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Thermodynamics of the complexation between salicylaldehyde thiosemicarbazone with Cu(II) ions in methanol–1,4-dioxane binary solutions

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Abstract: The complexation reaction between salicylaldehyde thiosemicarbazone, abbreviated as STSC, with Cu(II) ion was studied in binary mixtures of methanol–1,4-dioxane using UV–Vis spectrophotometric and conductometric methods at different temperatures. The formation constants (K_f) for the 1:1 complex, Cu(II)–STSC, were calculated from computer fitting of the absorbance and molar conductance data against various concentrations ratios (c_M:c_L or c_L:c_M) in different binary solvent mixtures. A non-linear correlation was observed for the variation of log K_f for the complex against the solvent compositions. Various thermodynamic parameters (ΔH, ΔS and ΔG) for the formation of the Cu(II)–STSC complex were also determined from the temperature dependence of the formation constants (K_f). The results showed that the complexation reaction is affected by the nature and composition of the mixed solvents.

Keywords: salicylaldehyde thiosemicarbazone; Cu(II); stability constants; binary mixtures; methanol; 1,4-dioxane.

INTRODUCTION

Schiff bases derived from the amines and aldehydes belong to an important class of ligands that coordinate to metal ions through the azomethine nitrogen.[1–3] In recent years, there has been considerable interest in the chemistry of transition metal complexes of thiosemicarbazone ligands, primarily because of their bioinorganic relevance.[4] In the solid state, these thiosemicarbazones exist in the thione form and in solution they tautomerize into the thiol form.[5] Complexation usually occurs through the dissociation of the acidic proton, resulting in the formation of a five-membered chelate ring and, when an additional donor site is incorporated or linked to the carbonylic carbon by one or two intervening atoms, tricoordination usually occurs.[5] Thiosemicarbazones of salicylaldehyde and their

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derivatives constitute a class of versatile tridentate (O, N and S) donors capable of stabilizing both higher and lower oxidation states of transition metal ions.[6–8] These ligands also have an ion-sensing ability, metal extraction properties, pharmacological properties, *etc*.[9–13] Among the first row transition metals, copper plays a pivotal role in cell physiology as a catalytic cofactor in the redox chemistry of mitochondrial respiration, iron absorption, free radical scavenging, elastin cross-linking,[14] *etc*. Copper is found in all living organisms and is a crucial trace element in redox chemistry, growth and development.[15] It is important for the function of several enzymes and proteins involved in energy metabolism, respiration and DNA syntheses. Very little information is available in the literature about the thermodynamic stability of the complexes of STSC and its derivatives, most probably due to their low water solubility that limits experimental exploration of their solution equilibria. However, the use of aqueous organic solvent mixtures can be useful for comparing the stability of complexes of different metal ions and a series of ligands in semi aqueous media.[16–18]

Among the various organic solvents, alcohols in nonpolar solvents can associate by means of hydrogen bonds into a series of *n*-mers. In dilute solutions, the predominant species are the unassociated molecules, while in concentrated solutions, both linear and *n*-mers coexist. In solvents such as 1,4-dioxane (DO) that can form hydrogen bonds with methanol (MeOH), the self-association of alcohols may be reduced or perturbed in favor of hydrogen-bonded structures when mixed together, leading to intermolecular association between MeOH and DO molecules.[19] Papanastasiou *et al.*[20] suggested that binary mixtures of DO and MeOH are characterized by the formation of two intermolecular complexes of the types (DO:MeOH) 1:1 and 1:2 and that DO can associate through hydrogen bonds involving either of its two oxygen atoms. Although, numerous literature data are available for complex formation of Schiff bases with metal ions in non-aqueous solvents and mixed solvent systems, thermodynamic data on complex formation of salicyaldehyde thiosemicarbazone (STSC) with Cu(II) ions in pure and mixed non-aqueous or semi aqueous solvents are rather scarce.[21–26] Hence in this work, the complexation behavior of STSC with Cu(II) ion in different MeOH–DO mixed solvents was studied in order to understand the thermodynamics of complex formation between STSC and Cu(II) in the studied mixed solvents.

