Monothiocyanatoiron(III) Complex in Dichloromethane–Methanol Solvent Mixture

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Complexation of Fe^{III} ion with thiocyanate in dichloromethane–methanol solvent mixture was studied because of our interest in the analytical uses of Fe^{II}-to-Fe^{III} transformations in non-aqueous media. Molar absorptivity and composition of the complex, as well as the solvolysis constant and the stability constant of the complex as a function of the solution composition were determined by spectrophotometry. The composition of the complex throughout the solubility range of the components was that of a monocomplex, $[FeNCS]^{2+}$. In highly acidic solutions, molar absorptivity of the complex was not influenced by acid concentration and was $(13\ 700 \pm 700)$ $dm^3\ mol^{-1}\ cm^{-1}$. The solvolysis constant was similar to the value in water, $K_s = 7.0 \times 10^{-3}$ $mol\ dm^{-3}$. The stability constant of the complex, on the other hand, was strongly influenced by acid concentration. Extrapolation to the infinite acid concentration yielded the stability constant $40\ 500$ $dm^3\ mol^{-1}$, which is adequate for analytical uses of the complex in non-aqueous media.

INTRODUCTION

Some uses of iron as a reagent in analytical chemistry have been based on the ability of Fe^{II} ions to undergo oxidation, on the one hand, and on the ease of the ensuing Fe^{III} ions to form strongly coloured complexes, on the other hand. The interplay of redox potentials, stability constants and optical absorptions of the involved species may result in favourable combinations of properties enabling analytical uses of iron: the oxidation of Fe^{II} ions is easily brought about by hydroperoxides[1] and ozone,[2] but not so readily by potentially interfering dialkyl peroxides[3] and oxygen from air;[4] Fe^{III} ion complexes with specific ligands and their absorption properties are rather different from those of Fe^{II} ions.[5]

Most applications of the oxidative transformation of Fe^{II} ions by various analytes refer to aqueous solutions. However, understanding of the optical absorption properties of the Fe^{III} ion in non-aqueous media would be desirable in the development of spectrophotometric methods, which could be applied in studies involving Fe^{III} ions in organic liquids, like in the corrosion of pipeline tubing,[6] in investigations involving environmental behaviour of hydrocarbons, in petroleum geology,[7] *etc*. Other potential applications include extension of the studies of oxidation reactions of iron(II) to non-aqueous solvents. Lower dielectric constants of non-aqueous solvents, as compared to water, enhance the effects of anion binding to iron, thus increasing the sensitivity of analytical methods[3] or providing a suitable reaction medium

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for studying the interactions of reactants that are only sparsely soluble in water.[8] However, data on the optical absorption properties of Fe^{III} ions in organic solvents are scarce.

This paper deals with the composition and properties of the thiocyanatoiron(III) complex in the solvent mixture dichloromethane–methanol ($\psi(CH_2Cl_2, MeOH)$ = 2 : 1). This solvent mixture has been recommended for the extraction of lipids instead of the Folch reagent because of the significantly lower carcinogenicity hazard of dichloromethane as compared to chloroform.[9] Most earlier authors employing the Fe^{III} thiocyanate assay for lipid hydroperoxides used to avoid chloroform by transferring the extract into another solvent for analysis, which, on the other hand, introduced a considerable and unnecessary risk of extra handling. In addition, working in dichloromethane does not require amylene as preservative, which was determined to be inappropriate in the Fe^{III} thiocyanate assay.[10]

EXPERIMENTAL

Reagent grade chemicals were used without further purification. Dichloromethane (CH_2Cl_2) and methanol (MeOH) (both from Kemika, Zagreb, Croatia) were *puriss.* grade, and were distilled before use on an all-glass adiabatic distillation column.

The stock solution of ammonium iron(III) sulphate (0.1 mol dm^{-3}) was prepared by dissolving $NH_4Fe(SO_4)_2 \cdot 12H_2O$ (Merck, Darmstadt, Germany) in 1.0 mol dm^{-3} solution of perchloric acid. The solution was standardized by titration with 0.1 mol dm^{-3} standard solution of potassium dichromate.

Stock solutions of thiocyanate were prepared by dissolving suitable quantities of KNCS (Merck) in MeOH. Methanolic stock solution of $NaClO_4 \cdot H_2O$ (Fluka, Buchs, Switzerland) was used to maintain a constant concentration of electrolytes.

