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STABILITY OF COMPLEX SILVER(I) AND COPPER(I) ION COMPOUNDS WITH UNSATURATED HYDROCARBONS AND AMMONIA

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The following research paper studies thermodynamics of complexing silver ion mixed complex compounds with 1,3-butadiene and ammonia in aqueous solutions. The study contains comparative analysis of stability of complex silver(I) and copper(I) ion compounds with ammonia and unsaturated hydrocarbons (2-methylpropene and 1,3-butadiene). It proves higher stability of complex silver(I) ions compared to hydrocarbon complexes. The results of the following study of complexing silver ion mixed complex compounds with 1,3-butadiene and ammonia in aqueous solutions are of interest for chemistry and engineering chemistry.

Introduction

Recently, studies of the thermodynamics of periodic table's 11th group's d-block metal ions complexing with various ligands in aqueous and non-aqueous solvents have attracted a lot of attention [1-7]. Despite the fact that these complex compounds have long been discovered, their importance in the fields of chemistry and engineering chemistry is increasing every decade. Known areas of application of these complex compounds are obtaining substances of high purity, the separation of hydrocarbon compounds, their use as catalysts in the processes of polymerization and oxidation. Currently, complex silver(I) and copper(I) ion compounds have attracted the attention of researchers for their potential clinical use as anti-cancer agents, as well as for the development of new biologically important drugs [8-12]. Research into the complexing of silver(I) and copper(I) ion mixed complex compounds is of particular interest due to the instability of gold(I) oxidation state in a number of various solvents.

Experimental

This study presents thermodynamic data on the silver ion mixed complex compounds complexing with 1,3-butadiene and ammonia in aqueous solutions. It also presents a comparative analysis of stability of complex silver(I) and copper(I) ion compounds with ammonia and unsaturated hydrocarbons (2-methylpropene and 1,3-butadiene).

In previous studies [13-16] about the complexing of complex silver(I) and copper(I) ion compounds with unsaturated hydrocarbons, it was established how pi-complexes with 1:1 composition can be formed, and they determined the equilibrium constants and thermodynamic characteristics of the reactions. The formation of complex silver(I) and copper(I) ion compounds with ammonia and unsaturated hydrocarbons is greatly relevant to this study. During the research into pi-complexes of silver ions with 2-methylpropene and ammonia [8], it was proven that the mixed complex compound $[Ag(NH_3)(C_4H_8)]^+$ can be formed.

We studied the complexing reaction of silver ion mixed complex compounds with 1,3-butadiene in aqueous ammonia solutions by applying potentiometry at atmospheric pressure and temperatures of 10–40 °C. The concentration of silver ions during the reaction was monitored by measuring the element's electromotive force, composed of silver and saturated calomel electrodes. To prepare the silver electrode, we deposited silver electrochemically onto a platinum wire from an aqueous salt solution at a current density of 0.003 A/cm^2. The change in the silver ion concentration in silver nitrate solutions was accompanied by a change in the potential of the silver electrode, which obeyed the Nernst equation. For the experiment, we used continuous-flow system while measuring the silver electrode potential with a high-resistance potentiometer with an accuracy of 0.1mV. Nitrogen was preliminarily put through the sample solution until a constant potential of the silver electrode was established. We applied the 1,3-butadiene gas-liquid chromatography method to the reaction. Its concentration, according to the adopted method, was constant and corresponded to its physical solvability. When passing 1,3-butadiene through the solution, the potential of the silver electrode decreased, since some of the silver ions were bound into a complex compound according to the model:

$$Ag^+ + C_4H_6 \leftrightarrow [Ag(C_4H_6)]^+$$

After reaching the equilibrium, hydrocarbon was no longer supplied, followed by adding the calculated amount of aqueous ammonia solution into the sample solution, which resulted in a decrease of silver electrode's potential due to the formation of ammonia and mixed complex compounds. The system quickly reached the equilibrium, and the potential of the silver electrode was constant for 15-20 minutes.

