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Stability Constants for the 18-Crown-6−Sodium Ion Complex in Mixtures of Water and Butan-1-ol or Butan-2-ol

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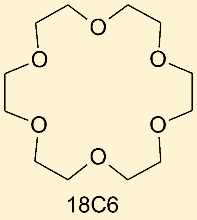
ABSTRACT: The complex formation constants of sodium ions with 18-crown-6 in mixtures of water and butan-1-ol or butan-2-ol at 298.15 K were determined by the potentiometric method with the use of sodium and chloride ion-selective electrodes. The correlations between the logarithm of the complex formation constants and the mole fraction of an alcohol in the mixed solvent were constructed based on the published data and the experimental results obtained in the present study. It was shown that the numerical value of the constant is to a great extent determined by the water-to-alcohol ratio and is virtually independent of the nature of the alcohol. The proposed correlations are suitable for the estimation of the stability constants of 18-crown-6 with sodium, potassium, and thallium ions in mixed aqua-alcohol solvents.



INTRODUCTION

Crown ethers were first isolated by Pedersen in 1962.[1] Pedersen stated the following simple rule for the estimation of the stability of metal complexes with cyclic polyethers: the stability of the complexes directly depends on the match between the cavity size of the crown ether and the metal ion radius. As more experimental data became available, it appeared that the observed selectivity of crown ethers is not always explained by this rule. The limitations of the applicability of the concept of the structural match are associated with the fact this concept does not account for some factors influencing the stability of the complexes (the nature of the solvent and the anion, the type of the substituent in crown ether, etc.). To reliably predict the results of interactions between metal ions and crown ethers, it is necessary to know the thermodynamic characteristics of the complex formation, in particular, the stability constants of ion−ligand complexes.

The aim of the present study was to investigate the influence of the composition of the solvent on the thermodynamic functions of the complex formation of 18-crown-6 ($C_{12}H_{24}O_6$) (see Figure 1) with sodium ions in water−butanol mixtures.

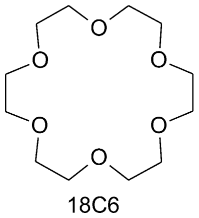


Figure 1. Structure of 18-crown-6.

It is known that 18-crown-6 selectively binds potassium ions. However, in the presence of sodium salts in the reaction mixtures, competitive reactions can occur, and their results substantially depend on the medium in which the reactions proceed. The complex formation constants of sodium ions with 18-crown-6 in different solvents published in the period from 1971 to 2000 were systematically analyzed in the study.[2] The numerical values of the complex formation constants in aqueous alcoholic solutions were reported in refs 3 to 19. It should be noted that the formation of the sodium crown ether complex was studied in most detail in water, methanol, and their mixtures, whereas poor data are available on the reactions in water−ethanol and water−propanol solutions; the data for butan-1(2)-ols are lacking.

Most of the authors dealing with the complex formation in mixed solvents made attempts to build correlations between the constants (or the standard Gibbs free energies) of the reactions and particular characteristics of the medium. For example, the linear correlation between the logarithm of the stability constant for the complexes with alkali metal cations in water−methanol solutions and the difference $(1 - 1/\varepsilon)$, where ε is the dielectric constant of the solvent, was found in the study.[20] However, in a more recent study[21] it was stated that the above-mentioned linear correlation is probably accidental because, in the general case, the local environment of the ions differs from the volume-averaged composition of the mixture. Actually, Abraham and Liszi[22] showed that, when transferred from water to a water-miscible solvent, a metal ion partially retains its hydration shell, and the ion is partially hydrated in a nonaqueous solution. In this case, the observed correlation is evident. In the case of a change in the water content in the mixture, this correlation reflects the resolvation of the cluster containing a cation and water molecules in its nearest environment, if the solvent outside the cluster is considered as a medium with a particular dielectric constant.

Based on their own data, Dishong and Gokel[23] suggested the linear correlation between the logarithm of the complex formation constant of sodium ions with crown ethers and the weight fraction of methanol in the water−methanol mixture (w_{Alc}). The regressive analysis showed that the experimental data can be described by the linear correlation with a

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satisfactory reliability; the correlation coefficient was approximately 0.97. Unfortunately, the extrapolation of this correlation to an alcohol-free mixture leads to the substantially overestimated logarithm of the formation constant of the complex $[\mathrm{Na}(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6)]^+$ in pure water (1.8 versus 0.8 ± 0.2),[2] which casts doubt on the correctness of the dependence $\log K \sim w_{\mathrm{Alc}}$. The Ukrainian research team performed a cycle of studies[17,19,24−26] on the influence of the composition of the mixed solvent on the degree of binding of sodium ions to macrocycles. To estimate the standard Gibbs free energy of the complex formation of 18-crown-6 with sodium salts in aqueous organic solvents (methanol, 2-propanol, acetone, acetonitrile, or dioxane as the organic component) at 298.15 K, the following multiparameter equation[19] was used:

$$\Delta G_{[\mathrm{Na}(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6)]^+} = A_0 + bE_T^N + cB_{\mathrm{KT}} + d\varepsilon^{-1} + k\delta^2 \tag{1}$$

