 is the Gibbs energy of complexation (ΔG) or the logarithm of the stability constant of the complex formed by a cation with the crown ether in an inert solvent; *b*, *c*, *d*, and *k* are the regression coefficients characterizing the sensitivity of the energy parameters of complexation to variation of the solvent properties; E_T^N is the normalized Dimroth–Reichardt empirical parameter of the solvent polarity, reflecting mainly the specific Lewis acidity (acceptor properties of solvents); B_{KT} is the Kamlet–Taft solvatochromic parameter characterizing the Lewis basicity (donor properties of solvents); ε is the dielectric permittivity; and δ^2 is the cohesion pressure related to the work of cavity formation in liquids.

In Table 1 are given the parameters of linear correlation (1) between the Gibbs energy of complexation of Na and K ions (M) with 18-crown-6 (L) [3–6] and the properties of the mixed solvents (B_{KT} and E_T^N [1], ε [7], δ^2 [8, 9]) at 298 K (Table 2) in the rational scale, obtained on the basis of the linear solvation energy relationships [1, 8].

The electron donor–acceptor properties of aqueous-organic solvents with protic and aprotic nonaqueous components (Table 2) favor coordination of the sodium and potassium cations with 18-crown-6 (Table 1,

1070-3632/03/7307-1021 $25.00

Table 1. Regression coefficients[a] of the equation $\log K(\Delta G) = A_0 + bE_T^N + cB_{KT} + d\varepsilon^{-1} + k\delta^2$

Parameter	A_0	b	c	d	$k \times 10^3$	r	σ^2	n
18-Crown-6Na$^+$								
$\log K$	7.25	0.104	0.217	–7.430	–2.116	0.98	0.04	24
ΔG	–41.2	–0.800	–1.277	41.80	12.07	0.98	1.16	24
18-Crown-6K$^+$								
$\log K$	7.94	0.991	0.152	–3.839	–2.139	0.94	0.11	24
ΔG	–44.8	–6.421	–1.041	22.83	12.26	0.94	3.46	24

[a] (r) Correlation coefficient, (σ^2) approximation variance, and (n) sample size.

Table 2. Thermodynamic parameters ($\log K$, ΔG) of formation of complexes 18-crown-6M$^+$ with sodium and potassium ions and parameters of aqueous-organic solvents: dielectric permittivity ε, empirical polarity parameters E_T^N and B_{KT}, and cohesion pressure[a] δ^2

Mole fraction of S	E_T^N	B_{KT}	ε	δ^2	ΔG_{NaL}	$\log K_{NaL}$	ΔG_{KL}	$\log K_{KL}$
Water–methanol								
0.00	1.00	0.19	78.4	2294.0	–12.9	2.24	–21.7	3.78
0.12	0.91	0.28	70.0	2120.0	–16.1	2.82	–23.3	4.09
0.27	0.85	0.42	60.9	1908.0	–19.0	3.33	–28.2	4.59
0.46	0.80	0.52	51.7	1645.0	–22.0	3.85	–30.0	5.26
0.69	0.79	0.54	42.6	1313.0	–25.9	4.54	–36.2	6.34
1.00	0.77	0.62	32.7	876.00	–32.5	5.69	–43.3	7.59
Water–2-propanol								
0.07	0.82	0.40	64.1	2206.0	–16.5	2.90	–23.6	4.14
0.17	0.70	0.58	49.7	2083.0	–15.7	2.75	–25.3	4.43
0.31	0.67	0.66	35.3	1902.0	–16.9	2.96	–26.3	4.61
0.55	0.63	0.72	23.7	1605.0	–21.3	3.73	–29.6	5.19
1.00	0.54	0.88	18.0	1030.0	–28.8	5.04	–29.9	5.23
Water–acetonitrile								
0.10	0.89	0.34	70.4	2126.0	–16.6	2.91	–23.4	4.10
0.23	0.83	0.40	60.6	1909.0	–18.5	3.23	–26.3	4.61
0.40	0.79	0.40	51.0	1618.0	–19.3	3.38	–28.4	4.98
0.64	0.74	0.43	42.9	1209.0	–26.4	4.63	–32.3	5.66
1.00	0.46	0.37	35.9	590.0	–34.2	6.00	–40.2	7.04
Water–acetone								
0.07	0.86	0.36	67.2	2159.0	–16.0	2.80	–22.9	4.01
0.17	0.75	0.47	54.8	1971.0	–18.7	3.28	–26.0	4.55
0.32	0.70	0.52	41.8	1696.0	–20.7	3.63	–28.6	5.01
0.55	0.66	0.56	29.6	1250.0	–23.6	4.14	–32.9	5.76
Water–dioxane								
0.05	0.86	0.28	62.1	2203.0	–15.5	2.71	–22.9	4.01
0.12	0.74	0.39	44.5	2070.0	–17.8	3.11	–25.2	4.42
0.23	0.66	0.47	27.2	1855.0	–19.4	3.40	–28.7	5.03
0.45	0.57	0.51	12.0	1451.0	–21.1	3.70	–30.4	5.33