Since the complexing of silver ions with unsaturated hydrocarbons and ammonia is a complex multistep process, the mixed complex compound's equilibrium constant was calculated after calculating equilibrium constants stepwise [15]. The activity coefficients of the reagents were assumed equal to unity, since the study used a 0.1M ammonium nitrate solution with low concentrations of ammonia (10^{-4}–10^{-2} mol/l) and 1,3-butadiene (0.004–0.04 mol/l).

Based on the experimental data, the equilibrium constants of the reactions of complexing and the equilibrium composition were calculated at 10^{-4}–10^{-3} mol/l concentrations of silver ions. The calculated equilibrium constants at various concentrations of silver and ammonia ions practically do not change, which proves the formation of a mixed complex compound with the composition of $[Ag(NH_3)(C_4H_6)]^+$.

The logarithm's dependence of the mixed complex's equilibrium constant on the reciprocal absolute temperature is shown in Fig. 1. From the tangent of the slope of this straight line, we calculated the standard change in the enthalpy of reaction. The standard change in the Gibbs energy was calculated using the isotherm equation.

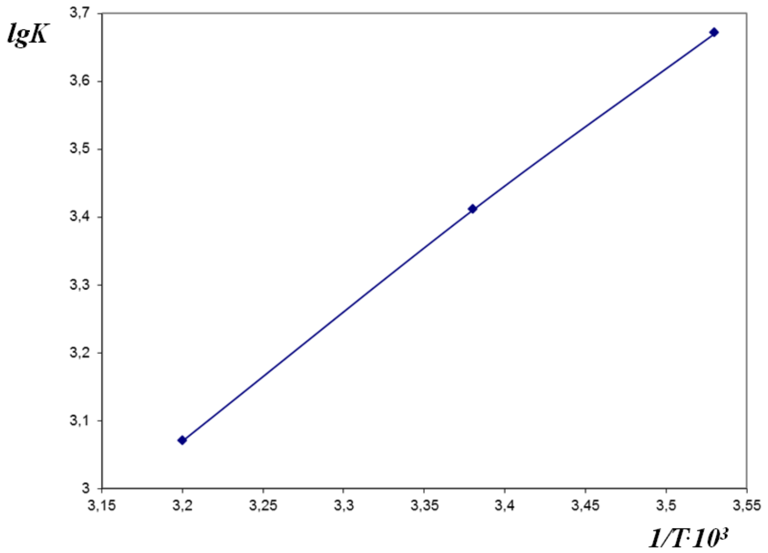

Fig. 1. Logarithm's dependence of the mixed complex's ($[Ag(NH_3)(C_4H_6)]^+$) equilibrium constant (*K*) on the reciprocal absolute temperature

The thermodynamic functions of complexing reactions at 25 °C calculated using the equilibrium constants are shown in Table 1.

The stability of the complex compounds can be judged from the equilibrium constants and standard changes in the Gibbs energy. Based on the data obtained, we determined that, in terms of their stability, the complex silver compounds with ammonia, unsaturated hydrocarbons, and mixed complex compounds in aqueous solutions can be arranged in the following order:

$$[Ag(NH_3)_2]^+ > [Ag(NH_3)(C_4H_8)]^+ > [Ag(NH_3)(C_4H_6)]^+ > [Ag(NH_3)]^+ > [Ag(C_4H_8)]^+ > [Ag(C_4H_6)]^+.$$

Table 1. Equilibrium constants and standard thermodynamic functions of complex copper(I) ion [13, 14] and silver(I) compounds with ammonia, 2-methylpropene [16] and 1,3-butadiene at 25 °C