where A_0 is the Gibbs free energy ($\mathrm{kJ \cdot mol^{-1}}$) or the proportional logarithm of the stability constant (the mole fraction scale) of the complex $[\mathrm{Na}(18\mathrm{C}6)]^+$ in an inert solvent, b, c, d, and k are the regression coefficients, E_T^N is the normalized empirical Dimroth−Reichardt parameter, B_{KT} is the Kamlet−Taft solvatochromic parameter characterizing the donor properties of the solvent, ε is the dielectric constant, and δ^2 is the cohesive energy density of the mixed solvent. Taking into account that the determination of the coefficients of the multiparameter equation (eq 1) in the case of a limited data set is the ill-posed problem (the solution is not unique), the parameters correlate with each other, and it is hardly possible to quantitatively estimate the individual terms of the expansion (eq 1). In this context, more simple equations proposed for the description of the complex formation in water−methanol mixtures:[27]

$$\Delta G_{[\mathrm{Na}(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6)]^+} = -1.9 - 13.2\varepsilon/\varepsilon_{\mathrm{H_2O}} \tag{2}$$

and water−2-propanol mixtures[28] are of interest:

$$\Delta G_{[\mathrm{Na}(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6)]^+} = -14 + 11\delta^2/\delta^2_{\mathrm{H_2O}} \tag{3}$$

To summarize, it should be noted that there are a few studies on the complex formation in mixed solvents, and the proposed correlations for the estimation of the stability constants of sodium crown ether complexes, although pretending to be physically substantiated, are in essence formally mathematical.

■ EXPERIMENTAL SECTION

Materials. Sodium chloride (99.8 % in mass), butan-1-ol (99.8 % in mass), butan-2-ol (> 98 % in mass), 18-crown-6 (00660-2-12-38 grade), and tetra-*n*-butylammonium hydroxide (TBAH; 10 % solution in water) were used in the experiments. The salt was predried in vacuo at 120 °C for 50 h. To remove moisture, the alcohols were stored over zeolites 4 A for 7 days and then distilled under atmospheric pressure. On distillation, two fractions were collected: one from the beginning until a rapid increase in the temperature was observed and another from the moment at which the temperature stopped rapidly rising and up to the end of the distillation. Electrochemical measurements were carried out with the use of alcohols from the second fraction. Their purity was confirmed by the fact that the observed refractive indices were equal to those published in the literature: $n_{\mathrm{D}}^{20} = 1.3978$ (1.39922) for butan-1-ol and $n_{\mathrm{D}}^{20} = 1.3964$ (1.39780) for butan-2-ol; the values reported in ref 29 are given in parentheses. Solutions were prepared with the use of deionized water with a specific conductance less than 0.2 $\mu\mathrm{S \cdot cm^{-1}}$ produced with an Elix Millipore water purification system. Crown ether was purified from impurities by standard recrystallization from acetonitrile. The sample was considered to be pure if there were no anomalies in thermoanalytical curves, which were measured by differential scanning calorimetry on a Netzsch DSC 204 F1 calorimeter, and if the melting point and the enthalpy of melting were equal to the published values for 18-crown-6: $T_{\mathrm{m}} = 312.25$ K, $\Delta_{\mathrm{m}}H = 35.5$ $\mathrm{kJ \cdot mol^{-1}}$ and $T_{\mathrm{m}} = 312.45$, $\Delta_{\mathrm{m}}H = 36.66$ $\mathrm{kJ \cdot mol^{-1}}$.[30]

Methodology. The equilibrium constant for the complex formation

$$\mathrm{Na}^+ + \mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6 = [\mathrm{Na}(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6)]^+ \tag{4}$$

is expressed in terms of the molal concentrations and the activity coefficients of the reagents and products according to the equation:

$$K_{\mathrm{m}} = \frac{m_{[\mathrm{Na}(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6)]^+}}{m_{\mathrm{Na}^+} m_{(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6)}} = K_{\mathrm{a}} \frac{\gamma_{\mathrm{Na}^+}\gamma_{(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6)}}{\gamma_{[\mathrm{Na}(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6)]^+}} \tag{5}$$

where K_{a} is the thermodynamic equilibrium constant of the reaction (eq 4) and γ_i is the activity coefficient of the ith particle in the solution. In highly dilute solutions, it can be assumed that the activity coefficient of the ligand $\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6$ is equal to unity, and the activity coefficients of the equally charged ions are equal and mutually canceled. Taking into account these assumptions, the constant K_{m} is equal to K_{a}:

$$\begin{aligned} K_{\mathrm{a}} &\cong \frac{m_{[\mathrm{Na}(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6)]^+}}{m_{\mathrm{Na}^+} m_{(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6)}} \\ &= \frac{m^0_{\mathrm{Na}^+} - m_{\mathrm{Na}^+}}{m_{\mathrm{Na}^+}(m^0_{(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6)} - m^0_{\mathrm{Na}^+} + m_{\mathrm{Na}^+})} \end{aligned} \tag{6}$$

In refs 31 and 32, it was shown that the concentration constant of the reaction eq 4 in a mixture of water and methanol remains virtually unchanged. and it is equal to the thermodynamic constant with the ionic strength varying in the range of 0.005 to 0.05 *m*.