Appropriate amounts of iron, acid and ligand stock solutions were mixed and topped with the solvent mixture CH_2Cl_2–MeOH (volume ratio, $\psi_{CH_2Cl_2, MeOH}$ = 2 : 1) to obtain working solutions. The solutions contained 2 % (1.1 mol dm^{-3}) water to enhance solubility. Half an hour after preparation, absorbance was measured against solvent. All measurements were made at room temperature.

A double-beam UV/Vis spectrophotometer, Model Cary 2200 (Varian, Mulgrave, Victoria, Australia), equipped with 1-cm rectangular quartz cells, was used for absorbance measurements.

RESULTS

For a given concentration of electrolytes, spectral characteristics of iron(III) solutions critically depend on the nature of the solvent, the presence of thiocyanate ligand and acid and water concentrations. Absorbance of
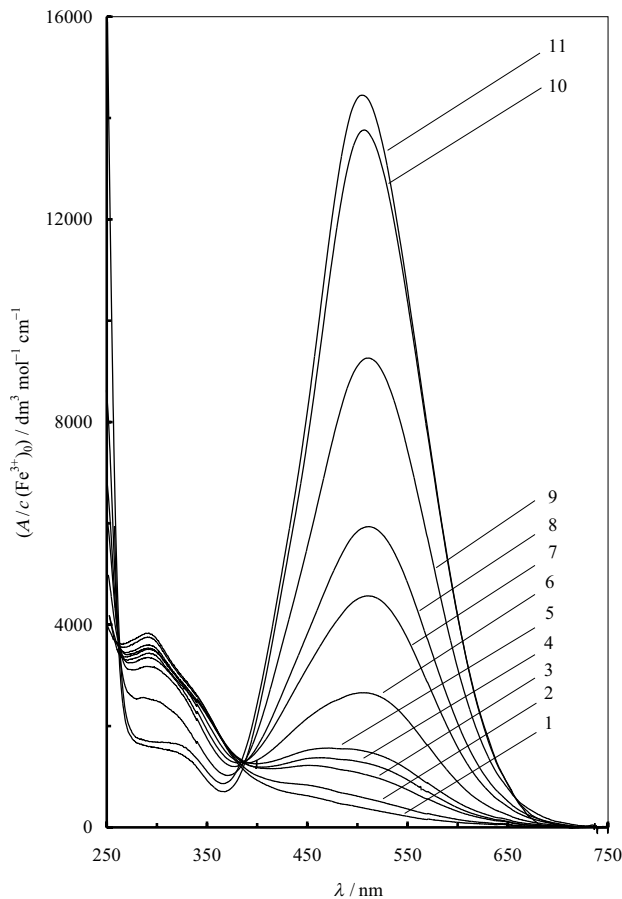
Figure 1. Absorbance of iron(III) solution normalized to the concentration of iron(III) in CH_2Cl_2–MeOH (2:1) solvent mixture as a function of thiocyanate ion concentration; $c(Fe^{3+})$ = 5.0×10^{-5} mol dm^{-3}; $c(HClO_4)$ = 8.0×10^{-4} mol dm^{-3}, $c(H_2O)$ = 1.1 mol dm^{-3}, $c(NaClO_4)$ = 2.3×10^{-2} mol dm^{-3}; $c(KNCS)$ = 5.0×10^{-6} (1), 2.0×10^{-5} (2), 4.0×10^{-5} (3), 5.0×10^{-5} (4), 6.0×10^{-5} (5), 1.0×10^{-4} (6), 2.0×10^{-4} (7), 3.0×10^{-4} (8), 5.0×10^{-4} (9), 2.0×10^{-3} (10), 6.0×10^{-3} (11) mol dm^{-3}.

thiocyanatoiron(III) complexes in the CH_2Cl_2–MeOH solvent mixture as a function of thiocyanate concentration at a constant concentration of iron, perchloric acid, water and at a constant concentration of electrolytes is shown in Figure 1. As the concentration of thiocyanate increases, the absorption maximum of the complex at 510 nm increases with the concomitant decrease of the absorption maximum at 290 nm belonging to hydroxoiron(III), and an isosbestic point at 385 nm indicates that only these two species are present. As the ligand concentration increases above 2 mmol dm^{-3}, formation of higher complexes becomes probable, as evidenced by the disappearance of the isosbestic point.

