

Article

Thermodynamics of Ag(I) Complex Formations with 2-Mercaptoimidazole in Water—Dimethyl Sulfoxide Solvents

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Abstract: The stability of coordination compounds of metal ions with ligands is of fundamental importance for elaborating upon practical sensors for the detection and quantification of metal ions in environmental samples. In this work, the stability constants of silver(I) complexes with 2-mercaptoimidazole (2MI) in a mixed water–dimethyl sulfoxide (DMSO) solvent were determined at 298.15 K and 308.15 K. It was found that with increasing temperature, the stability of the complexes decreases. The dependence of $\lg\beta_1$ on the water–DMSO solvent compositions has its minimum at a concentration of dimethyl sulfoxide of 0.1 mol. fr. To explain the effect of the solvent, the solvation characteristics of the reagents were analyzed. In this regard, the 2MI Gibbs energy of transfer from water to aqueous dimethyl sulfoxide solvents was determined, and the influence of the aqueous DMSO solvent on the thermodynamics of 2MI protonation was analyzed. The stabilization of the silver ion and 2MI during the transition from water to a water–DMSO solvent makes a negative contribution to the change in the Gibbs energy of complexation, while the solvation of a complex particle promotes the complex formation. As a result, the Gibbs energy transfer values are slightly increased. The results of these thermodynamic studies could be useful for the development of sensor materials based on mercaptoimidazoles.

Keywords: complexation; complex stability; distribution coefficient; inorganic ion sensors; 1-methyl-2-mercaptoimidazole; silver(I); solvation; thermodynamics; water–dimethyl sulfoxide solvents



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1. Introduction

In recent years, there has been a significant increase in the number of studies devoted to the search and study of new sensor materials and, in various approaches, aimed at improving the analytical characteristics of sensors made on the basis of these materials. Organic and inorganic materials–based colorimetric sensors are common and frequently used sensors with high sensitivity and selectivity. However, to monitor metal ions, a series of analytical methods have been developed, including inductively coupled plasma-mass spectrometry, atomic absorption spectrometry, electrochemistry, fluorescence, ion imprinting technology, surface-enhanced Raman scattering, and others [1].

Mercaptoimidazole derivatives are known for their use in pharmaceuticals [2,3]. Their use in the composition of various sensor materials for metal ions seems promising. Chemical sensors based on methylimidazole derivatives have the potential for various nanocompositions. For example, 2-mercaptoimidazole was immobilized onto surface silica so that the silica would have selective properties to extract the heavy metal chromium(III)

through the formation of a coordination compound between the 2-mercaptoimidazole and chromium(III) [4]. A novel Schiff base designated as a 5-[(3-methylthiophene-2-yl-methyleneamino)]-2-mercaptobenzimidazole sensor was successfully applied to the direct determination of copper(II) ions in tap water, river water, and dam water samples [5]. The biosensors screen-printed electrodes based on 1-methyl-2-mercaptoimidazole have been described [6].

The process of complexation of rhenium(V) with 2-mercaptoimidazole in a wide temperature range and HCl concentration was investigated using the developed redox system [7]. This type of electrode system could be useful for studying the process of complexation of metal ions in solutions by the potentiometric method. It is shown that 2-mercaptoimidazole in acidic solutions is oxidized under the action of molecular iodine to the corresponding disulfide with the loss of one electron according to the following scheme: $2R-SH-2e^- \leftrightarrow R-S-S-R+2H^+$. Reversibility and the standard electrode potential of the system were established, which was 165.3 mV.

The study [8] reported the development, characterization, and application of acetylcholinesterase biosensors based on a gold electrode modified with a mercaptobenzothiazole self-assembled monolayer and either poly(*o*-methoxyaniline) or poly(2,5-dimethoxyaniline) in the presence of polystyrene sulfonic acid. A new synthetic strategy for the self-assembly of Cu nanoparticles protected with imidazole-based bidentate ligands seems to be promising as a fluorimetric sensor. Biomedical applications of sensors in clusters are an active research field aimed at finding better fluorescent contrast agents and therapeutic pharmaceuticals for the treatment and prevention of diseases and the early diagnosis of cancers and other potent diseases.