Apparatus. In the present study, the concentration of sodium ions m_{Na^+} involved in the complex with 18-crown-6 was determined with the use of an electrochemical cell:

$$\begin{aligned} &\mathrm{Cl}^-\text{−ISE}|\mathrm{NaCl}(m) + \mathrm{TBAH} + \mathrm{H_2O}(100 - w_{\mathrm{Alc}}) \\ &\quad + 1(2)\text{-}\mathrm{C_4H_9OH}(w_{\mathrm{Alc}}) + \mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6|\mathrm{Na}^+\text{−ISE} \end{aligned}$$

where ISE is the ion-selective electrode, m is the molality of the solution with respect to sodium chloride, and w_{Alc} is the weight percentage of alcohol in the solvent. According to the Nernst equation, the electromotive force is proportional to the logarithm of the product of the molalities of sodium and chloride ions:

$$\begin{aligned} E &= E^0 + \frac{RT}{F}\ln(\gamma_{\mathrm{Na}^+}\gamma_{\mathrm{Cl}^-}) + \frac{RT}{F}\ln(m_{\mathrm{Na}^+}m_{\mathrm{Cl}^-}) \\ &= \alpha + \beta\ln(m_{\mathrm{Na}^+}m_{\mathrm{Cl}^-}) \end{aligned} \tag{7}$$

where E^0 is the standard electromotive force, R is the universal gas constant, T is the absolute temperature, F is the Faraday constant, γ_{Na^+} and γ_{Cl^-} are the activity coefficients of sodium and chloride ions, respectively, and m_{Na^+} and m_{Cl^-} are the concentrations of sodium and chloride ions. At a constant ionic strength, α is independent of the amount of the salt in the dilute solution. The parameter β should coincide with RT/F (the so-called Nernst slope), but manufacturers of ion-selective electrodes allow the deviation of the response of the electrode pair from the Nernst law, which is stated in the certificates of conformance for the electrodes. When determining the concentrations of ions from the results of electomotive force (EMF) measurements of the investigated cells, not the value of β (as it is in the case of mean-ion activity coefficients) but the fact that the parameter β remains constant is of principal importance. Hence, when designing experiments, particular attention was paid to the fact that the values of β during the calibration and in the course of experiments with crown ether were equal.

Both electrodes were calibrated upon measurements; their functional correctness was proved as described in ref 33. In the beginning of each experiment, the EMF of the investigated cell, which did not contain crown ether, was measured, and the calibration plots of E versus $\ln(m^0_{\mathrm{Na}^+} m^0_{\mathrm{Cl}^-})$ were constructed (the superscript 0 indicates that a complex-forming agent was absent in the solution). Then a complex-forming agent was added to the solutions under study using the weighting technique, and the measurements were repeated. The m_{Na^+} values were determined from the calibration plots, and then the constant K_a was calculated. The complex formation constant was determined for at least eight solutions with different salt-to-ligand ratios. For each NaCl concentration, a 5−10-fold excess of 18-crown-6 was used.

Tetra-*n*-butylammonium hydroxide (TBAH) was added to bind protons, which interfere with the selective determination of sodium ions, and to maintain the desired ionic strength, due to which the activity coefficients of sodium ions remained constant as the salt concentration was varied. Roberts and co-workers showed[34] that the stability constant of ammonium crown ether complexes in aqueous solutions decreases both with an increasing degree of replacement of hydrogen atoms in the ammonium cation by alkyl groups (in the series $\mathrm{NH_4^+} > \mathrm{EtNH_3^+} > \mathrm{Et_2NH_2^+} > \mathrm{Et_3NH^+}$) and with an increasing length of the hydrocarbon chain of the substituent (in the order $\mathrm{MeNH_3^+} > \mathrm{EtNH_3^+} > n\text{-}\mathrm{BuNH_3^+}$). Ammonium ions containing bulky substituents, whose size is much larger than the diameter of the cavity of the macrocycle, form pseudorotoxane complexes with polyethers only in the case of mono-, di-, and trialkylammonium ions. Hence, under the conditions of our experiments, tetra-*n*-butylammonium hydroxide can be considered as an inert electrolyte, which is not involved in the complex formation.

The electromotive force of the investigated cells was measured with the use of a Multitest IPL-103 ionomer (Research and Production Association Semiko, Russia) with an accuracy of ± 0.1 mV; the input impedance was not lower than 10^{12} Ω. Glass ESL-51-07SP (Gomel Measuring Equipment Plant, Belarus) and DX223-$\mathrm{Na^+}$ (Mettler Toledo, Switzerland) electrodes were used as the sodium ion-selective electrodes; OP-Cl-0711P (Radelkis, Hundary) and Elis-131 (Research and Production Association Izmeritelnaya Tekhnika IT, Russia) electrodes were used as the chloride ion-selective electrodes. The resistance of $\mathrm{Na^+}$-ISE and $\mathrm{Cl^-}$-ISE was at most (200 and 50) mΩ, respectively. The complex formation constants calculated from the data obtained with different electrodes agree with each other, which is additional support for the correctness of the results of electrochemical measurements. The temperature of the solutions was controlled by a TZh-TS-01/12K-20 cryothermostat (Russia); the temperature control accuracy was ± 0.05 K. In the course of the measurements, the solution was continuously magnetically stirred at a rate of 1 rev·s^{-1}. The measured EMF values of the cells were assumed to be equilibrium if the rate of the change in EMF was no higher than (0.01 to 0.02) mV·min^{-1}. As a rule, the equilibrium was established within 30 min.