EXPERIMENTAL

Materials

Reagent grade thiosemicarbazone (s), salicyaldehyde (l) and copper(II) nitrate trihydrate, $Cu(NO_3)_2\cdot 3H_2O$ (s) were procured from Thomas Baker, India, and used as received. Spectroscopic grade methanol (MeOH) and 1,4-dioxane (DO) (each of purity > 99 %, S. D. Fine Chemicals, India) were used without further purification. Salicylaldehyde thiosemicarbazone (STSC) was prepared according to a literature procedure and its purity was checked by spectroscopic and other analytical methods.[11] The various binary solvent mixtures were prepared by mass and necessary adjustments were performed to achieve exact mass fractions (w_1 = = 0.40, 0.60, 0.80 and 1.00) of MeOH in the binary solvent mixtures at 298.15 K under atmospheric pressure. The mass measurements were realized on a digital electronic analytical balance (Mettler, AG 285, Switzerland) with a precision of ±0.01 mg. The relative error in solvent composition was about 1%. The physical properties of these solvent mixtures are available in the literature.[27]

Preparation of the ligand

Thiosemicarbazone (0.746 g) was dissolved in 75 mL of doubly distilled deionized water by warming. To the obtained solution, salicylaldehyde (1 g) was added and the reaction mixture was refluxed for 3–4 h. Crystals of STSC were obtained from the solution on cooling. The thus-obtained crystals were separated by filtration, dried under vacuum and further purified by recrystallization from ethanol.

Analytical and spectral data of the ligand

The melting point of the ligand was determined by the open capillary method. The IR spectrum of the ligand salicyaldehyde thiosemicarbazone in the wavenumber range 400–4000 cm^{-1} was recorded on a Perkin–Elmer FT-IR spectrophotometer (RX-1). Elemental microanalyses were realized using a Perkin–Elmer (Model 240C) analyzer.

Salicyaldehyde thiosemicarbazone. White crystalline compound; Anal. Calcd. for $C_8H_9N_3OS$: C, 49.23; H, 4.61; N, 21.53; S, 16.41 %; IR (KBr, cm^{-1}): 3443.87 (3444[29]), 3320.97 (3321[29]), 3175.01 (3175[29]), 1236.84 (1237[29]), 1035.91 (1036[29]), 751.76 (752[29]).

The structure of the synthesized Schiff base is depicted in Fig. 1.

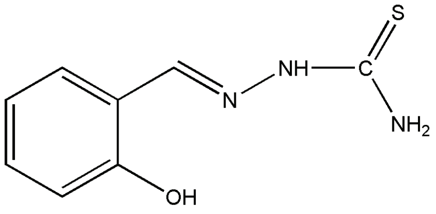

Fig. 1. Structure of salicylaldehyde semicarbazone (STSC).

UV–Vis spectrophotometric titration

The absorbance spectra were recorded on a Jasco V-530 spectrophotometer equipped with a thermostated bath. During the complexation studies, temperature of the quartz cell was maintained at 298.15±0.1 K. For the spectrophotometric titration, the stepwise additions of metal ion solution (1.3×10^{-3} mol dm^{-3}) to 2 mL of a solution of ligand (5.0×10^{-5} mol dm^{-3}) were realized using a 10 µL pre-calibrated micropipette. The absorbance (A) of the solution was measured after each addition of metal ion solution to the ligand solution.

Conductometric titration

The conductance measurements were performed with a Systronics-308 conductivity bridge (with a precision ±0.1 %) and a dip-type immersion conductivity cell (type CD-10) at a frequency of 1 kHz. Measurements were made in a water bath maintained at ±0.01 K of the desired temperatures. The cell was calibrated with standard KCl solution as described earlier[32] and the cell constant was 1.16 cm^{-1}. During the conductometric titration, a solution of copper nitrate (5.0×10^{-4} mol dm^{-3}, 15 mL) was placed in the conductivity cell and the conductance of the solution was measured. A solution of the ligand (2.5×10^{-2} mol dm^{-3}) was added stepwise to the conductivity cell with a pre-calibrated micropipette (50 μL) and the conductance of the resulting solution was measured after each addition. Addition of the ligand solution was continued until the total concentration of the ligand was approximately three times greater than that of the metal ion concentration (c_L:c_M = 3:1).