The current state of the use of graphene quantum dots (GQDs) as sensors for detecting metal ions is described [9]. Despite the success of GQDs in this area, the mechanisms that underpin GQD–metal ion specificity are rarely explored. This lack of information can result in difficulties when attempting to replicate published procedures and can limit the judicious design of new highly selective GQD sensors. Furthermore, there is a dearth of GQD examples that selectively detect biologically relevant metals.

A new fluorescent probe based on 3,3'-(((1E,1'E)-((3-oxo-1,3-dihydroisobenzofuran-1,1-diyl)bis(1-hydroxynaphthalene-4,2-diyl)))bis-(methanilyl-den))bis-(azanilidene))bis-(2-aminomaleonitrile) (PM) for the determination of Hg²⁺ in an aqueous solution of THF was developed [10]. Thanks to its excellent fluorimetric properties, a portable smart platform with smartphone support was created for convenient, cost-effective, and reliable Hg²⁺ detection. It is noteworthy that the detection of water samples from the environment in the field was achieved with good extraction using a portable platform.

The development of electrochemical sensors for monitoring heavy metal ions has rapidly increased [11–20]. These sensors use biological or biomimetic recognition elements, such as enzymes, antibodies, aptamers, and molecularly imprinted polymers, in direct contact with the electrode surface to provide quantitative or semi-quantitative detection of the target ions. This type of sensor offers high sensitivity, selectivity, and cost-effectiveness, making it an ideal tool for in situ monitoring of environmental contaminants. Factors contributing to the growing interest in this technology include the identification of suitable receptors and improved electrode designs and performances, including screen–printed electrodes, miniaturized devices, and portable potentiostats.

When developing new chemical sensors, in addition to the spectral characteristics of their sensory abilities, it is necessary to pay attention to the thermodynamic parameters of complexation processes and solvation characteristics of reagents, which determine the thermodynamics of selective binding processes in solutions [21–23]. Evaluating the influence of mixed solvent composition on the thermodynamic solvation parameters of both reagents and products (*G*, *H*, *S*) and deriving appropriate relationships between the solvation parameters of the interacting particles and those of the reaction allows to devise predictive models for complex formation. Therefore, it is possible to choose a suitable solvent for the synthesis of complexes with the desired thermodynamic properties, such

as stability and enthalpy of the complexation reaction. The thermodynamic parameters of complexation could probably be used as additional sensory characteristics [24].

The effect of solvent on acid–base properties and reactivity of methylimidazole derivatives was discussed in [25–29]. These results were an integral part of the studies of the reactions of complexation of the silver ion with sulfur–containing ligands in mixed solvents. To explain the solvent effects, the solvation of the ligand was studied, and the solvation contributions of the reagents to the change in the stability of complex particles was analyzed.

In particular, a potentiometric titration method was applied to study the process of complexation of silver(I) with N, N-ethylene urea; 1-formyl; and 1-acetyl-3-thiosemicarbazide in the temperature range 288–328 K in water and water–ethanol solvents [29]. It was found that the stability constant of the monosubstituted silver(I) complex with the studied ligands is twice as high as the stability of the two- and three-substituted complexes, which is associated with steric factors. The ionic strength of the solution does not affect the number of particles formed by the interaction of silver(I) with N, N-ethylene urea; 1-formyl; and 1-acetyl-3-thiosemicarbazide but affects the numerical values of the general and step stability constants. When the complexation reaction is transferred from water to water–ethanol solvents, the total stability constants of the complexes increase.

The Gibbs energies of resolution of 2-mercaptoimidazole (2MI) and 1-methyl-2-mercaptoimidazole (1MI) and their complexation with silver(I) in aqueous–ethanol solvents were studied [28]. Analysis of thermodynamic parameters showed that in all aqueous–ethanol solvent compositions, a compensatory effect of the solvation state of silver(I) ions and ligands in the $[\text{Ag}(2\text{MI})]^+$ and $[\text{Ag}(1\text{MI})]^+$ complex stability is observed. The changes in the solvate state of the complex particles ($[\text{Ag}(2\text{MI})]^+$, $[\text{Ag}(1\text{MI})]^+$) are key factors in the equilibrium shift of the reactions.