The complex formation of 18-crown-6 with sodium ions was studied in two steps. To elaborate the procedure for the determination of the stability constants of sodium crown ether complexes, in the first step we measured the EMF values of cells containing aqueous solutions whose K_a are known.[2] Once the reliability of the results was confirmed, the complex formation in a mixed water−alcohol solvent was investigated.

RESULTS AND DISCUSSION

The main source of errors in the determination of the complex formation constants by the potentiometric method is the error of the measurements of EMF. In the course of experiments with aqueous solutions of sodium chloride, the results obtained at considerable intervals (the experiments were performed at one month intervals) were well-reproduced. In addition, we minimized the possible contribution of the systematic shift of the EMF values in the course of the measurements to the error by performing calibration measurements for each new series of experiments. The random error was evaluated according to the conventional method. Thus, the rms deviation multiplied by Student's t value (for 95 % confidence interval and the corresponding number of the degrees of freedom) was calculated. The total error was determined according to the error-accumulation law. The results of calculations are given in Table 1. The complexes formation constant of sodium ions with 18-crown-6 in an aqueous solution at 298.15 K ($\log K_a = 0.86 \pm 0.1$) is in good agreement with the published data (0.8 ± 0.2).[2] Hereinafter, the common (decadic) rather than natural logarithms of the equilibrium constant are given for the convenience of the comparison of the results obtained in the present study with the data published in the literature.

Table 1. Experimental Values of Sodium Ions (1) and 18-Crown-6 (2) Molalities and Equilibrium Constants K_a (eq 6) in Water at Different Sodium Chloride to Crown Ether Ratios at 298.15 K[a]

m_1^0	m_2^0	m_1	
mmol·kg^{-1}	mmol·kg^{-1}	mmol·kg^{-1}	K_a
3.33	16.9	2.99	6.8
4.99	25.2	4.19	7.8
6.65	33.5	5.42	7.1
9.99	50.3	7.53	6.8
3.33	33.9	2.63	8.0
4.99	50.3	3.61	7.8
6.65	66.9	4.62	6.8
9.99	100.6	6.06	6.7
			avg 7.2

[a] m_1^0 and m_1 denote the molality of NaCl before and after the addition of 18-crown-6, and m_2^0 denotes the amount of crown ether added. The standard uncertainty m is 0.01 mmol·kg^{-1}, and the combined uncertainty K_a is $K_a = 1.2$ with a 0.95 level of confidence ($k \approx 2$)

Experiments with mixed solvents were carried out as described above. In one series of experiments, the successive measurements were performed for samples with a constant alcohol-to-water ratio but with different salt contents, starting with the lowest sodium chloride concentration ($\sim 5 \cdot 10^{-4}$ m) and up to the highest concentration (at most 10^{-2} m). Due to the phase separation in water—butan-1(2)-ol systems, it was impossible to determine the complex formation constants in a wide range of compositions of the mixed solvent. The electrode pair exhibited a linear EMF response versus the logarithm of the mean-ion molality for solutions containing alcohol up to 5 and 15 wt % for butan-1-ol and butan-2-ol, respectively (Figure 2). In alcohol-rich solutions, the function $E = f(\ln[m_{Na^+}m_{Cl^-}])$ showed a nonlinear behavior (Figure 2), and these mixtures were not investigated in the present study.

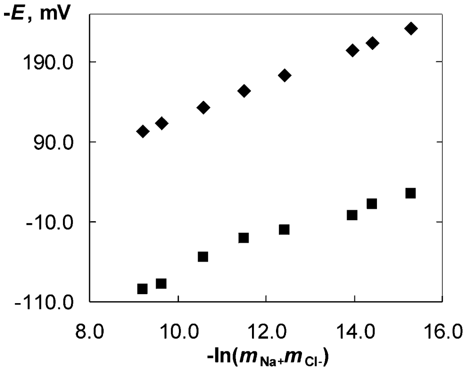

Figure 2. Plot of the response of the electrode pair versus the logarithm of the product of the sodium and chloride ion concentrations in aqueous 1-C_4H_9OH at 298.15 K. The results of the measurements for solutions with different alcohol contents are represented by graphical symbols: ♦, 4 wt % of butan-1-ol; ■, 90 wt % of butan-1-ol.

The results of the processing of the electrochemical data obtained in the cells containing a mixed solvent are given in Table 2 (the alcohol-to-water weight ratios are given in parentheses).