RESULTS

UV–Vis spectrophotometric titration

The UV–Vis spectra of the STSC ligand and its Cu(II) complex in pure MeOH and in the binary mixtures of MeOH with DO are presented in Fig. 2, which shows that the absorption spectrum of the solution of STSC ligand (initially 5.0×10^{-5} mol dm^{-3}) underwent marked changes when a solution of Cu(II) cations (1.3×10^{-3} mol dm^{-3}) was added to the ligand solution in a stepwise fashion until the contentratrions ratio, c_M:c_L, of 3:1 at 298.15 K was achieved. The UV–Vis spectrum of STSC showed two characteristic bands at around 291 and 332 nm. These bands originate from the azomethine chromophore and the phenol moiety, respectively. During the spectrophometric titration, complex formation was indicated by a gradual decrease in the intensity of the 332 nm peak and by the development of a peak at around 394 nm. These changes in UV–Vis spectra were due to the coordination of Cu(II) ion through imine nitrogen atom, sulfur atom with an additive effect from the deprotonation of the phenolate group upon chelation, resulting in the formation of six and five-membered ring systems between the metal atom and the ligand in the complex.[16] However, the peak at 291 nm overlapped with that of the free NO_3^- at around 298 nm[29] and increased gradually in intensity in pure MeOH as more and more electrolyte solution was added, but the peak showed no such changes for the solutions in the binary mixtures; probably due to low dielectric constants of the binary mixtures. Hence, the analysis of the spectrophotometric data was performed with the absorbance values at λ = 394 nm as shown in Fig. 3. It is evident from Fig. 3 that when the ligand STSC reacted with Cu(II) ions in MeOH and its binary mixtures with DO, a 1:1 complex is formed. The mass balance for the ML complex is given by the relation:[31]

$$\mathrm{M} + \mathrm{L} \rightleftarrows \mathrm{ML} \tag{1}$$

and the formation constant (K_f) could be given by:

$$K_\mathrm{f} = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]} \tag{2}$$

where [M], [L] and [ML] stand for the concentrations of free metal ion, free ligand and formed complex in equilibrium, respectively. The mass balance for Eq. (1) can be solved provided that the following relations for the concentrations of total metal ion and ligand remain valid in equilibrium:

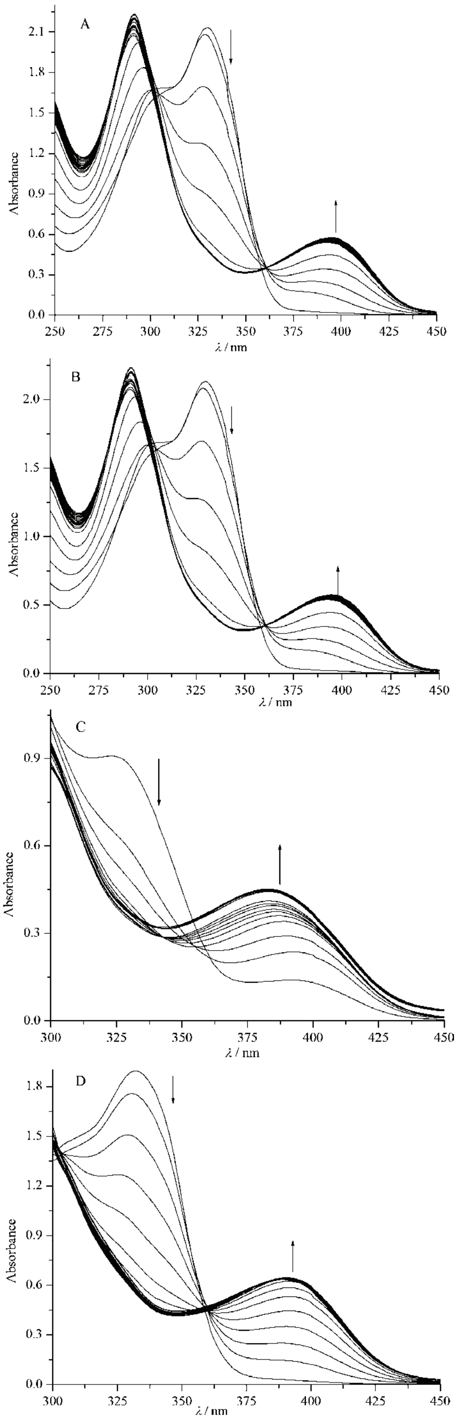

Fig. 2. UV–Vis spectra of the STSC ligand (5×10^{-5} mol dm^{-3}) in the presence of increasing concentrations of Cu(II) ions in different solvent mixtures with MeOH mass fractions (w_1) at 298.15 K: A, w_1 = 1.00; B, w_1 = = 0.80; C, w_1 = 0.60; D, w_1 = 0.40.

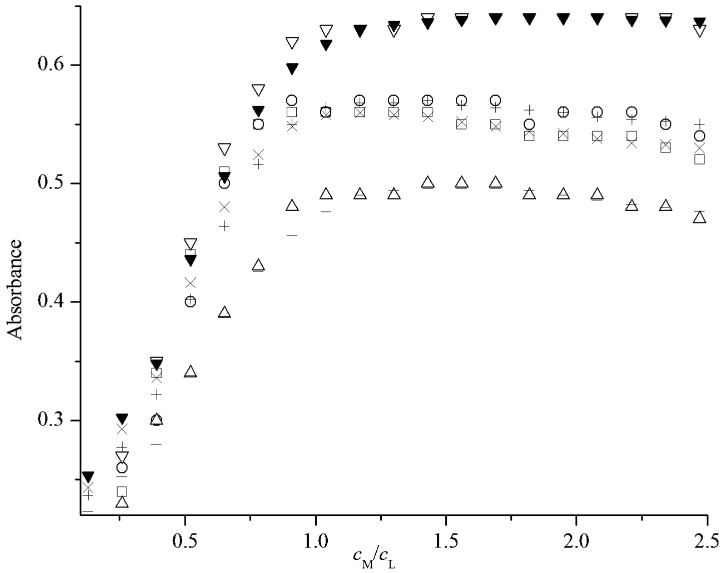

Fig. 3. Absorbance plot () for the ligand STSC with Cu(II) ion against c_M:c_L for different mass fractions (w_1) of MeOH in different solvent mixtures at 298.15 K. Symbols for the experimental data: □, w_1 = 1.00; ○, w_1 = 0.80; Δ, w_1 = 0.60; ∇, w_1 = 0.40. Symbols for the calculated data: ×, w_1 = 1.00; +, w_1 = 0.80; –, w_1 = 0.60; ▼, w_1 = 0.40.

$$c_M = [M] + [ML] \tag{3}$$

$$c_L = [L] + [ML] \tag{4}$$

When the [M] and [L] values, obtained from Eqs. (3) and (4), are substituted in Eq. (2), one obtains K_f as:

$$K_f = \frac{[ML]}{(c_M - [ML])(c_L - [ML])} \tag{5}$$

If only the complex absorbs at a particular wavelength, the total absorption (A) at this wavelength can be given by:

$$A = \varepsilon l[ML] = \varepsilon [ML] \tag{6}$$

where ε is the molar absorption coefficient of the complex and the path length l = 1 cm. Hence, from the above relation, [ML] is given by:

$$[ML] = A/\varepsilon \tag{7}$$

Therefore, when $c_M >> c_L$, Eq. (5) can be rearranged as:

$$K_f = \frac{[ML]}{c_M(c_L - [ML])} = \frac{A/\varepsilon}{c_M(c_L - A/\varepsilon)} \tag{8}$$