The solvation of 1-methyl-2-mercaptoimidazole (1MI) in aqueous–dimethyl sulfoxide solvents was studied by the interfacial distribution method with a control of analyte concentration by UV spectrophotometry [27]. It was found that with an increase in the DMSO content in the solution, the Gibbs resolution energy ($\Delta_{\text{tr}}G^0$) takes a negative value, which is a consequence of a better solvation of 1MI in DMSO than in water.

The analysis of the literature data illustrates the possibility of practical application of water–organic solvents to obtain more stable complexes of thioamide ligands with silver(I) ions in comparison with aqueous solutions. This should be especially important to detect metal ions presented in industrial waste water containing organic solvents.

The aim of this work is to determine the stability of silver(I) coordination compounds with 2MI in water–DMSO solvents and to study the effect of the binary water–DMSO solvent composition on the complex formation by a solvation–thermodynamic approach. The solvation–thermodynamic analysis is based on the obtained thermodynamics parameters for the solvate state of 2-mercaptoimidazole and the acid–base equilibria of the ligand, which are obtained in this work. The results of the presented thermodynamic studies could be useful, in our opinion, for the development of sensor materials based on mercaptoimidazoles.

2. Results

To establish the influence of the solvent nature on the acid–base properties and the equilibrium of complexation using the solvation–thermodynamic approach, it is necessary to know the Gibbs energy ($\Delta_{\text{tr}}G^0$) of the transfer of reagents and reaction products. For the Ag^+ ion, the Gibbs energy of transfer from water to aqueous DMSO solvents is given in [30], but such data are not available in the literature for 2MI. The Gibbs energy of 2MI transfer was determined by the method of interphase distribution of a substance between two immiscible phases. Table 1 shows experimental data on the determination of the equilibrium concentration of 2MI in water and aqueous DMSO solvents, calculated distribution coefficients of 2MI in H_2O –Hex and H_2O –DMSO–Hex systems, as well

as changes in the Gibbs energy of the 2MI transfer from water to aqueous–dimethyl sulfoxide solvents.

Table 1. Equilibrium concentrations of 2MI in water and aqueous–dimethyl sulfoxide solvents; distribution coefficients of 2MI in H₂O–Hex and H₂O–DMSO–Hex systems; and changes in the Gibbs energy of 2MI transfer from water to aqueous–DMSO solvents, T = 298.15 K.

$[2MI]^{H_2O-DMSO} \times 10^5, \text{ mol L}^{-1}$	$[2MI]^{hex} \times 10^5, \text{ mol L}^{-1}$	K_1	K_2	$\Delta_{tr}G^0, \text{ kJ/mol}$
9.55	0.45			
9.60	0.40	0.045 ± 0.01	-	0
9.83	1.70			
9.84	1.60	-	0.017 ± 0.003	-2.38 ± 0.40
9.82	1.80			
9.90	0.10			
9.92	0.80	-	0.009 ± 0.002	-4.00 ± 0.70
9.91	0.90			
9.45	5.50			
9.49	5.10	-	0.056 ± 0.004	-1.55 ± 0.70
9.46	5.40			

From the data in the Table 1, it can be seen that when transferring 2MI from water to H₂O–DMSO solvents, a minimum of $\Delta_{tr}G^0$ (2MI) is observed at the DMSO concentration range of 0.1–0.25 mol. fr. In general, when transferring from water to a water–DMSO solvent, the oversolvation of 2MI is observed. Previously, we found a similar oversolvation for 1-methyl-2-mercaptoimidazole when transferred from water to H₂O–DMSO solvents up to DMSO 0.3 mol. fr. (Figure 1) [27].