The formation of a complex can be represented by the equation:

$$m \text{ Fe}^{3+} + n \text{ NCS}^- = [\text{Fe}_m(\text{NCS})_n]^{3m-n} \qquad (1)$$

The cumulative stability constant β_n of the complex is given by the equation:

log (c(Fe^{3+})$_0$ / mol dm^{-3}), log (c(NCS$^-$)$_0$/ mol dm^{-3})

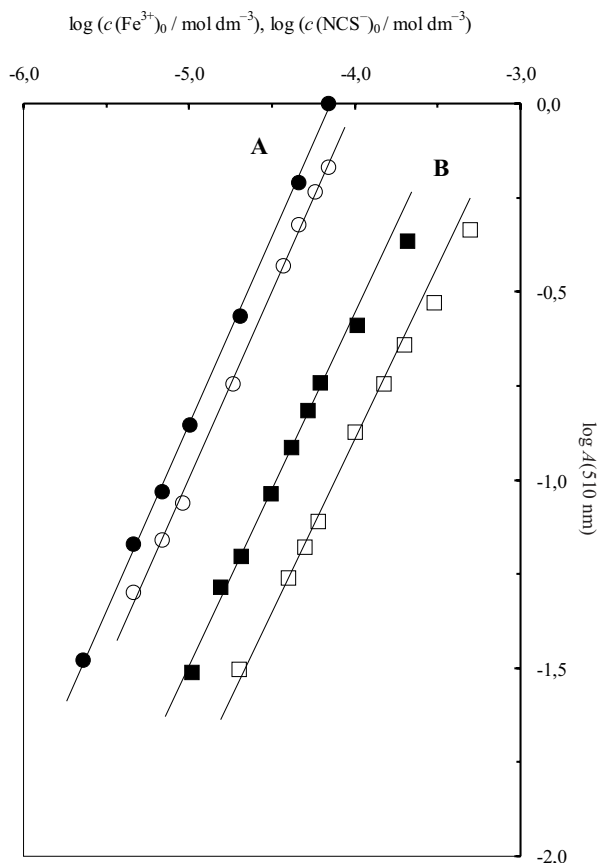

Figure 2. Dependence of the absorbance of iron(III) solutions at 510 nm in CH$_2$Cl$_2$–MeOH (2:1) solvent mixture at c(H$_2$O) = 1.1 mol dm^{-3} and c(HClO$_4$) = 2.3 × 10^{-2} mol dm^{-3} according to Eq. (3); Group A: on iron(III) concentration, c(NCS$^-$) = 2.0 × 10^{-3} (●), 5.0 × 10^{-4} (O) mol dm^{-3}; Group B: on NCS$^-$ concentration at c(Fe^{3+}) = 5.0 × 10^{-5} mol dm^{-3}, c(HClO$_4$) = 2.3 × 10^{-2} (■), 8.0 × 10^{-4} (□) mol dm^{-3}.

$$\beta_n = c(\text{Fe}_m\text{NCS}_n)^{3m-n} / (c(\text{Fe}^{3+})^m \, c(\text{NCS}^-)^n) =$$
$$A(\lambda_{\max}) / (\varepsilon(\text{Fe}_m\text{NCS}_n)^{3m-n} \, c(\text{Fe}^{3+})^m \, c(\text{NCS}^-)^n) \quad (2)$$

Taking the logarithm of (2), we obtain:

$$\log (A(\lambda_{\max})) = m \log c(\text{Fe}^{3+}) + n \log c(\text{NCS}^-) +$$
$$\log \varepsilon(\text{Fe}_m\text{NCS}_n)^{3m-n} + \log \beta_n \quad (3)$$

The composition of the complex was elucidated by means of equation (3). By varying the concentration of Fe^{3+} ion at a constant concentration of thiocyanate (Figure 2, group A), straight lines with the slopes independent of the thiocyanate concentration, $m = 0.99 \pm 0.01$, were obtained.

By varying the concentration of thiocyanate at a constant concentration of Fe^{3+}, straight lines were also obtained (group B). The slope of the straight lines in group B was $n = 0.95 \pm 0.03$. The two groups of experiments indicate that the composition of the complex is [FeNCS]$^{2+}$.