Table 2. Experimental Values of Sodium Ions (1) and 18-Crown-6 (2) Molalities, and Equilibrium Constants K_a (eq 6) in Mixed Solvents at Different Sodium Chloride to Crown Ether Ratios at 298.15 K[a]

solvent	m_1^0 mmol·kg^{-1}	m_2^0 mmol·kg^{-1}	m_1 mmol·kg^{-1}	K_a
butan-2-ol—water (5:95)	3.36	16.8	2.92	9.1
	5.01	25.2	4.07	9.5
	7.99	41.1	5.83	9.5
	10.00	50.4	7.30	7.8
	3.36	33.6	2.69	7.6
	5.01	50.4	3.42	9.5
	7.99	82.2	4.71	8.8
	10.00	100.6	5.57	8.3
				avg 8.8
butan-2-ol—water (15:85)	3.59	18.5	3.01	10.8
	5.51	28.4	4.31	10.2
	7.43	38.5	5.30	11.1
	10.01	51.6	6.55	11.0
	3.59	37.1	2.61	10.4
	5.51	56.7	3.37	11.6
	7.43	77.0	4.01	11.6
	10.01	103.1	4.61	11.95
				avg 11.0
butan-1-ol—water (6:94)	3.19	16.7	2.74	10.0
	5.03	25.0	4.22	8.0
	8.05	40.0	6.00	9.0
	10.00	50.0	7.31	7.8
	3.19	33.4	2.43	9.6
	5.03	50.1	3.51	8.9
	8.05	80.0	4.67	9.5
	10.00	100.0	5.59	8.3
				avg 8.9

[a] m_1^0 and m_1 denote the molality of NaCl before and after the addition of crown ether; m_2^0 denotes the amount of crown ether added. The standard uncertainty u is $u(m) = 0.01$, and the combined expanded uncertainties U are $U(K_a) = 1.7$ for 5 and 6 wt % of butan-2-ol or butan-1-ol and $U(K_a) = 1.3$ for 15 wt % of butan-2-ol with a 0.95 level of confidence ($k \approx 2$).

A comparison of the results of the present study and the published data on the stability constants of sodium crown ether complexes in water—alcohol solvents is presented in Figure 3. Figure 3 shows the logarithms of the complex formation constants of sodium ions with 18-crown-6 in mixtures of water with methanol, ethanol, 2-propanol,[2] butan-1-ol, and butan-2-ol (the present study). Since the complex formation constants reported in the review[2] were calculated on the molality concentration scale, the results presented in Table 2 were recalculated taking into account the data on the densities of the mixtures under study. Under the experimental conditions used in the present study, the density of the solution determined by pycnometry was found to be equal to the density of the water—alcohol solution up to four decimal places.

As can be seen from Figure 3, the following general rule is true for alcohols belonging to different homologous series and containing a hydrocarbon skeleton of different length: the higher content of the organic component in the mixture, the higher stability of the complex. There is the linear correlation between the logarithm of the constant and the mole fraction of alcohol in the solvent. The deviations of the experimental values of log K_a from the straight line are smaller than the error in the determination of the complex formation constant in water by different methods, such as conductometry, polarography, calorimetric titration, and NMR spectroscopy. This is evidence that the influence of alcohols of the general formula $C_nH_{2n+1}OH$ on the binding of alkali metal cations to crown ether $C_{12}H_{24}O_6$ in mixed solvents is virtually independent of the lengths and structure of the hydrocarbon chain and is determined only by the water-to-organic component ratio in the solvent. On the basis of the above-described results, the following correlation that relates the logarithm of the complex formation constant at 298.15 K to the mole fraction of alcohol in the mixed solvent can be derived:

$$\log K_a = a \cdot x_{Alc} + b \qquad (8)$$

where a and b are the parameters of the equation and x_{Alc} is the mole fraction of alcohol in the mixed solvent. The approximation of a total data set for alcohols with $n = 1 \div 4$ by eq 8 gave the following parameters: $a = 3.32 \pm 0.1$, $b = 0.838 \pm 0.07$; the maximum deviation of the calculated stability constants of the sodium crown ether complex from the initial values is 0.36 logarithmic units; the rms deviation is 0.16. The largest deviation is observed for two mixtures of water and 2-propanol. Since the complex formation constants of sodium ions with 18-crown-6 in solutions containing 2-C_3H_7OH were determined in the only study, these data are preliminary.