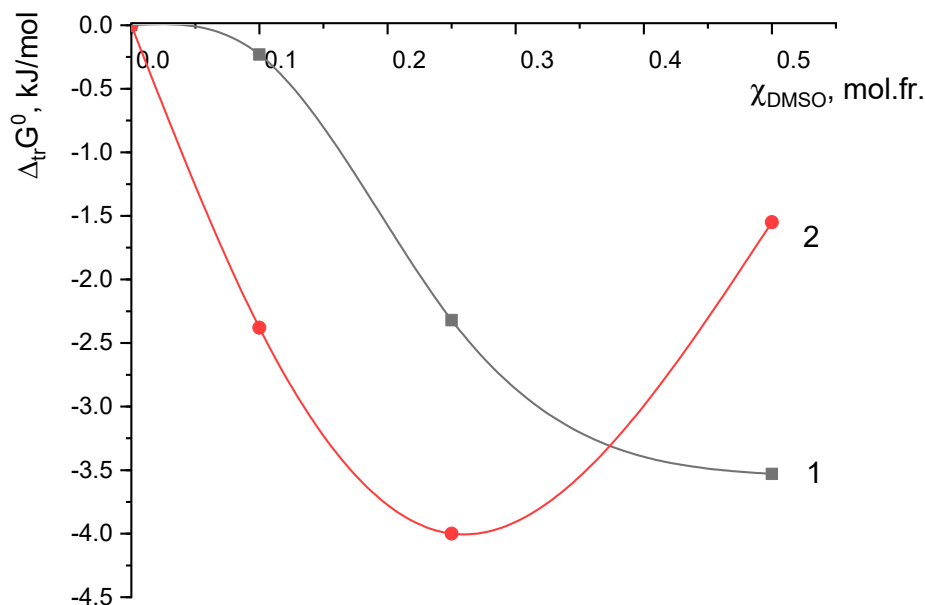


Figure 1. The Gibbs energy change during the transfer of 2–mercaptoimidazole (1) and 1–methyl–2–mercaptoimidazole (2) from water to aqueous–dimethyl sulfoxide solvents at 298 K.

One of the conditions for obtaining the most accurate thermodynamic values of the complexation reaction in aqueous organic solvents is to study the equilibrium of proton addition in ligand solutions. We studied the acid–base equilibrium of 2–mercaptoimidazole in an aqueous solution (pK_a value = 2.97 ± 0.04). In continuation of these studies, we determined the values of pK_a 2–mercaptoimidazole in aqueous DMSO solvents at 298 K by applying the potentiometric method. Table S1 (in Supplementary Materials) shows the pH-metric titration data of 2MI at 298 K in a mixed solvent containing 0.1 mol. fr. DMSO. The values of 2–mercaptoimidazole pK_a in water and aqueous–dimethyl sulfoxide solvents with variable DMSO content at 298.15 and 308.15 K are presented in the Table 2.

Table 2. The values of 2-mercaptoimidazole pK_a in water and water–dimethyl sulfoxide solvents at 298.15 and 308.15 K.

	X _{DMSO} , mol. fr.			
	0.0	0.1	0.25	0.5
298.15	2.97 ± 0.04	1.93 ± 0.07	2.34 ± 0.02	2.72 ± 0.08
308.15	2.76 ± 0.05	1.76 ± 0.04	2.23 ± 0.03	2.63 ± 0.07

The pK_a = f(χ_{DMSO}) dependence has an extreme form with a minimum in the range of DMSO concentration corresponding to 0.1 mol. fr.. A further increase in the content of DMSO leads to a slight increase in the basic properties of 2MI.

3. Discussion

To analyze the effect of the H₂O–DMSO solvent compositions on the thermodynamics of the protonation process of 2MI, information on the solvation of all participants in the acid–base equilibrium is needed. Data on the solvation of 2MI (Δ_{tr}G⁰_{2MI}) were presented in the Table 1. The change in the Gibbs energy of proton transfer (Δ_{tr}G⁰_{H⁺}) was taken from the literature [30]. Using Equation (1) and data from Table 3, the values of the Gibbs energy change of the 2MI protonation reaction during transfer from water to aqueous–dimethyl sulfoxide solvents (Δ_{tr}G⁰_r) are calculated. Using Equation (2), the values of the Gibbs energy of the protonated particle H2MI⁺ (Δ_{tr}G⁰_{H2MI⁺}) were calculated.

$$\Delta_{tr}G^0_r = \Delta_{tr}G^0_{H_2O - EtOH} - \Delta_{tr}G^0_{H_2O} \quad (1)$$

$$\Delta_{tr}G^0_r = \Delta_{tr}G^0_{H_2MI^+} - \Delta_{tr}G^0_{H^+} - \Delta_{tr}G^0_{2MI} \quad (2)$$

Table 3. The stability constants of silver(I) complexes with 2MI in a water–DMSO mixed solvents at 298.15 K and 308.15; I = 0.1 mol L^{−1} NaClO₄.