Taking the concentrations of ions at equilibrium, the stability constant of the complex K_1 is:

$$K_1 = \frac{c(\text{FeNCS}^{2+})}{(c(\text{Fe}^{3+})_0 - c(\text{FeNCS}^{2+}))\,(c(\text{NCS}^-)_0 - c(\text{FeNCS}^{2+}))} \quad (4)$$

In excess of NCS$^-$ and under conditions where [FeNCS]$^{2+}$ is predominant and no higher complexes are formed, $(c(\text{NCS}^-)_0 - c(\text{FeNCS}^{2+})) \approx c(\text{NCS}^-)_0$, the absorbance of Fe^{3+} solutions at an optical length of 1 cm, in the presence of the ligand, corrected for the absorbance of solutions in the absence of ligand, can be related to $c(\text{NCS}^-)_0$ by the equation:

$$A = \varepsilon(\text{FeNCS}^{2+}) \, c(\text{FeNCS}^{2+}) =$$
$$\frac{\varepsilon(\text{FeNCS}^{2+}) \, K_1 \, c(\text{Fe}^{3+})_0 \, c(\text{NCS}^-)_0}{1 + K_1 \, c(\text{NCS}^-)_0} \quad (5)$$

Taking the reciprocal of equation (5), one obtains:

$$1 / A = 1 / (\varepsilon(\text{FeNCS}^{2+}) \, c(\text{Fe}^{3+})_0) +$$
$$1 / (\varepsilon(\text{FeNCS}^{2+}) \, K_1 \, c(\text{Fe}^{3+})_0 \, c(\text{NCS}^-)_0) \quad (6)$$

and

$$c(\text{Fe}^{3+})_0 / A =$$
$$1 / \varepsilon(\text{FeNCS}^{2+}) + 1 / (\varepsilon(\text{FeNCS}^{2+}) \, K_1) \cdot 1 / c(\text{NCS}^-)_0 \quad (7)$$
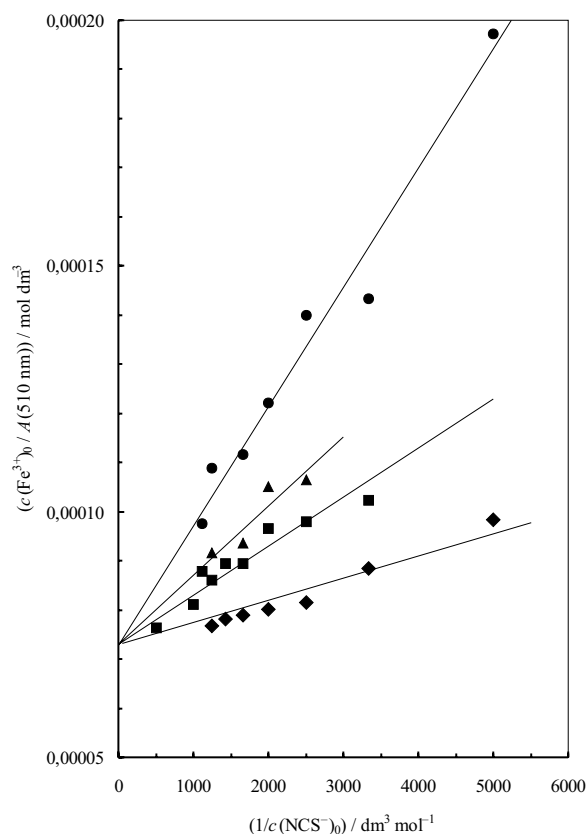