Rearranging the above relation, one obtains:[31]

$$\frac{c_\mathrm{M}c_\mathrm{L}}{A}=\frac{c_\mathrm{M}}{\varepsilon}+\frac{1}{\varepsilon K_\mathrm{f}} \tag{9}$$

Thus a linear regression of $c_\mathrm{M}c_\mathrm{L}/A$ against c_M gives the molar absorption coefficient (ε) from the slope and K_f from the intercept. Using these ε and K_f values, obtained from Eq. (9) as initial guess values, the absorbance ($A_{\mathrm{cald.},i}$) of each solution was iteratively calculated and then the final ε and K_f values were obtained from Eq. (10) by using the Newton–Raphson Method with the aid of a C-program. Eq. (10) was obtained after some rearrangement of Eq. (5):

$$\left(A/\varepsilon\right)^2-\{(c_\mathrm{M}+c_\mathrm{L})+1/K_f\}\left(A/\varepsilon\right)+c_\mathrm{M}c_\mathrm{L}=0 \tag{10}$$

The standard errors (σ) in the absorbances were calculated from the following the relation:

$$\sigma=\left[\sum_{i=1}^{n}\{A_{\mathrm{exp.},i}-A_{\mathrm{cald.},i}\}^2/n\right]^{1/2} \tag{11}$$

where n stands for the number of solutions. The obtained standard errors (σ) were 0.035, 0.025, 0.039 and 0.042 in the solvent mixtures with w_1 = 0.40, 0.60, 0.80 and 1.00, respectively.

Conductometric titration

It is known that the equilibrium for 1:1 complexation is represented by Eq. (1) and the formation constant (K_f) is given by:

$$K_\mathrm{f}=\frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]}\frac{f_\mathrm{ML}}{f_\mathrm{M}f_\mathrm{L}} \tag{12}$$

where the f terms stand for the activity coefficients of the species indicated in subscripts. Under the employed dilute concentration range, the activity coefficient of the uncharged ligand (f_L) can be assumed to be unity.[33,34] According to the Debye–Huckel limiting law $f_\mathrm{M}\approx f_\mathrm{ML}$, the activity coefficients in Eq. (12) cancel each other.[35] The fraction of the total metal ion concentration (α), remaining free at equilibrium, can be expressed by the relation:

$$\alpha=\frac{\Lambda_\mathrm{m}-\Lambda_\mathrm{ML}}{\Lambda_\mathrm{MA}-\Lambda_\mathrm{ML}} \tag{13}$$

where Λ_m, Λ_MA and Λ_ML stand for the total molar conductance, and the molar conductance of the electrolyte and the complex, respectively. The Λ_ML values were calculated by a least square linear regression of the data points (Λ_m *vs.* $c_\mathrm{L}/c_\mathrm{M}$) after the curve changed its slope at higher c_L:c_M ratios (Fig. 4). Then, the α values were calculated from Eq. (13) for each solution and an initial K_f value