[a] The cohesion energy densities of mixed solvents were calculated by the additive scheme: $\delta^2(H_2O\text{–}S) = X_{H_2O}\delta^2(H_2O) + X_S\delta^2(S)$ (X is the mole fraction of the corresponding component in the mixed solvent).

Table 3. Components of the Gibbs energy of complexation of 18-crown-6 with sodium and potassium cations in aqueous-organic solvents at 298 K (kJ mol^{-1}): $\Delta G_{NaL} = -41.2 - 0.800E_T^N - 1.277B_{KT} + 41.80\varepsilon^{-1} + 12.07\times10^{-3}\delta^2$, $\Delta G_{KL} = -44.8 - 6.421E_T^N - 1.041B_{KT} + 22.83\varepsilon^{-1} + 12.26\times10^{-3}\delta^2$

Mole fraction of S	$\Delta G_{ML}(E_T^N)$		$\Delta G_{ML}(B_{KT})$		$\Delta G_{ML}(\varepsilon)$		$\Delta G_{ML}(\delta^2)$	
	Na^+	K^+	Na^+	K^+	Na^+	K^+	Na^+	K^+
				Water–methanol				
0.00	–0.8	–6.4	–0.2	–0.2	0.5	0.3	27.7	28.1
0.12	–0.7	–5.8	–0.4	–0.3	0.6	0.3	25.6	26.0
0.27	–0.7	–5.5	–0.5	–0.4	0.7	0.4	23.0	23.4
0.46	–0.6	–5.1	–0.7	–0.5	0.8	0.4	19.9	20.2
0.69	–0.6	–5.1	–0.7	–0.6	1.0	0.5	15.8	16.1
1.0	–0.6	–4.9	–0.8	–0.7	1.3	0.7	8.2	8.3
				Water–2-propanol				
0.07	–0.7	–5.3	–0.5	–0.4	0.7	0.4	26.6	27.0
0.17	–0.6	–4.5	–0.7	–0.6	0.8	0.5	25.1	25.5
0.31	–0.5	–4.3	–0.8	–0.7	1.2	0.7	22.9	23.3
0.55	–0.5	–4.0	–0.9	–0.8	1.8	1.0	19.4	19.7
1.0	–0.4	–3.5	–1.1	–0.9	2.3	1.3	12.4	12.6
				Water–acetonitrile				
0.10	–0.7	–5.7	–0.4	–0.4	0.6	0.3	25.7	26.1
0.23	–0.7	–5.3	–0.5	–0.4	0.7	0.4	23.0	23.4
0.40	–0.6	–5.1	–0.5	–0.4	0.8	0.5	19.5	19.8
0.64	–0.6	–4.8	–0.6	–0.5	1.0	0.5	14.6	14.8
1.0	–0.4	–3.0	–0.5	–0.4	1.2	0.6	7.1	7.2
				Water–acetone				
0.07	–0.7	–5.5	–0.5	–0.4	0.6	0.3	26.1	26.5
0.17	–0.6	–4.8	–0.6	–0.5	0.8	0.4	23.8	24.2
0.32	–0.6	–4.5	–0.7	–0.5	1.0	0.6	20.5	20.8
0.55	–0.5	–4.2	–0.7	–0.6	1.4	0.8	15.1	15.3
				Water–dioxane				
0.05	–0.7	–5.5	–0.4	–0.3	0.7	0.4	26.6	27.0
0.12	–0.6	–4.8	–0.5	–0.4	0.9	0.5	25.0	25.4
0.23	–0.5	–4.2	–0.6	–0.5	1.5	0.8	22.4	22.7
0.45	–0.5	–3.7	–0.7	–0.5	3.5	1.9	17.5	17.8

$b < 0$, c 0). The contributions of the donor properties of the solvents, $\Delta G_{ML}(B_{KT})$ (here and hereinafter, the cations are given without charges), to the stability of the complexes are virtually equal, and the electron-acceptor properties, $\Delta G_{ML}(E_T^N)$, are manifested to a greater extent in stabilization of the potassium complex (Table 3).