Figure 3. Determination of the stability constant K_1 of [FeNCS]$^{2+}$ according to Eq. (7) in CH$_2$Cl$_2$–MeOH (2:1) solvent mixture as a function of perchloric acid concentration; c(Fe^{3+}) = 2.3 × 10^{-5} mol dm^{-3}, c(H$_2$O) = 1.1 mol dm^{-3}, c(NaClO$_4$) + c(HClO$_4$) = 2.3 × 10^{-2} mol dm^{-3}, c(HClO$_4$) = 4.2 × 10^{-3} (◆), 2.2 × 10^{-3} (■), 1.0 × 10^{-3} (▲), 1.3 × 10^{-4} (●) mol dm^{-3}.
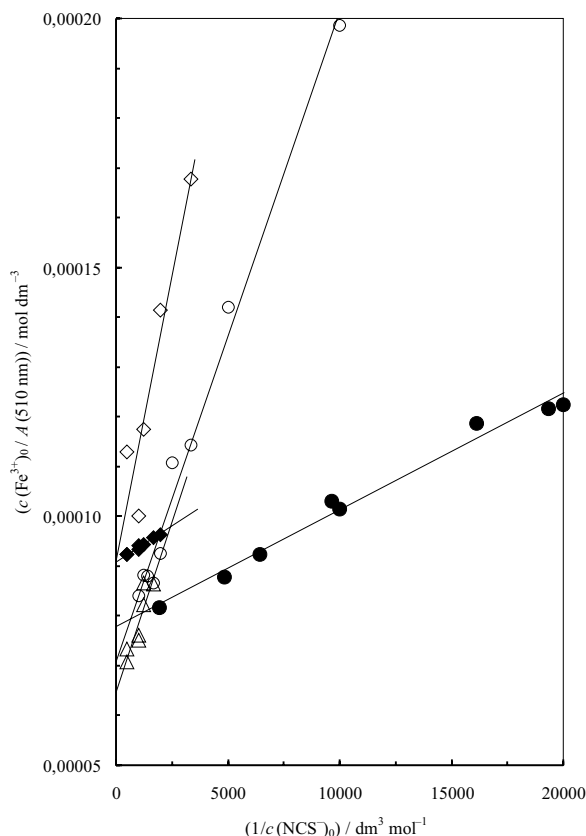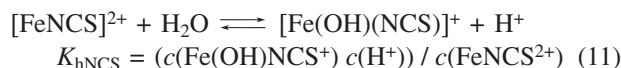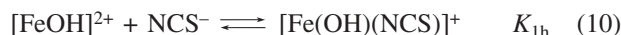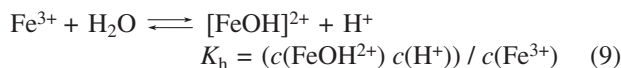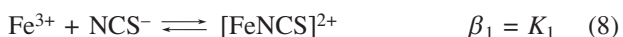
Figure 4. Determination of the stability constant K_1 of $[FeNCS]^{2+}$ according to Eq. (7) in CH_2Cl_2–MeOH (2:1) solvent mixture, $c(H_2O) = 1.1$ mol dm^{-3}; at $c(HClO_4) = 2.3 \times 10^{-2}$ mol dm^{-3}, $c(Fe^{3+}) = 5.0 \times 10^{-6}$ (●), 5.0×10^{-5} (◆) mol dm^{-3}; at $c(HClO_4) = 8.0 \times 10^{-4}$ mol dm^{-3}, $c(Fe^{3+}) = 5.0 \times 10^{-5}$ mol dm^{-3} (◇); $c(Fe^{3+}) = 5.0 \times 10^{-5}$ mol dm^{-3} (△), $c(NaClO_4) = 2.2 \times 10^{-2}$ mol dm^{-3}; $c(Fe^{3+}) = 1.2 \times 10^{-5}$ mol dm^{-3} (○), $c(NaClO_4) = 2.2 \times 10^{-2}$ mol dm^{-3}.

$\varepsilon(FeNCS^{2+})$ and K_1 can be determined from the intercept and the slope of the straight line obtained by plotting $c(Fe^{3+})_0 / A$ vs. $1 / c(NCS^-)_0$.

The increase of the perchloric acid concentration at the same concentration of electrolytes did not change the molar absorptivity of the complex (common intercept in Figure 3), but it did increase the stability constant. On the other hand, the increase of the concentration of electrolytes at the same concentration of perchloric acid did not change the stability constant (common slope in Figure 4), but molar absorptivity was increased.

From these results, molar absorptivity was $(13\ 700 \pm 700)$ dm^3 mol^{-1} cm^{-1}. Also, an increase of the observed stability constants with increasing acid concentration was obtained (Figure 5). The complexation of Fe^{3+} with thiocyanate was described in terms of the parallel path mechanism, and the reaction scheme in water was put forward[11] as follows:

$$Fe^{3+} + NCS^- \rightleftharpoons [FeNCS]^{2+} \qquad \beta_1 = K_1 \quad (8)$$

$$Fe^{3+} + H_2O \rightleftharpoons [FeOH]^{2+} + H^+$$
$$K_h = (c(FeOH^{2+})\ c(H^+)) / c(Fe^{3+}) \quad (9)$$

$$[FeOH]^{2+} + NCS^- \rightleftharpoons [Fe(OH)(NCS)]^+ \qquad K_{1h} \quad (10)$$