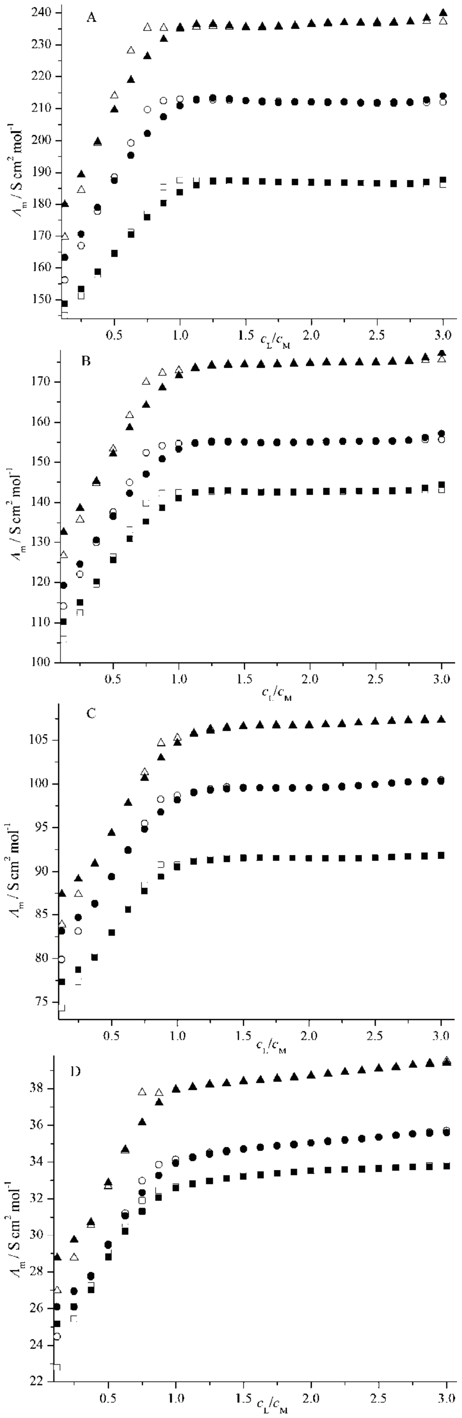

Fig. 4. Molar conductance (Λ_m) *vs*. mole ratio plot (c_L:c_M) for the Cu(II)–STSC complex in pure MeOH and different binary mixtures of MeOH–DO at different temperatures: A, w_1 = = 1.00; B, w_1 = 0.80; C, w_1 = 0.60; D, w_1 = 0.40. Symbols for the experimental data: □, T = 298.15 K; ○, T = 308.15 K; Δ, T = 318.15 K and symbols for the calculated data: ■, T = = 298.15 K; ●, T = 308.15 K; ▲, T = 318.15 K.

for each solution was calculated using the [M] and [L] values. Eq. (12) can also be rearranged as:[36]

$$K_f[\mathrm{ML}]^2 - \{1+(c_M+c_L)K_f\}[\mathrm{ML}] + K_f c_M c_L = 0 \qquad (14)$$

The final K_f values and [ML] were then calculated iteratively using the Newton–Raphson Method and successive approximations with the aid of a C-program.

DISCUSSION

The nature of a solvent can strongly influence the stoichiometry of a complex and complexation of transition metal ions in solution. The stability of transition metal complexes with polydentate ligand depends on several factors, such as the number and type of the donor sites present in the ligand, the number and size of the chelate rings formed on complexation, *etc.*[37] In addition, the stability also depends upon the donor strengths and dielectric constants of solvent–solvent mixtures.[38] Although the STSC solution had negligible conductance, its addition to the metal ion solution caused a rather large and continuous increase in molar conductance in all solvents. As can be seen from Fig. 4, the addition of STSC to Cu(II) ions in pure MeOH as well as in the binary solvent mixtures at different temperatures resulted in increases in molar conductivity. This fact indicated that the Cu(II)–STSC complex is more mobile than solvated Cu(II) ions and to the existence of some ion pairs in the initial salt and the release of some high-mobility protons and NO_3^- into the solution.[39,40] The slope of Λ_m *vs.* c_L/c_M plots for all solvent mixtures showed significant changes in slopes when c_L:c_M was about 1 thus indicating the formation of a relatively stable 1:1 complex (ML) between Cu(II) ions and STSC. From Fig. 4, it is also evident that the curvature of the molar conductivity plots for the Cu(II)–STSC complex decreased as the experimental temperature increased. This fact indicated to the formation of a weaker complex at higher temperatures. This is also evident from Table I wherein log K_f for Cu(II)–STSC complex in pure MeOH as well as in the binary solvent mixtures decreased with increasing temperature. However, slightly higher values of log K_f were obtained at 318.15 K for solvent mixtures with w_1 = 0.40 and 0.60 than those at 308.15 K.