X _{DMSO} , mol. fr.	298 K		
	lgβ ₁	lgβ ₂	lgβ ₃
0	6.84 ± 0.03	10.56 ± 0.03	12.27 ± 0.04
0.1	7.18 ± 0.04	10.49 ± 0.09	12.64 ± 0.3
0.25	6.58 ± 0.01	10.46 ± 0.01	-
0.50	5.86 ± 0.01	10.17 ± 0.01	-
		308 K	
0	6.79 ± 0.03	10.36 ± 0.03	11.93 ± 0.4
0.1	6.88 ± 0.01	9.96 ± 0.02	11.60 ± 0.2
0.25	6.42 ± 0.01	9.72 ± 0.01	-
0.50	5.62 ± 0.01	9.81 ± 0.05	-

Figure 2 shows the dynamics of reagents solvation contributions to the change in the Gibbs energy of the 2MI protonation in water–dimethyl sulfoxide solvents.

When transferring from water to aqueous–DMSO solvents, a slight weakening of the reaction of protonation of 2-mercaptoimidazole is observed (Figure 2). In an aqueous DMSO solvent, protonation of 2MI is characterized by significant increase in H⁺ and H2MI⁺ solvation. In contrary, the solvation of 2MI is slightly increased. It can be assumed that the weakening of the protonation of 2MI is associated with a compensatory contribution between H⁺ and H2MI⁺ and a slight increase in the solvation state of 2MI.

It was found that in aqueous solutions, silver(I) with 2MI forms three complex particles. In contrast to imidazole [28], the stability of stepwise-formed silver(I) complexes with 2MI decreases with increasing temperature.

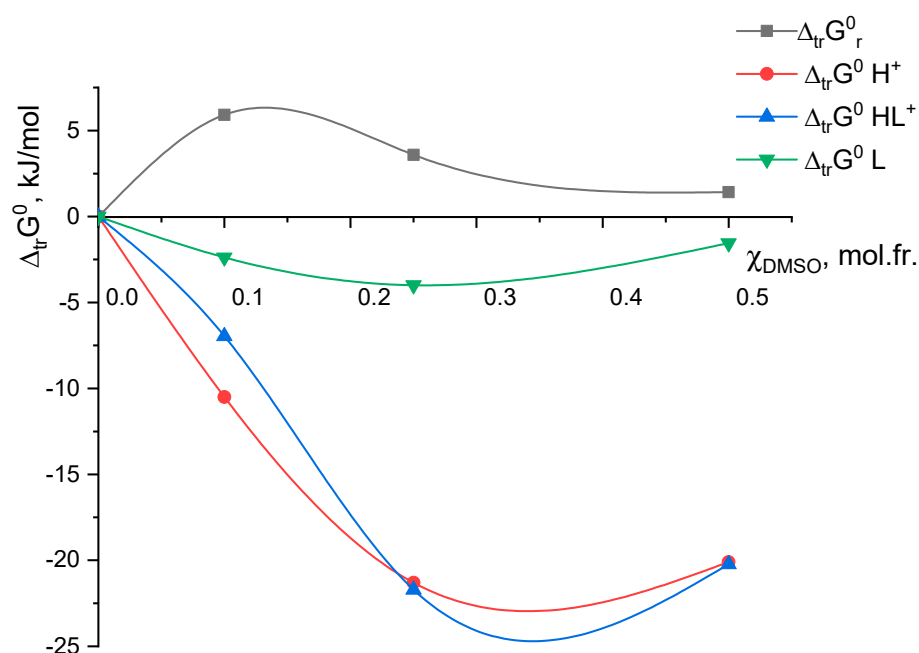


Figure 2. The reagents solvation contributions to the change in the Gibbs energy of the 2MI protonation in water–dimethyl sulfoxide solvents.