Complex compound	*K*, l/mol	ΔH^0_{298}, kJ/mol	ΔS^0_{298}, J/(mol·K)	ΔG^0_{298}, kJ/mol
$[Ag(NH_3)]^+$	$2.1 \cdot 10^3$	-30.1	-37.2	-18.8
$[Ag(NH_3)_2]^+$	$16.2 \cdot 10^3$	-52.7	-38.5	-41.4
$[Ag(C_4H_8)]^+$	47.3	-29.7	-68.6	-9.6
$[Ag(C_4H_6)]^+$	30.5	-14.6	-21.3	-7.9
$[Cu(C_4H_8)]^+$	$31.3 \cdot 10^3$	-29.5	-13.0	-25.6
$[Cu(C_4H_6)]^+$	$169.7 \cdot 10^3$	-34.5	-15.5	-29.8
$[Ag(NH_3)(C_4H_8)]^+$	$7.0 \cdot 10^3$	-31.4	-22.0	-30.9
$[Ag(NH_3)(C_4H_6)]^+$	$2.6 \cdot 10^3$	-32.6	-19.3	-45.6

As can be seen from the table, complex silver compounds with 2-methylpropene are more stable. Compared to hydrocarbon complex compounds ($[Ag(C_4H_8)]^+$, $[Ag(C_4H_6)]^+$), mixed complex silver ion compounds are more stable. The formation of a mixed complex compound can be represented as the reaction of the addition of an ammonia molecule to the pi-complex, or as a reaction of displacement of water molecules from the pi-complex by an ammonia molecule:

$$[Ag(C_4H_6)(H_2O)]^+ + NH_3 = [Ag(NH_3)(C_4H_6)]^+ + H_2O$$

With an increase in the ammonia concentration, the hydrocarbon molecule is displaced from the silver ion's inner coordination sphere and $[Ag(NH_3)_2]^+$ is formed.

The relatively close values of the $[Ag(NH_3)]^+$ formation's equilibrium constants and mixed complex compounds can also be explained by the fact that monoamine–silver, in addition to ammonia, contains a water molecule in the internal coordination sphere. It follows that the stability of complex silver compounds with two types of ligands barely depends on the nature of the second ligand (water or hydrocarbon).

The reaction is enabled by a decrease in enthalpy and an increase in entropy. The stability of mixed complex compounds is dominated by the enthalpy factor. If we consider the change in the enthalpy of reaction a characteristic of the bond strength in hydrocarbon complex compounds, then the same sequence can be observed, both for the stability and for the change in the enthalpies of the complex compounds' formation reactions.

The change in entropy in the complexing process is mainly associated with the replacement of the translational motion of the metal and ligand ions with the rotational and vibrational motion of the resulting complex compound. Since the first component contributes mainly to the total change in entropy, the change in the entropy of complexing reactions is negative. In addition, different degrees of hydration of the metal ion and neutral ligand influence the change in entropy. An uncharged ligand is less hydrated than a metal ion. Therefore, complexing is accompanied by a partial destruction of the metal's hydration shell and a decrease in the negative value of entropy. The presence of a conjugated double bond in a hydrocarbon molecule in mixed complex compounds leads to a decrease in the negative value of entropy.

To assess the influence of the metal's nature on the complexing process, the formation's reactions of silver hydrocarbon complexes were compared with the data available in the literature on complexes with copper(I) ions [13, 14]. A data comparison shows that the complex copper(I) ion compounds of hydrocarbons are more stable than complex silver ion compounds. Obviously, the copper(I) ion is a stronger donor and acceptor than the silver ion, since it has a higher electron affinity energy. In addition, the ionization potential of the copper ion is lower than that of silver. Therefore, the strength of the metal-ligand bond, due to both donor-acceptor and back donations, will be higher for copper complex compounds.

Conclusion

The following work studied thermodynamics of silver ion mixed complex compounds complexing processes with 1,3-butadiene and ammonia in aqueous solutions. It includes the comparative analysis of stability of complex silver(I) and copper(I) ion compounds with ammonia and unsaturated hydrocarbons (2-methylpropene and 1,3-butadiene). The results of the following study on stability of complex compounds with silver ion mixed complex compounds complexing with unsaturated hydrocarbons presents and interest for fields of chemistry and engineering chemistry.

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