TABLE I. log K_f values for the Cu(II)–STSC complex obtained from complexometric titrations in MeOH–DO binary mixtures at different temperatures; w_1 is the mass fraction of MeOH in the binary solvent mixtures. Standard errors are given in the parenthesis

w_1	T / K		
	298.15	308.15	318.15
1.00	5.28 (±0.23)	4.90 (±0.21)	4.89 (±0.19)
0.80	5.14 (±0.21)	4.84 (±0.18)	4.76 (±0.16)
0.60	4.92 (±0.16)	4.75 (±0.15)	4.80 (±0.11)
0.40	4.97 (±0.18)	4.83 (±0.15)	5.00 (±0.12)

MeOH has a higher Gutmann donor number (*DN* = 19) that that of DO (*DN* = = 14.8).[41] However, a comparison of the stability constants given in Table I and III revealed that Cu(II) ion was weakly solvated and easily complexed by the ligand in the solvent mixtures with higher contents of MeOH and the stability constants decreased with increasing concentration of DO in the binary solvents. This fact is in accordance with the reverse order of their solvating ability as represented by their Gutmann donor numbers. It is known that the solvating ability of the solvent plays an important role in different complexation reactions. Moreover, the stability and selectivity of the formed complexes are affected by a number of molecular factors, such the number and character of the donor atoms in the Schiff base, the polarizibility and charge density of the metal ion, the nature of substituents and the character of the co-anion with the cationic species.[42,43] In the Cu(II)–STSC complex, the ligand binds a Cu(II) ion through its three binding sites (O, N and S) and the fourth coordination site is most probably occupied by the solvent molecules, *i.e.*, MeOH or DO.[16] However, as per the polarity and steric factors for MeOH and DO, it is expected that MeOH will preferentially occupy the fourth coordination site. Regardless, the variation of the log K_f for the Cu(II)–STSC complex as a function of solvent composition is presented in Fig. 5, which shows that the changes in the stability constants for Cu(II)–STSC complex *vs*. the solvent composition are not linear. This evidence reflects that changes might be occurring in the structure of the solvent mixtures[20] and these changes probably alter solvations of the metal ion, the Schiff base and even the resulting complex as well as the preferential solvation of these species in the mixed solvents.[44] Preferential solvation of ions by one of the components of a mixed solvent system depends on two factors: the relative donor–acceptor abilities of the

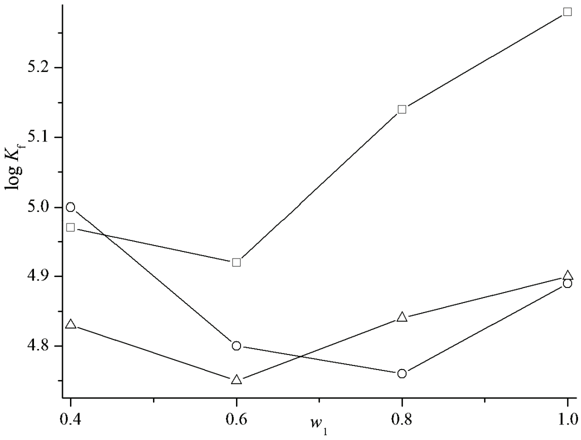

Fig. 5. Variation of formation constants (K_f) for Cu(II)–STSC complex against mass fractions (w_1) of MeOH in the binary solvent mixtures at different temperatures. Symbols: □, 298.15 K; Δ, 308.15 K; ○, 318.15 K.

component molecules towards the ion and the interactions between solvent molecules themselves. The solvating properties of the components in mixed solvents can even be significantly modified by solvent–solvent interactions when the energy of the latter is comparable with the energy difference of ion–solvent interactions for both of the components.[45]

Anyway, the stability constants given in Tables I and II have nearly the same order although the formation constants evaluated by the two methods are not the same but are similar in magnitude. This is because the experimental data were analyzed by two different approaches in the two methods used to determine the stability constants (K_f) and they have their own intrinsic error limits.