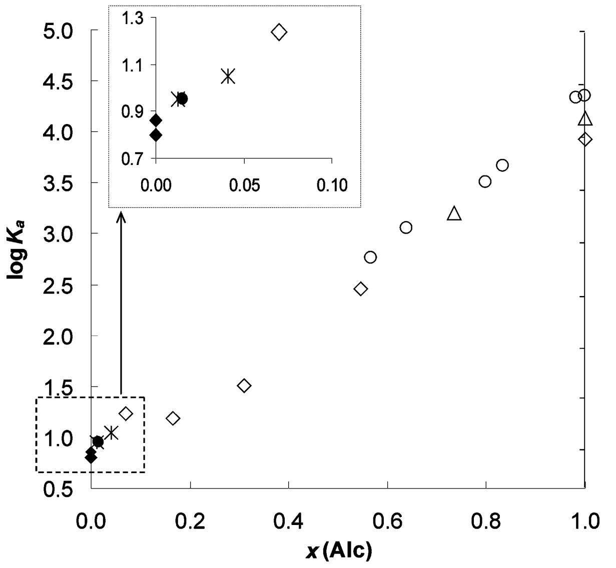

Figure 3. Plot of the logarithm of the complex formation constant of sodium chloride with 18-crown-6 (K_a, eq 6) versus the alcohol content in the mixed solvent (x_{Alc}) at 298.15 K: ◆, Arnaud-Neu et al.,[2] pure water; ○, Arnaud-Neu et al.,[2] water−methanol solvent; △, Arnaud-Neu et al.,[2] water−ethanol solvent; ◇, Arnaud-Neu et al.,[2] water−propan-2-ol solvent; ●, from Table 2, water−butan-1-ol solvent; ∗, from Table 2, water−butan-2-ol solvent. The inset shows a fragment of the diagram in the composition range up to 10 mol % of alcohol.

The correlation between the degree of binding of metal cations to 18-crown-6 and the percentage of the organic component in water−alcohol solvents was confirmed by the data on the complex formation with potassium[2,15,16,35] and thallium[36] ions (Figures 4 and 5). Investigations of systems containing 18-crown-6 with thallium salts in different water−alcohol mixtures ($H_2O-C_nH_{2n+1}OH$, $n = 3$) by the Polish research group[36] showed that in all cases under study the stability constant of the thallium crown ether complex decreases with increasing water content in the mixed solvent regardless of the specific properties of pure alcohols (the dielectric constant, the magnetic moment, etc.). It was hypothesized that the effect of alcohol in its mixtures with water is reduced.

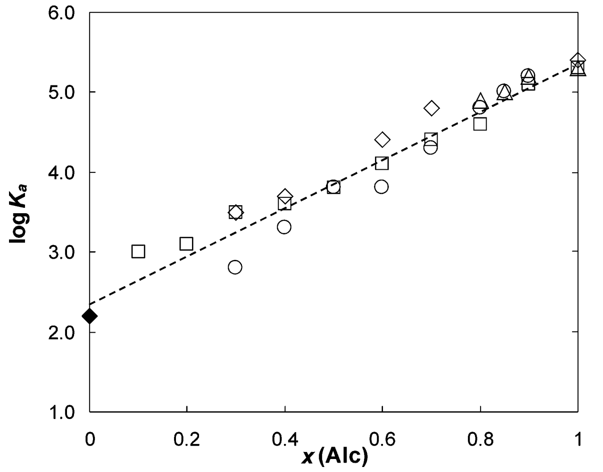

Figure 4. Plot of the logarithm of the complex formation constants of 18-crown-6 with thallium ions versus the alcohol content x_{Alc} in the mixed solvent at 298.15 K. The experimental data for different solvents are represented by symbols: ◆, Arnaud-Neu et al.,[2] pure water; ○, Lada et al.,[36] water−methanol solvent; △, Lada et al.,[36] water−ethanol solvent; ◇, Lada et al.,[36] water−propan-2-ol solvent; □, Lada et al.,[36] water−propal-1-ol solvent; the calculated logarithm constants (log K_a) with the use of the eq 8 are shown as a dashed line.

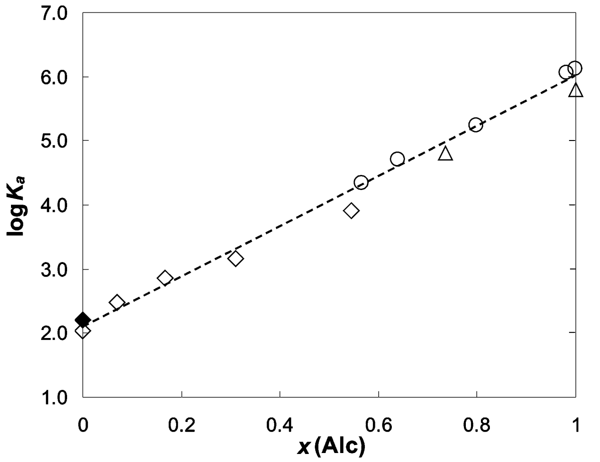

Figure 5. Plot of the logarithm of the complex formation constants of 18-crown-6 with potassium ions versus the alcohol content x_{Alc} in the mixed solvent at 298.15 K. The experimental data for different solvents are represented by symbols: ◆, Arnaud-Neu et al.,[2] pure water; ○, Arnaud-Neu et al.,[2] water−methanol solvent; △, Luca and Azab,[15] Bogatskii et al.,[16] water−ethanol solvent; ◇, and Didi and Bondarev,[35] water−propan-2-ol solvent; the calculated logarithm constants (log K_a) with the use of the eq 8 are shown as a dashed line.

The calculated coefficients of eq 8 for the potassium crown ether complex are $a = 3.96 \pm 0.1$, $b = 2.057 \pm 0.07$; the coefficients for the thallium crown ether complex are $a = 2.99 \pm 0.1$, $b = 2.383 \pm 0.09$. In the experiments with potassium, the maximum error of the approximation is 0.31 logarithmic units, and the rms deviation is 0.13; for thallium, the corresponding values are 0.48 and 0.19.

