

COMPLEX FORMATION OF Ag^+ WITH POLYETHER 18-CROWN-6 Calorimetric and potentiometric methods*

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Abstract

The complex formation of Ag^+ with polyether 18-crown-6 (18C6) and their solvation have been studied using calorimetric and potentiometric methods in H_2O –EtOH solvents in wide range of ethanol concentration. The standard enthalpies of dissolution AgNO_3 , AgClO_4 and 18C6 in aqueous-ethanol solvents are obtained. The stability of a complex $[\text{Ag}18\text{C}6]^+$ grows with increasing the EtOH content a solvent.

Using the method based on the thermodynamic characteristics of solvation of metal-ion, ligand and complex-ion the interpretation of the results has been given.

Keywords: binary solvents, complex formation, complex stability, 18-crown-6, ethanol, silver(I) ion, transfer enthalpy change

Introduction

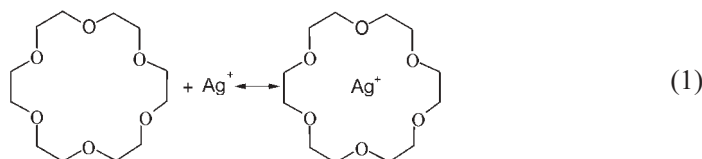
The interest in studying crown-ethers is based upon their selectivity towards the reaction of metal cations. In many areas this property is important: design sensing elements for cation selective electrodes, development of carrier-membrane systems, study of transport mechanisms of biological ions, increasing of solubility of salts in solvents of low polarity [1].

The complex stability depends on the nature and the composition of mixed solvents. The formation of complexes is competitive with the solvation of all participants of the reaction. The thermodynamic parameters of a complex formation are interlinked to the solvation of a cation, ligand and complex, therefore the thermodynamic of solvation of reagents determines a complex stability in a mixed binary solvent. The establishment of interrelation between the reagent solvation and thermodynamics of the reactions is an important problem in solution chemistry.

The study of thermodynamics of complex formation Ag^+ with 18-crown-6 in aqueous ethanol:

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and the reagents solvation has been presented in this work.

Materials and procedures

Silver nitrate (pure grad) was dried at 90°C under vacuum up to a constant mass. Silver perchlorate was obtained by the method described in [2]. The purity of salts AgNO_3 (99.9%) and AgClO_4 (99.0%) was checked by potentiometric titration. Crown-ether 18C6 ('IREA', Moscow) was dried using P_2O_5 [3]. The analysis has shown the carbon content 99.97% in relation to calculated by the formula $\text{C}_{12}\text{H}_{24}\text{O}_6$. Ethanol was purified by distillation. The water content in EtOH was determined by precise measuring of density and was taken into account at preparation of a mixed solvent.

Enthalpies of reaction (1) and enthalpies of dissolution AgNO_3 , AgClO_4 and 18C6 are obtained calorimetrically.

It has utilised the isoperibolic calorimeter of our own desing and construction, which is similar to the one described in [4]. The cell of 110 cm^3 volume for a calorimetric titration was made of stainless steel. The calorimetric cell for measuring the dissolution effect has a volume 72 cm^3 and is supplied with a holder and a breaker for a glass ampoule.

Both cells have a rotational stirrer and semiconductor thermometer on the base Co–Mn oxide. The calorimeter vessel was located within nickel plated brass cylinder which can be submerged into the thermostat regulated by means PID-regulator at $25 \pm 0.002^\circ\text{C}$. The heat capacity of the calorimetric system was determined electrically by calibration with an accuracy of $\pm 0.2\%$ over the total temperature range of 0.1°C .

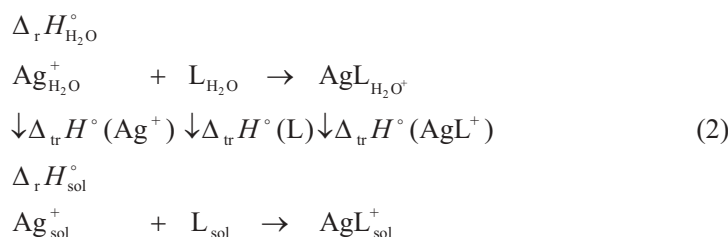
The measured enthalpy of dissolution $\Delta_{\text{sol}}H_{298.15}^\circ$ (KCl , H_2O) corresponds to the standard SRM 1655 NBS [6] within 0.4%.

Stability constants of $[\text{Ag18C6}]^+$ in EtOH–water solvents are obtained potentiometrically by 'CRYTUR' Ag^+ -selective electrode. The calibration of an electrode was made on EtOH–water solutions of silver nitrate (10^{-3} – $10^{-2}\text{ mol L}^{-1}$) directly ahead of the experiment. In each composition of a mixed solvent 10–14 potentiometric measurings at $25 \pm 0.1^\circ\text{C}$ were carried out. The analytical concentration of silver ion was equal 10^{-3} – $10^{-2}\text{ mol L}^{-1}$, the concentration of a ligand was 10^{-3} – $10^{-2}\text{ mol L}^{-1}$.