TABLE II. log K_f values for the Cu(II)–STSC complex obtained from UV–Vis spectrophotometry in MeOH–DO binary mixed solvents at 298.15 K; w_1 is the mass fraction of MeOH in the binary solvent mixtures. Standard errors are given in the parenthesis

w_1	log K_f
1.00	4.87 (±0.13)
0.80	4.77 (±0.12)
0.60	4.76 (±0.10)
0.40	4.65 (±0.13)

Thermodynamic parameters

In order to obtain a better understanding of the thermodynamics of the complexation reaction between Cu(II) and STSC, it is useful to determine the contributions of enthalpy and entropy of the reaction. The thermodynamic parameters were calculated from the temperature dependence of the complexation constants (van't Hoff plot):

$$2.303\log K_f = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

where R is the gas constant. For all the solvent mixtures, the plots of log K_f *vs.* $1/T$ were almost linear and the ΔS and ΔH values were determined in the usual way from the slope and the intercept of the plots, respectively. The calculated thermodynamic parameters are listed in Table III. The ΔH and ΔS values associated with the complexation reaction were negative for all the solvent mixtures except for the solvent mixture with $w_1 = 0.40$. The ΔG values for the complexation reaction were negative indicating the spontaneity of the reaction. Thus, it is evident that the reactions were spontaneous and enthalpy-driven except for the solvent mixture with $w_1 = 0.40$. For this solvent mixture, the complexation reaction was observed to be entropy-driven. These trends, as reflected by the thermodynamic parameters for the complexation reaction, are the overall results of several factors, such as solvation/desolvation of the species involved in the complexation reaction and the variation in flexibility of Schiff base during the complexation process, as well as the degree of ion–solvent, ligand–solvent, complex–solvent and solvent–solvent interactions.[46,47]

TABLE III. Thermodynamic parameters (Δ*H*, Δ*S* and Δ*G*) for the formation of the Cu(II)–STSC complex in different binary mixtures of MeOH with DO

w_1	ΔG / kJ mol^{-1}			ΔH / kJ mol^{-1}	ΔS / J mol^{-1} K^{-1}
	298.15 K	308.15 K	318.15 K		
1.00	–29.81 (±0.23)	–29.61 (±0.22)	–29.41 (±0.21)	–35.77 (±0.23)	–19.97 (±0.22)
0.80	–29.15 (±0.12)	–28.96 (±0.12)	–28.78 (±0.11)	–34.71 (±0.13)	–18.65 (±0.13)
0.60	–27.89 (±0.15)	–28.45 (±0.13)	–29.01 (±0.15)	–11.11 (±0.13)	56.27 (±0.14)
0.40	–28.09 (±0.20)	–29.11 (±0.23)	–30.13 (±0.22)	2.42 (±0.20)	102.31 (±0.23)

CONCLUSIONS

The formation constants for the complexation of Cu(II) ion with STSC were determined conductometrically at different temperatures and spectrophotometrically at 298.15 K. Thermodynamic parameters for the complexation were determined from the temperature dependence of the formation constant. The stoichiometry of the Cu(II)–STSC complex in pure MeOH and in all the MeOH–DO binary mixtures was found to be 1:1. The negative values of Δ*G* show the ability of the studied ligand to form stable complex with Cu(II) ion and the complexation proceed spontaneously.

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ИЗВОД

ТЕРМОДИНАМИКА ФОРМИРАЊА КОМПЛЕКСА Cu(II) СА САЛИЦИЛАЛДЕХИД-ТИОСЕМИКАРБАЗОНОМ У БИНАРНИМ РАСТВОРИМА МЕТАНОЛ–1,4-ДИОКСАН

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Реакција комплексирања Cu(II) и салицилалдехид тиосемикарбазона (STSC) испитивана је у бинарним растворима метанол–1,4 диоксан применом метода спектрофотометрије у ултраљубичастој и видљивој области и кондуктометрије на различитим температурама. Константе формирања (K_f) за 1:1 комплекс, Cu(II)–STSC, су израчунате коришћењем података о апсорбанцији и моларној проводљивости у функцији различитих односа концентрација (c_M:c_L или c_L:c_M) у бинарним ратсворима. Добијена је нелинерана корелација између промене log K_f комплекса и састава раствора. Из температурске зависности константи формирања одређени су термодинамички параметри (Δ*H*, Δ*S* и Δ*G*) формирања Cu(II)–STSC комплекса. Добијени резултати показују да природа и састав коришћених раствора утичу на реакција комплексирања.

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