$$[FeNCS]^{2+} + H_2O \rightleftharpoons [Fe(OH)(NCS)]^+ + H^+$$
$$K_{hNCS} = (c(Fe(OH)NCS^+)\ c(H^+)) / c(FeNCS^{2+}) \quad (11)$$

where K_1 and K_{1h} are the stability constants of the corresponding complexes, while K_h and K_{hNCS} are the hydrolysis constant of Fe^{3+} and the acid dissociation constant of the complex, respectively. The observed equilibrium constant for the binding of thiocyanate, K_{obs}, would be given by:

$$K_{obs} = \frac{c(FeNCS^{2+}) + c(Fe(OH)NCS^+)}{c(NCS^-)\ (c(Fe^{3+}) + c(FeOH^{2+}))} \quad (12)$$

The value for the acid dissociation constant of $[FeNCS]^{2+}$ (Eq. 11) in water is rather small, $K_{hNCS} = 6.5 \times 10^{-5}$ mol dm^{-3}.[12] Under the conditions of high acid concentrations in dichloromethane–methanol, an even lower value may be expected, so that the second term in the numerator of Eq. (12) can be neglected. This leads to
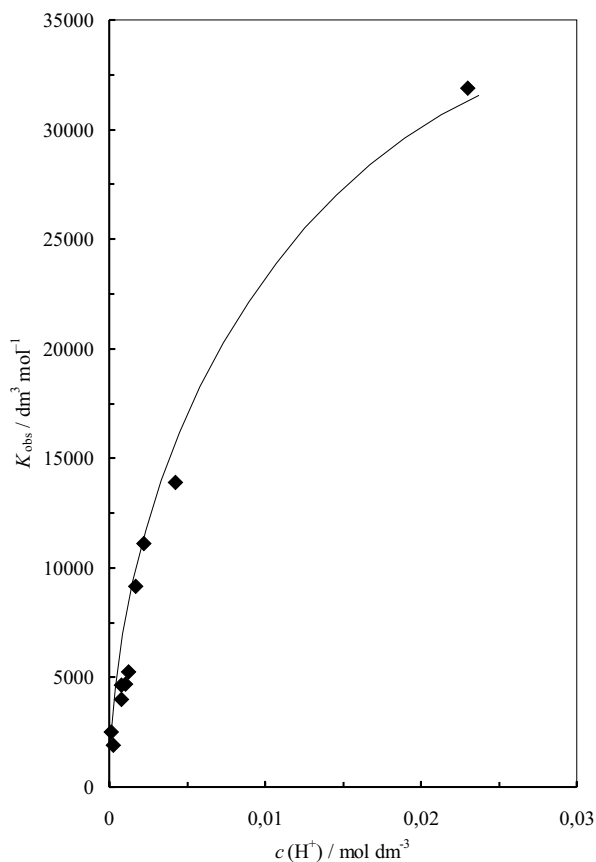

Figure 5. Dependence of the observed equilibrium constant for the binding of thiocyanate, K_{obs}, on perchloric acid concentration in CH_2Cl_2–MeOH (2:1) solvent mixture; $c(H_2O) = 1.1$ mol dm^{-3}; $c(NaClO_4) + c(HClO_4) = 2.3 \times 10^{-2}$ mol dm^{-3}.
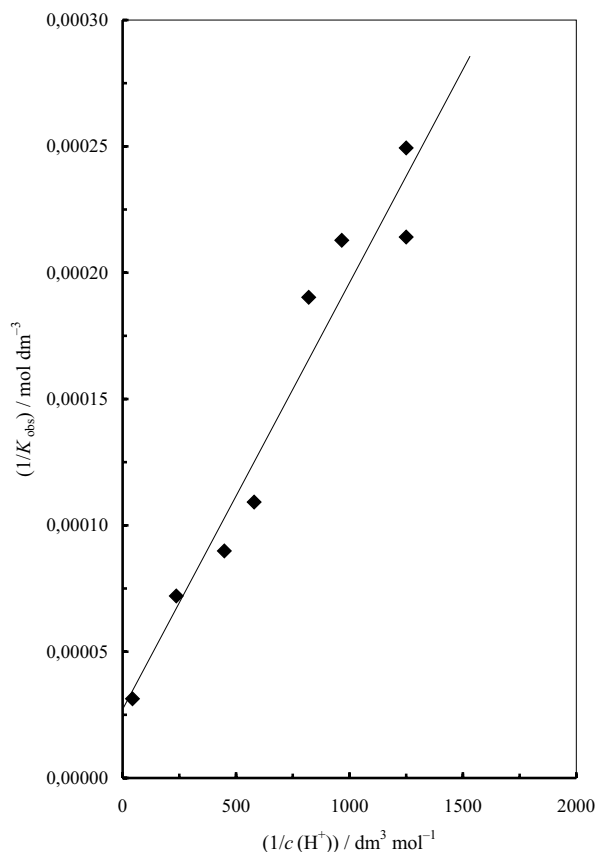
Figure 6. Determination of the stability constant K_1 of $[FeNCS]^{2+}$ and the solvolysis constant of Fe^{3+} ion according to Eq. (14) in CH_2Cl_2–MeOH (2:1) solvent mixture, as a function of perchloric acid concentration; $c(H_2O) = 1.1$ mol dm⁻³; $c(NaClO_4) + c(HClO_4) = 2.3 \times 10^{-2}$ mol dm⁻³.