For the determination of enthalpies of dissolution AgNO_3 , AgClO_4 and 18C6 the heats of dissolution 0.03–0.16 g of reagent were measured. In each binary solvent 4–5 experiments were made. The standard enthalpies of dissolution was obtained by linear extrapolation of dependences $\Delta_{\text{sol}}H^m = f(m^{1/2})$ to infinite dilution. Concentration dependence of dissolution's heat 18C6 was not revealed.

The proposed method

The change of parameters of complex formation with solvent composition can be submitted via the following schema:



The following equation for the change of reaction heat at transfer of reaction from water to other solvent was obtained from a thermodynamic cycle (2):

$$\Delta_{\text{tr}} H^\circ = \Delta_r H_{\text{sol}}^\circ - \Delta_r H_{\text{H}_2\text{O}}^\circ = \Delta_{\text{tr}} H^\circ (\text{AgL}^+) - \Delta_{\text{tr}} H^\circ (\text{Ag}^+) - \Delta_{\text{tr}} H^\circ (\text{L}) \quad (3)$$

where $\Delta_{\text{tr}} H^\circ$, $\Delta_{\text{tr}} H^\circ (\text{Ag}^+)$, $\Delta_{\text{tr}} H^\circ (\text{L})$, $\Delta_{\text{tr}} H^\circ (\text{AgL}^+)$ – the transfer enthalpies of reaction and reagents accordingly. The stability of a complex depend on the parameters of reagents solvation similarly:

$$-RT \ln K_{\text{sol}}^\circ / K_{\text{H}_2\text{O}}^\circ = \Delta_{\text{tr}} G^\circ = \Delta_{\text{tr}} G^\circ (\text{AgL}^+) - \Delta_{\text{tr}} G^\circ (\text{Ag}^+) - \Delta_{\text{tr}} G^\circ (\text{L}) \quad (4)$$

Following Eq. (3) it is possible to calculate the contribution of each reagent into the transfer enthalpy of reaction. It enables to estimate the role of solvation effects in investigated reaction. The enthalpies of reaction (1) and transfer enthalpy of reagents from water to water-ethanol solvents were experimentally determined for this purpose.

For the determination of $\Delta_{\text{tr}} H^\circ$ the heat of dilution (Q'_{dil}) of a ligand solution (18C6) and the heat (Q_{mix}) of its mixing with a solution AgNO₃ (or AgClO₄) were measured at 298.15 K. The ligand solution was placed in an ampule. The composition of a solvent in an ampoule and in a cell was identical.

Q_{mix} includes the heat of a complex formation (Q_{cpl}), the heat and the heat of dilution of a solution there contained in a cell (Q''_{dil}):

$$Q_{\text{mix}} = Q_{\text{cpl}} + Q'_{\text{dil}} + Q''_{\text{dil}} \quad (5)$$

Q''_{dil} was very small because the solution volume in a cell was incremented approximately by 1% during the experiment and the reagent concentrations in a cell did not exceed 0.15 mol L⁻¹.

Therefore the Eq. (5) can be written as:

$$\Delta_{\text{cpl}} H_i = \Delta_{\text{mix}} H_i - \Delta_{\text{dil}} H_i \quad (6)$$

where $\Delta_{\text{cpl}} H_i$, $\Delta_{\text{mix}} H_i$ and $\Delta_{\text{dil}} H_i$ – molar enthalpies of a complex formation in process, enthalpies of mixing and dilution calculated on 1 mol of an added ligand in *i*-th experience.

The program HEAT [6], which is intended for the calculation of reactions enthalpies and equilibrium constants in systems with arbitrary stoichiometry, made the processing of the experimental data. The algorithm HEAT executes the minimisation of function F :

$$F = \sum_{i=1}^N \omega_i (\Delta_{\text{cpl}} H - \Delta_{\text{calc}} H)_i^2 \quad (7)$$

where N – number of experimental points; ω_i – weighing factors taking into account unequal precision of measurements; $\Delta_{\text{calc}} H$ – calculated enthalpies by given stoichiometrical model; $\Delta_{\text{cpl}} H$ – experimentally measured enthalpies of process.

By Eqs (8)–(10) there is an opportunity to calculate the standard value of $\Delta_r H^\circ$ for a simple model including only complex ML :

$$\Delta_{\text{cpl}} H = [ML] \Delta_r H^\circ / X_L^\circ \quad (8)$$

where C_L° – the analytical concentration of a ligand, $[ML]$ – the equilibrium concentration of a complex to the end of the experiment.