Experimental potentiometric titration data for the analysis of equilibrium processes involving 2-mercaptoimidazole and silver in aqueous DMSO solvents were processed using KEV software [31]. To calculate the equilibrium of complex formation, the following equilibria were introduced into the program in the form of a matrix:



The most correct stoichiometric composition of silver(I) complexes with 2MI was determined by varying the stoichiometric matrix in KEV, choosing one that gave the smallest standard deviation for the stability constant and values of electrode potentials. Using the described approaches, it was shown that coordination compounds of the composition $[\text{Ag}(2\text{MI})]^+$, $[\text{Ag}(2\text{MI})_2]^+$, and $[\text{Ag}(2\text{MI})_3]^+$ were formed in the silver(I)–2MI–H₂O–DMSO. Figure 3 shows diagrams of particles distribution in the silver(I)–2MI–0.10 mol. fr. DMSO system at 298.15 K.

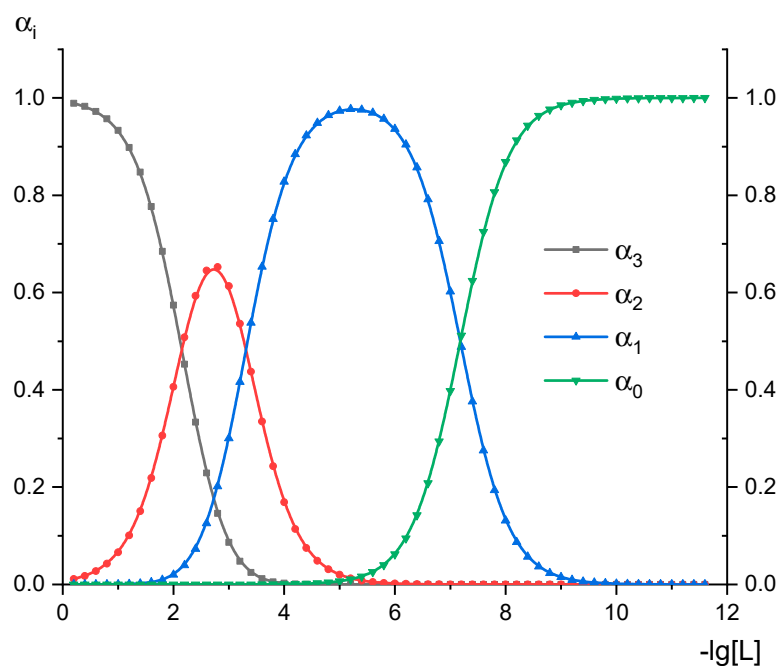


Figure 3. Diagram of the particles distribution the silver(I)–2MI–0.10 mol. fr. DMSO system at 298.15 K: α_0 –[Ag]⁺; α_1 –[Ag(2MI)]⁺; α_2 –[Ag(2MI)₂]⁺; α_3 –[Ag(2MI)₃]⁺.

Analysis of the distribution diagrams shows that when silver(I) interacts with 2MI, a step-by-step complexation occurs, and each complex form has a limit of its formation depending on the concentration of the organic ligand.

According to the literature data [32], 1-methyl-2-mercaptoimidazole is coordinated by silver(I) due to the sulfur atom of the thione group. It can be assumed that 2-mercaptoimidazole is also coordinated with silver(I) by the sulfur atom, forming a three-substituted complex (Figure 4).