Variation of the intensity of intermolecular interactions [cohesion energy density, $\Delta G_{ML}(\delta^2)$] and dielectric properties, $\Delta G_{ML}(\varepsilon)$, causes opposite effects, i.e., the complexes with the crown ether become less stable in going from inert to aqueous-organic solvents. It should be noted also that electrostatic interactions exert a stronger destabilizing effect on the sodium complex: $\Delta G_{NaL}(\varepsilon) > \Delta G_{KL}(\varepsilon)$ (Table 3).

The relationship between the thermodynamic functions of complexation (ΔG_{ML}) and energy characteristics of solvation (ΔG_s) of reactants (L, M^+) and products (ML^+) is as follows [10]:

$$\Delta G_{ML} = \Delta G_{ML}(\text{vacuum}) + \Delta G_{s,ML} - \Delta G_{s,M} - \Delta G_{s,L}. \quad (2)$$

Then, the change $\Delta\Delta G_{ML}$ in the Gibbs energy of complexation (i.e., in the stability of the complexes) due to solvation activity of the solvent (ΔG_{tr}) upon replacement of water by an organic or aqueous-organic solvent S is as follows:

Table 4, Regression coefficients of Eq. (4)

Parameter of transfer	b_i	c_i	d_i	$k_i \times 10^3$	r	σ^2	n
Water–methanol, water–2-propanol							
$\Delta\Delta G_{NaL}$	22.09	19.07	35.85	16.43	0.995	0.33	11
$\Delta\Delta G_{KL}$	–30.37	–26.90	256.35	13.94	0.963	2.7	11
Water–acetonitrile, water–acetone							
$\Delta\Delta G_{NaL}$	12.24	–1.82	250.68	10.62	0.992	0.56	10
$\Delta\Delta G_{KL}$	8.56	2.91	–49.50	8.06	0.999	0.08	10

$$\Delta\Delta G_{ML} = \Delta G_{ML}(S) - \Delta G_{ML}(H_2O) = \Delta G_{tr,ML} - \Delta G_{tr,M} - \Delta G_{tr,L}. \quad (3)$$

Taking into account (1), the relationship between the thermodynamic characteristics of transfer of the complexation reaction ($\Delta\Delta G_{ML}$) and those of transfer of reactants and products (ΔG_{tr}) from water to a nonaqueous and aqueous-organic solvent takes the form

$$\Delta\Delta G_{ML} = b_i\Delta E_T^N + c_i\Delta B_{KT} + d_i\Delta\varepsilon^{-1} + k_i\Delta\delta^2, \quad (4)$$

where b_i, c_i, d_i, and k_i are the regression coefficients characterizing the sensitivity of the parameters of transfer of the reaction, reactants, and products to the properties of the nonaqueous or aqueous-organic solvent; $\Delta\varepsilon^{-1} = \varepsilon^{-1}(S–H_2O) - \varepsilon^{-1}(H_2O)$.

In Table 4 are given the coefficients of multiparameter equation (4) describing the linear correlation between the Gibbs energies of transfer of the complexation reaction of Na^+ and K^+ with L, on the one hand, and changes in the chemical and dielectric properties of the medium, on the other hand (Table 5).

Table 5. Gibbs energies of transfer of the complexation reaction (kJ mol^{-1}) and changes in the chemical and dielectric properties of aqueous-organic solvents with protic and aprotic organic components at 298 K