From the equation of material balance of reaction follows:

$$C_L^\circ = [ML] + [L] \quad (9)$$

where $[L]$ – equilibrium concentrations of a ligand.

Hence Eq. (8) can also be submitted as

$$1/\Delta_{\text{cpl}} H = 1/\Delta_r H^\circ + 1/K^\circ \Delta_r H^\circ [Ag] \quad (10)$$

where $[Ag]$ – equilibrium concentration of Ag⁺-ion.

Equation (10) can be presented as a linear plot (Fig. 1).

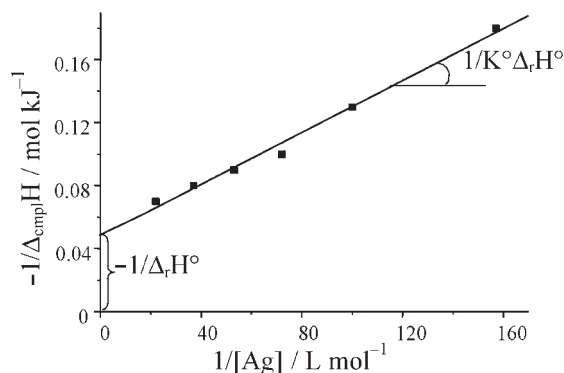


Fig. 1 Calculation $\Delta_r H^\circ$ and $\lg K^\circ$ by Eq. (10)

Diversions of experimental points from a linear plot are explained rather by inexactness of value $\lg K^\circ$ than by errors of calorimetric measurements.

$\lg K^\circ$ is obtained potentiometrically and is utilised at calculation $\Delta_r H^\circ$ by means of the HEAT program. For obtaining reliable $\Delta_r H^\circ$, it is necessary that the yield of a complex was whenever possible maximal.

The concentrations [Ag⁺] at potentiometric and calorimetric measurements were approximately identical. The ionic strength μ of a solution was created by silver salts and was equal to $4 \cdot 10^{-3} - 2 \cdot 10^{-1}$. The influence of an ionic environment on the reaction is insignificant at such small values μ and it can be neglected.

Results and discussion

The standard enthalpies of dissolution AgNO₃, AgClO₄ and 18C6 in EtOH–water solvents are shown in Table 1. The transfer enthalpies of Ag⁺ and A[−] ion from water to binary solvents are calculated as

$$\Delta_r H^\circ(\text{Ag}^+, \text{A}^-) = \Delta_{\text{sol}} H_s^\circ - \Delta_{\text{sol}} H_{\text{aq}}^\circ \quad (11)$$

where A[−] is or ClO₄[−].

Equation (11) follows from a thermodynamic cycle (12).

Table 1 Enthalpies of dissolution AgNO₃, AgClO₄ and 18C6 in H₂O–EtOH mixtures at 298.15 K

X _{EtOH} , mol fr	0.00	0.10	0.20	0.30	0.50	0.70	0.85	0.90
$\Delta_{\text{sol}} H_{(\text{AgNO}_3)}^\circ \pm 0.3 \text{ kJ mol}^{-1}$	22.7	27.5	25.3	20.8	13.9	28.3	–	–
$\Delta_{\text{sol}} H_{(\text{ClO}_4)}^\circ \pm 0.3 \text{ kJ mol}^{-1}$	8.6	–	–	–	–	–7.5	–	–11.6
$\Delta_{\text{sol}} H_{(18\text{C}6)}^\circ \pm 0.2 \text{ kJ mol}^{-1}$	–21.8	–1.5	8.5	11.1	14.5	17.9	25.1	30.9

The transfer enthalpy of single ion Ag⁺ were obtained using data $\Delta_{\text{sol}} H^\circ(\text{NH}_4\text{NO}_3)$ [7] and $\Delta_{\text{tr}} H^\circ$ of ions and [8, 9] calculated by guess $\text{Ph}_4\text{B}^- = \text{Ph}_4\text{P}^+$ assumption. The solvation of Ag⁺ in water is a less exothermic process than in ethanol (Fig. 2). The extremum of $\Delta_{\text{tr}} H^\circ(\text{Ag}^+)$ is found at 0.1 mol fraction of ethanol. A similar dependence $\Delta_{\text{tr}} H^\circ(\text{M}^+) = f(X_{\text{EtOH}})$ was found previously for cations of alkali metals [10] and probably is explained by structural changes of a solvent at this compositions. The transfer enthalpy of [Ag18C6]⁺ were determined by Eq. (3).

The composition of a solvent influences more strongly on ligand solvation than on solvation of a metal ion (Fig. 2). Hence, $\Delta_{\text{tr}} H^\circ$ of all participants of reaction (1) yield a representative contribution in stability of a complex [Ag18C6]⁺ as follows from Eqs (3) and (4).