equation (13), which takes into account that a fraction of the iron(III) concentration is involved in the solvolysis (in Eq. (13) K_h for the hydrolysis constant is substituted for K_s for the solvolysis constant of Fe^{3+}):

$$K_{obs} = c(FeNCS^{2+}) / (1 + K_s / c(H^+)) c(Fe^{3+}) c(NCS^-)$$
$$= K_1 / (1 + K_s / c(H^+)) \qquad (13)$$

Consequently, the corrected value of the stability constant K_1 can be obtained by multiplying the observed stability constant K_{obs} by factor $(1 + K_s / c(H^+))$. The constants K_1 and K_s can be calculated from the intercept and the slope of the straight line (14) obtained as a reciprocal of equation (13) (Figure 6). In this way, the stability constants $K_1 = 40\,500$ dm³ mol⁻¹ and $K_s = 7.0 \times 10^{-3}$ mol dm⁻³ were obtained.

$$1 / K_{obs} = 1 / K_1 + K_s / (K_1\, c(H^+)) \qquad (14)$$

DISCUSSION

The position of maximum absorption at 510 nm of the complex $[FeNCS]^{2+}$ in CH_2Cl_2–MeOH (2 : 1), as com-
pared to 460 nm in water, is consistent with the lower dielectric constant of the solvent mixture.[13] However, the dielectric constant alone cannot account for the hypsochromic shift, and specific solvent effects should also be held responsible. In our solutions, only methanol and water can be expected to participate in solvent – solute interactions. On the other hand, the presence of water up to 1 mol dm⁻³ had no appreciable effect on the spectra of monochloroiron(III) complex in N-methylacetamide according to the literature,[14] and we feel confident that the same concentration of water in the mixture with methanol has a comparatively negligible effect.

The nature of the methanol solvation sheath in the presence of water should be similar to that of ethanol, which is described in the literature:[15] on gradual addition of water to the initially anhydrous ethanol solution of neodymium, ethanol molecules were eventually completely displaced by the water molecules added. It is reasonable to assume that both hexaaqua- and hexamethanol- coordinated Fe^{III} ions exist in solution, as well as all their sterically possible intermediate combinations.

The hydrolysis/solvolysis of the solvated ion introduces one hydroxyl/methoxyl group in the coordination shell, which has a strong effect on the reaction kinetics. Both solvent exchange and anation reaction rates are much faster on the hydrolyzed/solvolyzed than on the unhydrolyzed/unsolvolyzed ions. Water exchange rates on the hydrolyzed Fe^{III} ions are faster than on the unhydrolyzed ion by a factor of 1000.[16] The anation of the hydrolyzed iron(III) ion by thiocyanate (reaction 10) is two orders of magnitude faster than that of hexaaquairon(III) ion in water (reaction 8).[11] The activity of the hydrogen ion in solution is therefore of particular importance.

The kinetics in methanol is even faster than in water. The relative solvent exchange rate for Fe^{III} ions is three orders of magnitude larger in methanol than in water.[17] There are no kinetic measurements of the anation reaction of the Fe^{III} ion by thiocyanate in methanol, but it is reasonable to expect that solvolysis in methanol would be more severe than in water due to the lower dielectric constant. Two factors contribute to the formation of complexes in CH_2Cl_2–MeOH: on the one hand, activity coefficients of ions are larger compared to aqueous solutions of the same concentration; on the other hand, lowering of the dielectric constant would increase the tendency of ions to associate forming ion pairs and complexes. This behaviour is possible at concentrations that are lower in comparison to aqueous solutions.