Mole fraction of S	ΔE_T^N	ΔB_{KT}	$\Delta\varepsilon^{-1} \times 10^3$	$\Delta\delta^2$	$\Delta\Delta G_{NaL}$	$\Delta\Delta G_{KL}$
Water–methanol–Na^+, K^+–18-crown-6						
0.00	0	0	0	0	0	0
0.12	–0.09	0.09	1.531	–174.0	–3.2	–1.6
0.27	–0.15	0.23	3.665	–387.0	–6.1	–4.5
0.46	–0.20	0.33	6.587	–649.0	–9.1	–8.3
0.69	–0.21	0.35	10.719	–981.0	–13.0	–14.5
1.00	–0.23	0.43	17.826	–1418.0	–19.6	–21.6
Water–2-propanol–Na^+, K^+–18-crown-6						
0.07	–0.18	0.20	2.846	–181.0	–3.7	–2.0
0.17	–0.30	0.39	7.366	–302.0	–2.9	–3.7
0.31	–0.33	0.47	15.574	–399.0	–4.1	–4.7
0.55	–0.37	0.53	29.439	–663.0	–8.5	–8.0
1.00	–0.46	0.69	42.801	–1264.0	–16.0	–8.3
Water–acetonitrile–Na^+, K^+–18-crown-6						
0.00	0	0	0	0	0	0
0.10	–0.11	0.15	1.449	–168.0	–3.7	–1.8
0.23	–0.17	0.21	3.747	–385.0	–5.6	–4.7
0.40	–0.21	0.21	6.853	–676.0	–6.4	–6.8

Table 5. (Contd.)

Mole fraction of S	ΔE_T^N	ΔB_{KT}	$\Delta\varepsilon^{-1} \times 10^3$	$\Delta\delta^2$	$\Delta\Delta G_{\mathrm{NaL}}$	$\Delta\Delta G_{\mathrm{KL}}$
Water–acetonitrile–Na^+, K^+–18-crown-6						
0.64	–0.26	0.24	10.555	–1085.0	–13.5	–10.7
1.00	–0.54	0.18	15.100	–1704.0	–21.3	–18.6
Water–acetone–Na^+, K^+–18-crown-6						
0.07	–0.14	0.17	2.126	–136.0	–3.1	–4.0
0.17	–0.25	0.28	5.493	–323.0	–5.8	–6.3
0.32	–0.30	0.33	11.168	–599.0	–7.8	–11.7
0.55	–0.34	0.37	21.030	–1045.0	–10.7	–19.8

The values and signs of the regression coefficients in Table 4 show how, and to what extent, the donor–acceptor (solute–solvent), intermolecular (solvent–solvent), and electrostatic interactions affect the stability of NaL and KL (Table 5) on replacement of water by aqueous-organic solvents.

As the concentration of an organic component in a mixed aqueous-organic solvent is increased, the solvent structure should undergo changes associated with the break of the hydrogen bond network. Thus, additions of protic and aprotic components to water facilitate formation of local cavities in mixed aqueous-organic solvents. Therefore, as the concentration of a nonaqueous component is increased, the destabilizing contribution of the cohesion energy density to the Gibbs energy of complexation of the Na^+ and K^+ ions with 18-crown-6 decreases (Table 3). Table 4 shows that changes in the intensity of intermolecular interactions in going from water to aqueous-organic solvents are accompanied by enhancement of the stability of NaL and KL ($k_i > 0$, $\Delta\delta^2 < 0$).

It should be noted in this connection that enhancement of the stability of KL in aqueous-organic solvents with protic organic component, compared to water, is also due to enhancement of the donor properties of the medium ($c_i < 0$, $\Delta B_{KT} > 0$), whereas the electron-acceptor properties and electrostatic interactions decrease the stability of the complex ($b_i < 0$, $\Delta E_T^N < 0$; $d_i > 0$, $\Delta\varepsilon^{-1} > 0$). In aqueous-organic solvents with aprotic organic component, on the contrary, the stability of KL grows with increasing dielectric and acceptor properties ($b_i > 0$, $\Delta E_T^N < 0$; $d_i < 0$, $\Delta\varepsilon^{-1} > 0$) and decreases with increasing electron-donor power of aqueous-organic solvents ($c_i > 0$, $\Delta B_{KT} > 0$).

The differences in the solvent effect on the stability of NaL on replacement of water by aqueous-organic solvents are due to the electron-donor activity of these solvents. In solvents with the protic nonaqueous component, the stability of the complex decreases ($c_i > 0$, $\Delta B_{KT} > 0$), and in aqueous-aprotic solvents, increases ($c_i < 0$, $\Delta B_{KT} > 0$) with increasing solvent basicity.

Thus, electrostatic and chemical aspects of solvation are many-sided and complicated. Understanding of factors affecting complexation of cations with electron-donor ligands in solutions requires further development of the thermodynamic and correlation methods of quantitative analysis of the solvent effects.

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