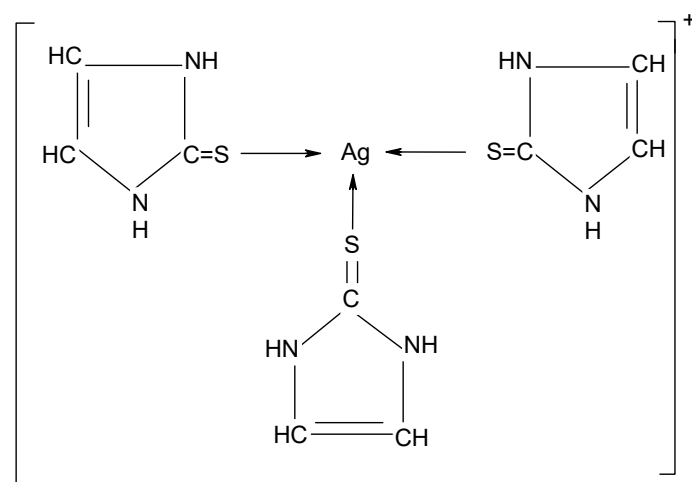


Figure 4. Silver(I) complex with 1-methyl-2-mercaptoimidazole: 1-methyl-2-mercaptoimidazole molecules coordination during [Ag(2MI)₃]⁺ complex formation.

Table 3 shows the stability constants of silver(I) complexes with 2MI in a water–DMSO mixed solvent at 298.15 K and 308.15 K. With increasing temperature, regardless of the composition of the water–organic solvent, the stability of the complexes decreases. The composition of the solvent affects not only the stability of the resulting complexes but also their stoichiometry. The dependence of $\lg\beta_1$ on the composition of the aqueous DMSO solvent has an extremum at a concentration of 0.1 mol. fr. DMSO. In general, for mono-

and bis-complexes, the stability of complexes decreases during the transition from water to water–DMSO solvents.

The change in $\Delta_{tr}G^0$ of the mono-ligand complex formation reaction and the solvation of the participants in this process in aqueous DMSO solvents is shown in Figure 5. The stabilization of the silver ion during the transition from water to aqueous–DMSO solvents makes a negative contribution to the equilibrium of complexation, with an insignificant contribution from changes in the solvate state of 2MI. The changes in the solvate state of the complex particle are similar to that of silver ion. As a result, the Gibbs energy transfer values are slightly increased up to 5 kJ/mol at 0.5 mol. fr. DMSO.

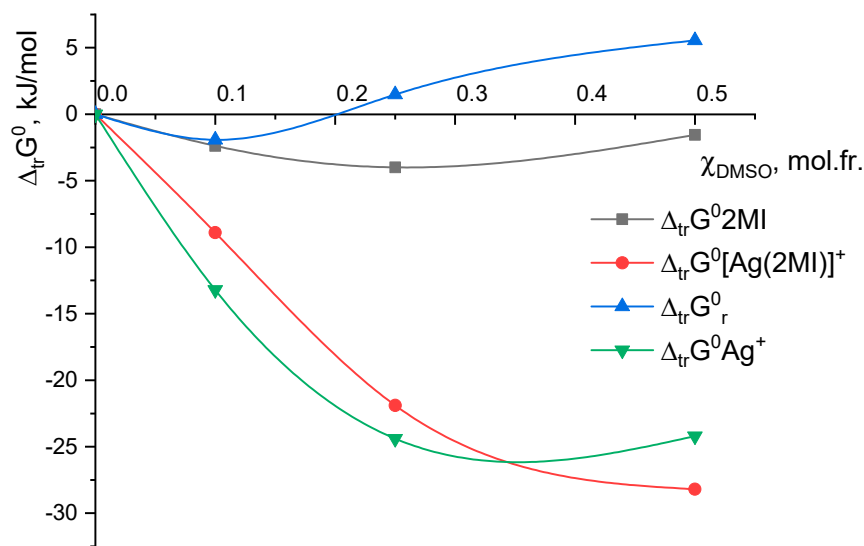


Figure 5. Influence of water–DMSO solvents on the Gibbs energy transfer and reagents solvation.

4. Materials and Methods

The Gibbs energy of the 2MI transfer from water to aqueous–dimethyl sulfoxide solvents was determined as described in [27]. To determine the protonation constants of 2-mercaptoimidazole in the aqueous–DMSO solvent, a galvanic cell consisting of glass and silver chloride electrodes was used. A hydrochloric acid solution with a concentration of 0.01 mol L^{-1} in an aqueous DMSO solvent was used as a titrant. The pH values were measured using a PH-150MP pH meter. The temperature in the cell was kept constant using a water thermostat with an accuracy of maintaining a temperature of $\pm 0.1 \text{ }^\circ\text{C}$.