The high concentration of protons needed to suppress solvolysis in methanol may not be attainable because of the incomplete dissociation of the acid; consequently, there will always be solvolyzed Fe^{III} species in methanol, as evidenced by the brownish colour of the solutions, already observed by Rabinowitch.[18]

These qualitative differences are reflected in the large quantitative difference between stability constants in water and those measured in the solvent mixture in this work: while the value of about 130 dm³ mol⁻¹ was reported in the literature,[11,19] about 300 times higher value was obtained in the present work.

On the other hand, the solvolysis constant K_s obtained in this work is of the same order of magnitude as the hydrolysis constant K_h obtained in water.[20] This would indicate that not only would the forward solvolysis reaction be accelerated in the solvent mixture, but that the reverse reaction would also be accelerated to the approximately same degree.

The dependence of the equilibrium constant on ionic strength is described by the Debye-Hückel equation:[21]

$$\log K_s = \log K_h - 2.04 \sqrt{\mu} / (1 + 2.97 \sqrt{\mu}) \quad (15)$$

Conversely, it can be used to estimate the ionic strength responsible for a certain value of the equilibrium constant. We shall take the hydrolysis constant at zero ionic strength $K_h = 6.5 \times 10^{-3}$ mol dm⁻³ in water[20] to estimate the ionic strength at which one would obtain solvolysis constants $K_s = 7.0 \times 10^{-3}$ mol dm⁻³, obtained in this work. The calculation gives $\mu = 3.5 \times 10^{-4}$, a value which is an order of magnitude lower than the actual concentration, which is of the order of millimoles in these experiments. This illustrates the weaker dissociation of electrolytes in the solvent mixture and, on the other hand, lower requirements on the ionic strength for the same effect in the solvent mixture as compared to water. This estimate is not very sensitive to the small variations of the coefficient in the denominator, which contains the distance of the closest approach.[21] Hence, we find this extrapolation from water to solvent mixture justified for this type of qualitative estimate.

CONCLUSION

The stability constant of the [FeNCS]²⁺ complex in aqueous solution is not large ($K_1 = 146$ dm³ mol⁻¹),[11] and partition of iron(III) in complexes with other ligand anions is possible. Consequently, no high precision of any analytical method based on the quantitation of the [FeNCS]²⁺ complex in water may be expected. Reduction of the Fe^III into Fe^II ion and subsequent complexation with organic ligands (dipyridyl, *o*-phenanthroline) has therefore been developed.

On the other hand, the composition of the [FeNCS]²⁺ complex in the solvent mixture dichloromethane–methanol is well defined over a range of concentrations, and the stability constant is high enough to make this complex a suitable means of visualizations of Fe^II-to-Fe^III transformations in non-aqueous media.

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SAŽETAK

Kompleks monotiocijanatoželjeza(III) u smjesi otapala diklormetan–metanol

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Kompleksiranje iona željeza(III) s tiocijanatom u smjesi otapala diklormetan–metanol istraživano je zbog našega zanimanja za analitičke primjene koje se temelje na promjenama željezo(II)-željezo(III) u nevodenim sredinama. Molarna apsorptivnost i sastav kompleksa, kao i konstanta solvolize i konstanta stabilnosti kompleksa u ovisnosti o sastavu otopine određene su spektrofotometrijski. U području topljivosti komponenata u otopini kompleks je bio u obliku monokompleksa, $[FeNCS]^{2+}$. Na molarnu apsorptivnost kompleksa u vrlo kiselim otopinama nije utjecala koncentracija kiseline i iznosila je $(13\ 700 \pm 700)$ dm^3 mol^{-1} cm^{-1}. Vrijednost konstante solvolize bila je slična onoj u vodi, $K_s = 7{,}0 \times 10^{-3}$ $mol\ dm^{-3}$. S druge strane, konstanta stabilnosti kompleksa bila je pod jakim utjecajem koncentracije kiseline. U približenju beskonačno velikoj koncentraciji kiseline dobivena je konstanta stabilnosti $40\ 500$ dm^3 mol^{-1}, koja je primjerena za analitičke primjene kompleksa u nevodenoj sredini.