■ CONCLUSIONS

The fact that not only the reaction under consideration but also related reactions with other metal ions are characterized by the linear correlation (eq 8) suggests that eq 8 will allow one to estimate the complex formation constants at 298.15 K in any water−alcohol solvent without additional experiments. The main uncertainties of these estimations are the errors of primary experimental data. To confirm the validity of the correlation eq 8, it is desirable to measure the K_a of reaction (eq 4) in solutions with propanols additionally.

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■ REFERENCES

(1) Pedersen, C. J. Cyclic polyethers and their complexes with metal salts. *J. Am. Chem. Soc.* **1967**, *89*, 2495−2496.

(2) Arnaud-Neu, F.; Delgado, R.; Chaves, S. Critical evaluation of stability constants and thermodynamic functions of metal complexes of crown ethers (IUPAC Technical Report). *Pure Appl. Chem. Soc.* **2003**, *75*, 71−102.

(3) Izatt, R. M.; Terry, R. E.; Nelson, D. P.; Chan, Y.; Eatough, D. J.; Bradshaw, J. S.; Hansen, L. D.; Christensen, J. J. Calorimetric titration study of the interaction of some uniand bivalent cations with benzo-15-crown-5, 18-crown-6, dibenzo-24-crown-8, and dibenzo-27-crown-9 in methanol-water solvents, at 25 °C and $\mu = 0.1$. *J. Am. Chem. Soc.* **1976**, *98*, 7626−7630.

(4) Krakowiak, K. E.; Zhang, X. X.; Bradshaw, J. S.; Zhu, C. Y.; Izatt, R. M. New 2-methylenepropylene-bridged cryptands with high sodium ion selectivity: A thermodynamic study of complexation. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1995**, *23*, 223−231.

(5) Lehn, J. M.; Vierling, P. The [18]-N_2O_3 aza-oxa macrocycle: a selective receptor unit for primary ammonium cations. *Tetrahedron Lett.* **1980**, *21*, 1323−1326.

(6) Haymore, B. L.; Lamb, J. D.; Izatt, R. M.; Christensen, J. J. Thermodynamic origin of the macrocyclic effect in crown ether complexes of sodium(1+), potassium(1+), and barium(2+). *Inorg. Chem.* **1982**, *21*, 1598−1602.

(7) Frensdorff, H. K. Stability constants of cyclic polyether complexes with univalent cations. *J. Am. Chem. Soc.* **1971**, *93*, 600−606.

(8) Smetana, A. J.; Popov, A. I. On the influence of ionic strength on the equilibrium constant of an ion−molecule reaction. *J. Chem. Thermodyn.* **1979**, *11*, 1145−1149.

(9) Michaux, G.; Reisse, J. Solution thermodynamic studies. Part 6. Enthalpy-entropy compensation for the complexation reactions of some crown ethers with alkaline cations: a quantitative interpretation of the complexing properties of 18-crown-6. *J. Am. Chem. Soc.* **1982**, *104*, 6895−6899.

(10) Buschmann, H. J. Stabilitatskonstanten und thermodynamische Werte fur die Bildung von 1:1- und 2:1-Komplexen von Kronenethern mit Alkali-und Erdalkali-Ionen in Methanol. *Chem. Ber.* **1985**, *118*, 2746−2756.

(11) Strasser, B. O.; Popov, A. I. Influence of solvent properties on the kinetics of complexation of the sodium ion with 18-crown-6. *J. Am. Chem. Soc.* **1985**, *107*, 7921−7924.

(12) Zollinger, D. P.; Bos, M.; van Veen-Blaauw, A. M.W.; van der Linden, W. E. Microcomputer-controlled polarographic instrumentation and its use in the determination of stability constants of crown ether complexes. *Anal. Chim. Acta* **1985**, *167*, 89−96.

(13) Buschmann, H. J. A comparison of different experimental techniques for the determination of the stabilities of polyether, crown ether and cryptand complexes in solution. *Inorg. Chim. Acta* **1992**, *195*, 51−60.

(14) Solov'ev, V. P.; Strakhova, N. N.; Kazachenko, V. P.; Solotnov, A. F.; Baulin, V. E.; Raevsky, O. A.; Rudiger, V.; Eblinger, F.; Schneider, H.-J. Steric and Stereoelectronic Effects in Aza Crown Ether Complexes. *Eur. J. Org. Chem.* **1998**, 1379−1389.

(15) Luca, C.; Azab, H. A. A Study of Formation Equilibria of the Complexes of Some Metal Cations with Polyoxa Macrocyclic Ligands. *Anal. Lett.* **1984**, *17*, 1937−1946.

(16) Bogatskii, A. V.; Luk'yanenko, N. G.; Popkov, Y. A.; Zakharov, K. S.; Vavra, V. M. Synthesis and complex-forming ability of tricarbonyl analogs of crown ethers. *J. Org. Chem. USSR* **1981**, *17*, 1062−1069.