When studying the complexation of silver(I) with 2MI, the initial concentrations of AgNO_3 and 2MI and were $1.0 \times 10^{-4} \text{ mol L}^{-1}$ and $1.0 \times 10^{-2} \text{ mol L}^{-1}$, respectively. The ionic strength of the titrant and solution in the potentiometric cell was kept constant ($0.1 \text{ mol L}^{-1} \text{ NaClO}_4$). A plate made of pure silver was used as an indicator electrode. The reference electrode was a silver chloride electrode. Titration of the AgNO_3 solution with a solution of 2MI was carried out in aqueous–DMSO solvents containing 0.10, 0.25, and 0.50 mol. fr. DMSO. The potential measurement of the Ag^+/Ag system during potentiometric titration was carried out using a PH–150 MP pH meter with an error of $\pm 0.1 \text{ mV}$. The calculation of the equilibrium composition of the particles present in the solution was carried out using the KEV program [31], taking into account the $\lg K(\text{H}^+)$ of 2MI obtained in this work in the binary solvents under study.

Quantitative results on particles concentration in equilibrium could also provide information useful to develop some sensor materials in $\text{Ag–2MI–H}_2\text{O–DMSO}$ systems. Tables S1 and S2 (in Supplementary Materials) show, as an example, the equilibrium concentrations of the complexes formed in an aqueous–DMSO solvent containing 0.10 mol. fr. calculated according to the KEV program.

5. Conclusions

The values of the Gibbs energy transfer of the 2-mercaptoimidazole were determined by the interphase distribution method. It is shown that when 2MI is transferred from water to water–DMSO, enhancement of the solvation of the protonated form occurs. The change in the solvate state of 2MI is insignificant.

The stepwise complex formation of silver(I) with 2-mercaptoimidazole in water–DMSO solvents of variable composition has been established. The change in $\Delta_{tr}G^0_r$ for the mono–ligand complex is discussed in the solvation–thermodynamic approach.

Stabilization of the silver ion during the transition from water to water–DMSO solvent makes a negative contribution to the equilibrium of complexation, with an insignificant contribution from changes in the solvate state of 2MI. The solvate state of the mono-complex particle is similar to the change in the solvation state of silver(I) ion. As a result, the Gibbs energy transfer values are slightly increased.

The thermodynamic parameters of complexation and solvation of the reagent obtained in this work are of interest for fundamental science for understanding the processes of coordination of silver(I) ions with thioligands in aqueous organic solvents. This knowledge is also necessary to develop the sensor materials based on 2-mercaptoimidazole for the quantitative identification of silver ions in water–organic solvents. In addition, the potentiometric method traditionally used to determine the stability of complex compounds could be useful for quantitative determination of the equilibrium composition of particles in an analyte.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics11050199/s1>. Table S1: pH-metric titration data of 2-mercaptoimidazole and calculated pKa values of 2-mercaptoimidazole in the H₂O–DMSO solvent at $\chi_{DMSO} = 0.1$ mol. fraction, $C_{2MI} = 0.01$ mol L^{−1}. Table S2: Potentiometric titration data of AgNO₃ solution by 2MI solution at T = 298.15 K, $\chi_{DMSO} = 0.10$ mol. fr., I = 0.1 mol L^{−1} NaClO₄

Author Contributions: Conceptualization, S.S. and T.U.; methodology, A.S., S.B. and K.A.; formal analysis, S.S., T.U., D.A., A.S., S.B. and K.A.; investigation, S.S., T.U., D.A., A.S., E.M., S.B. and K.A.; resources, S.S., T.U., D.A., A.S., S.B. and K.A.; writing—original draft preparation, S.B.; writing—review and editing, S.B., A.S., S.S., Y.M. and T.U.; visualization, S.S., T.U., D.A., A.S., S.B. and K.A.; project administration, S.S. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding authors.

Conflicts of Interest: The authors declare no conflict of interest.

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