It was determined that the solvation of 18C6 is stronger in water than ethanol (Table 1). The dissolution of 18C6 at 0.0–0.1 mol fr. EtOH occurs exothermically, and in the most concentrations – endothermically.

The stoichiometrical model providing the formation of an only one complex [Ag18C6]⁺ is well featured by calorimetric and potentiometric data. The thermodynamic functions of complex formation in water (Table 2, Fig. 3) agree with the liter-

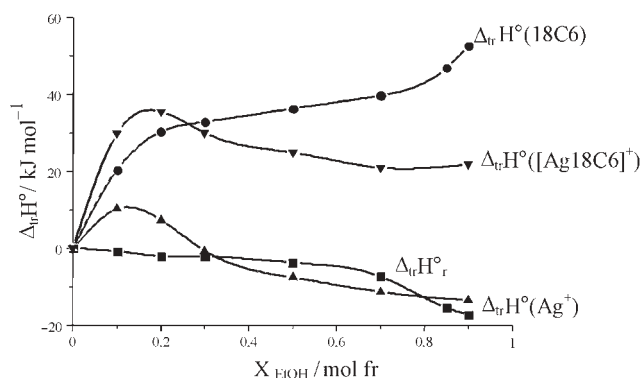


Fig. 2 The enthalpy of transfer from water to EtOH–water solvents for the reaction ($\Delta_{tr}H_r^\circ$) and reagents

ary data: $\lg K^\circ = 1.5$ [11], $\lg K^\circ = 1.6$ [12, 13], $\Delta_r H^\circ = 9.7 \text{ kJ mol}^{-1}$ [11]. The stability constant grows with the increasing EtOH content in a solvent.

Table 2 The stability constants of $[\text{Ag}18\text{C}6]^+$ in H_2O –EtOH solvents at 298.15 K

X_{EtOH} mol fr	0.0	0.1	0.2	0.3	0.5	0.7	0.85	0.9
$\lg K^\circ \pm 0.02$	1.40	1.81	1.98	2.08	2.40	2.76	3.30	3.47

Figure 3 presents the dependence of thermodynamic parameters of reaction (1) on the composition of solvent. Increasing the concentration of the ethanol implement decreases the enthalpy of the complex formation. The enthalpy contribution is a dominant factor, which provides the complex stability in solvent of any compositions.

The calculations with Born's equation show that the electrostatic contribution to value $\Delta_{tr}H^\circ$ ($\Delta_{tr}H^\circ([\text{Ag}18\text{C}6]^+)$) is very small owing to the big radius of a complex ion. The considerable distinctions in values $\Delta_{tr}H^\circ(\text{AgL}^+)$, $\Delta_{tr}H^\circ(\text{L})$ and

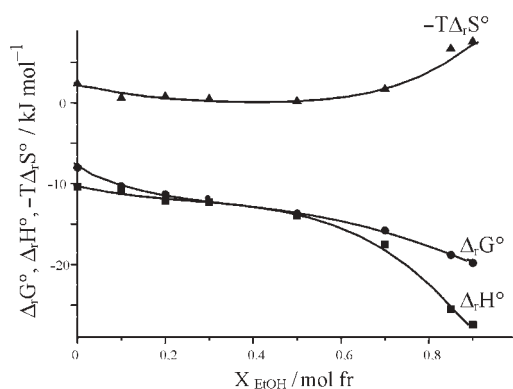
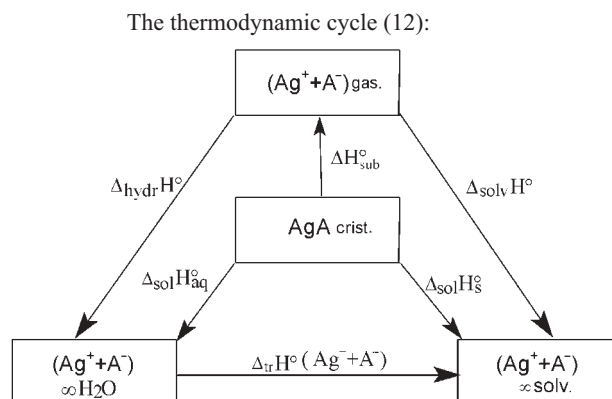


Fig. 3 The thermodynamic parameters of reaction (1) in EtOH–water solvents



$\Delta_{\text{tr}}H^\circ(\text{Ag}^+)$ at 0.7–0.9 mol fr. EtOH prove that the solvation of a complex occurs differently from the same of a ligand or a metal ion.

Conclusions

The stability constants of a complex in water–ethanolic solvents depend on thermodynamic parameters of the solvation of all reagents: ion Ag^+ , ligand, and complex ion. The parameters of the solvation of complex $[\text{Ag}18\text{C}6]^+$ has considerable differences from the same both macrocycle and metal ion. These distinctions are caused by specific interaction of reagents with components of a mixed solvent.

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