(17) Didi, Y.; Tsurko, E. N.; Bondarev, N. V. Stability constants of the Na^+ complex with 18-crown-6 in aqueous 2-propanol at 298.15−318.15 K. *Russ. J. Gen. Chem.* **1997**, *67*, 885−888.

(18) Didi, Y.; Kern, A. P.; Tsurko, E. N.; Bondarev, N. V. Thermodynamics of complex formation and solvation in the systems M-18-crown-6−H_2O−2-propanol (M = Na^+, K^+). *Russ. J. Gen. Chem.* **1998**, *68*, 758−762.

(19) Zaitseva, I. S.; El'tsov, S. V.; Kabakova, E. N.; Bondarev, N. V. Correlation analysis of the solvent effects on the on the thermodynamic functions of complexation of sodium and potassium ions with 18-crown-6 ether in aqueous−organic solvents. *Russ. J. Gen. Chem.* **2003**, *73*, 1079−1084.

(20) Pullman, B.; Goldblum, N., Eds. *Metal-Ligand Interactions in Organic Chemistry and Biochemistry*; Reidel Publishing Company: Dordrecht, 1977.

(21) Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D., Eds. *Inclusion Compounds*; Academic Press: New York, 1984.

(22) Abraham, M. H.; Liszi, J. Calculations on ionic solvation. Part 1. Free energies of solvation of gaseous univalent ions using a one-layer continuum model. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1604−1614.

(23) Dishong, D. M.; Gokel, G. W. Crown cation complex effects. 16. Solvent dependence of the 15-crown-5 and 18-crown-6 equilibriums with sodium cation. *J. Org. Chem.* **1982**, *47*, 147−148.

(24) Pereselko, V. F.; Lipovetskaya, E. E.; Kabakova, E. N.; Bondarev, N. V. Thermodynamics of complex formation of Na^+ with 18-crown-6 in methanol−water mixtures. *Russ. J. Gen. Chem.* **1995**, *65*, 366−368.

(25) Lipovetskaya, E. E.; Kabakova, E. N.; Bondarev, N. V. Thermodynamics of complex formation of metal ions with crown ethers. Na^+−18-crown-6−H_2O−methanol system. *Russ. J. Gen. Chem.* **1996**, *66*, 204−207.

(26) Kabakova, E. N.; Bondarev, N. V. Thermodynamic parameters of complex formation of Na^+ and K^+ ions with 18-crown-6 in water−methanol mixtures. *Russ. J. Phys. Chem.* **1998**, *72*, 1196−1199.

(27) Bondarev, N. V. Solvation-thermodynamic effects of the water-methanol solvent on the coordination of Na^+, K^+, NH_4^+, and Ag^+ ions with 18-crown-6. Gibbs energies of complexation and resolvation of reagents. *Russ. J. Gen. Chem.* **2006**, *76*, 13−18.

(28) Larina, O. V.; Bondarev, N. V.; Kern, A. P. Solvent effects and complex formation of sodium, potassium, ammonium, and silver(I) salts with 18-crown-6 in water.propan-2-ol solvents. *Vestn. Kharkiv. National Univ.* **2007**, *770*, 301−312.

(29) Weissberger, A., Proakauer, E. S., Riddick, J. A., Toops, E. E., Eds. *Organic solvents*, 2nd ed.; Wiley (Interscience): New York, 1955.

(30) Domanska, U.; Venkatesu, P. Measurement and Correlation of Solid-Liquid Equilibria of 18-Crown-6 in Alcohols. *J. Chem. Eng. Data* **1998**, *43*, 919−924.

(31) Zavada, J.; Pechanec, V.; Zajicek, J.; Stibor, I.; Vitek, A. Effects of salt concentration and counterion on stability of alkali ion−18-crown-6 complexes in aqueous and methanolic solution: A conflicting evidence from potentiometric and sodium-23 NMR studies. *Collect. Czech. Chem. Commun.* **1985**, *50*, 1184−1193.

(32) Smetana, A. J.; Popov, A. I. On the influence of ionic strength on the equilibrium constant of an ion−molecule reaction. *J. Chem. Thermodyn.* **1979**, *11*, 1145−1149.

(33) Uspenskaya, I.; Konstantinova, E.; Veryaeva, E.; Mamontov, M. In *Electromotive Force Measurements and Thermodynamic Modelling of Sodium Chloride in Aqueous−Alcohol Solvents, Electromotive Force and Measurement in Several Systems*; Sadik, K., Ed.; InTech: Rijeka, Croatia, 2011.

(34) Roberts, J. L.; McClintock, R. E.; El-Omrani, Y.; Larson, J. W. Stability Constants for 18-Crown-6−Alkylammonium Ion Complexes. *J. Chem. Eng. Data* **1979**, *24*, 79−80.

(35) Didi, Y.; Bondarev, N. V. Stability constants of the complex [K-18C6]$^+$ in water−2-propanol mixtures. *Russ. J. Phys. Chem.* **1996**, *66*, 1267−1270.

(36) Lada, E.; Koczorowska, A.; Lei, X.; Kalinowski, M. K. Complexation of Thallium(I) Ions by 18-Crown-6 in Alcohol−Water Binary Mixtures. *Pol. J. Chem.* **1993**, *67*, 211−217.